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Waste Recovery and Decarbonization: a Sustainable Synergy

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Nowadays, the decarbonization of the sector of energy and the transformation of the whole economy chain in climate-neutral economy are targets in the political agenda of more than 50 Countries. The replacing of carbon-based fuels with hydrogen is one of the main ways to reach the decarbonization of the energy sector and reducing of impact on climate. Anyway, the production of hydrogen by recurring to electrolysis of the water molecules requires a large energy amount so that its sustainability must be increased by realizing more efficient system or synergy with other industrial sectors such as clean energy recovery. Possible well recognized sources of sustainable energy are biomasses, solar, and wind; in this paper an additional resource, a biowaste produced by anthropic activity, the sewage sludge, is considered as a possible source of energy for green hydrogen on the basis of a life-cycle perspective: the avoided burdens of landfill and incineration of sludges balance the low efficiency of the overall system for hydrogen production.
The paper illustrates a model that combines biowaste treatment with hydrogen production. The mathematical model of the system allowed to calculate the mass balance and the feedstock energies distribution. The output variables of the model are hydrogen yield, electricity to the grid (surplus), and CO_2 sequestrated; the input data to the model are the biowaste mass rate (and the composition), the power demand for hydrogen production by electrolysis and the electricity and heat consumption of the plant. The model results demonstrated that the hydrothermal carbonization of the given biowaste, that is sewage sludge from a waste-water treatment plant and the enriched air gasification of the resulted hydrochar converted into biofuel allowed to produce about 20kg/h of green hydrogen by covering all the energy demand of the plant, both heat, and electricity.

1. Introduction

European Union (European Commission, 2018) and the United States of America adopted a roadmap with 2050 as the deadline, China aims to reach carbon-neutrality in 2060 (Yang et al., 2022). The main transformations of the economic sectors can be summarized in: a) decarbonization of electricity production; b) electrifying end uses and switching to other clean fuels; c) cutting energy wastes; d) reducing methane and other non-CO2 emissions; e) scale-up CO_2 removal. Aiming to this ambitious target will require investing in realistic technological solutions and aligning actions in key areas such as industrial policy, finance and research. Two important areas of the industrial sector that need to be decarbonize and obtain carbon-neutrality are waste treatment and energy production. The waste treatment sector is responsible of emission of methane for approximately 14.5% of the total released in the ambient (EPA, 2022) due to disposal of non-inertised biowaste such as sludges, food waste, high TOC wastewater, etc. The energy production in USA is today based for more than 60% of fossil fuels, coal, natural gas, petroleum, and other gases (EIA, 2022) and similar percentages can be found in EU Countries. The sustainability of the waste management systems overall the world requires the renouncing of incineration in large plants, landfilling and long transportation overseas or between Countries' boundaries. The integration between the waste producers, at least the industrial ones, and the energy providers can realise the targets in term of reduced environmental impact of both sectors: waste management and energy production. The energy production from organic-based waste i.e. the biowaste, is often inefficient due to the high moisture content and low carbon content; making the energy from biowaste really interesting for the energy providers is one of the target of new processing and technological development. The use of pre-treatment that promotes the carbon mineralization, nutrients extraction and dehydration such as hydrothermal carbonization can allow the transition

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from the status of biowaste to that of biofuel (Vallejo et al., 2020). The biofuel can be converted into a synthetic gas by using pyrolysis and gasification processes that require smaller plant respect to combustors and are characterized by greater flexibility. The fluidized bed gasifier (BFBG) is a technological choice that allows great performance of carbon conversion, particularly when the gasification process is carried out with oxygen and enriched air (Liu et al., 2018) that improves the diffusional resistances during the solid conversion into syngas. The syngas can be then used to produce energy in engines, gas turbines, steam boilers, etc. depending on its degree of cleaning and calorific value (Valderrama Rios et al., 2018). The syngas can also be used to produce hydrogen by using the steam-reforming process (Rostrup-Nielsen et al., 2002); this option is quite interesting because since it is not applied to natural gas but to syngas coming from biofuel, it should be considered green hydrogen as well.

2. Conceptual model

2.1 System boundary

The model is applied to a system that includes three self-reliant sub-systems connected each to other by energy and/or by-product flows in such a way to optimize the material and energy use and applied circular economy principles. The sub-systems are: B1) the sludge conversion into syngas and energy, B2) the green hydrogen production via electrolysis and B3) the optional line of blue hydrogen production via water-gas shift WGS. The unit processes composing the overall system, grouped for the subsystems are reported in the following table 1.

Table 1. Subsystems and unit processes list

Subsystem B1 – sludge conversion into bio-fuel, syngas production and energy production	Subsystem B2 – Green hydrogen production via electrolysis of recovered water	Subsystem B3 – Blue hydrogen production via water-gas shift and sequential sequestration
Hydrothermal carbonization of sludge from industrial waste-water treatment	Water recovery and purification via reverse osmosis	Syngas upgrading via water-gas shift reaction
Bio-fuel production: dewatering, drying and granulation	Hydrogen production from purified water via electrolysis	Hydrogen separation
Gasification with O_2-enriched air	Oxygen production	Residual syngas valorization via energy recovery
Syngas conditioning		
Energy production via gas turbine		

The qualitative description of the main unit processes is reported in the following paragraph.

2.2 Unit processes' description

2.2.1 Hydrothermal carbonization

HTC is a thermochemical process occurring in the liquid phase that converts biomass into hydrochar by several different steps with mild reaction conditions at low temperatures (180–250 °C), absence of oxygen and sub-critical water conditions. The HTC process is convenient when biomass is wet since it can carbonize substrate with a water content up to 90% by weight without prior drying, which results in an expensive and long process (Wang et al., 2018). In an HTC process, water has the role to promote the heat transfer throughout the bulk of the biomass during the process, enhancing the efficiency of heat transfer, and promoting the hydrolysis reactions. Chemical dehydration, decarboxylation reactions and polymerization and aromatization are the main chemical reactions that allow the concentration of carbon and its mineralization. HTC requires an appropriate heating system in order to attain the set-up temperature because exothermal reactions are not able to balance the unavoidable loss of heat throughout the reactor wall. The process is carried out in a reactor at 250°C, under an autogenous pressure of about 39bar for 6 hours. The reactor is fed batchwise with a mixture of sludge and water in a ratio able to reach a 12-20% of solids content.
This process has been applied to sludge produced by the industrial wastewater treatment plant with the scope to convert it into a biologically inactive product, with a decreased content of nitrogen and nutrients as well as TOC. This product can be managed with minor environmental issues such as bad odors release, and with the possibility to be stored longer being inactive, almost inert.

2.2.2 Bio-fuel preparation

In the model illustrated before, the hydrochar from sludge is converted into a bio-fuel by recurring to the mechanical operations that are: dewatering, drying and agglomeration. The water removed from these operations is sent to a waste-water treatment for nutrient recovery and water reuse. The heat to be used is recovered by the energy generation system so no fossil fuel is used for the scope. The composition of the bio-fuel depends on the biowaste used; in the following that obtained by experiments with sludge is used. The hydrochar, and then the biofuel obtained from its drying and pelletizing, is characterized by an ultimate composition depending on the severity of the HTC process parameters and by the initial composition of the biowaste. More specifically, the H/C and O/C ratios depend on the HTC process conditions while the ash fraction depends on the initial biowaste composition. Another important feature is the carbon structure in the hydrochar: starting from cellulosic biomass, a granular and porous hydrochar is produced, starting from a sludge, for which the carbon is dissolved in water, a carbon-rich powder is obtained.

2.2.3 Waste-water treatment and pure demineralised water preparation

The waste-water treatment plant is used to recover the amount of pure water to feed the electrolysis process for hydrogen production and recover nutrients. The water used in the HTC reactor is rich in nutrients, dissolved and suspended carbon, and soluble metals. The processes utilized to produce a stream of water suitable to be recovered as pure water for hydrogen production are well known in the industry and scientific literature (Bouchareb et a., 2022, Beswick et al., 2021). In the model we consider a hybrid process including evaporation and reverse osmosis (RO) membrane that results to be effective and applicable to the case study. Obviously, the RO process is applied only to the water stream addressed to H_2 production to keep the cost low. These processes are not described in detail in the model and in the following calculations.

2.2.4 Bubbling Fluidized Bed Gasifier

Gasification can be defined as the conversion of carbonaceous material into a gaseous product that consists of hydrogen, carbon monoxide, carbon dioxide, methane, lower amounts of light hydrocarbons (C2-C8), and nitrogen (if air is used as gasifying agent). The gasification process is performed in the presence of a gasifying agent (in this specific case a mixture of air and oxygen) at elevated temperatures (850-1000°C) and at atmospheric pressure. Bubbling fluidized bed gasification plants can be configured to utilize more efficient energy conversion systems, such as gas engines and gas turbines which potentially have higher electrical generation efficiencies. The utilization of oxygen-enriched air as gasifying agent is expected favorable to the production of valuable gas. Its utilization could produce a gas with a higher calorific value and a lower concentration of tar compare with the use of air.

2.2.5 Energy generation

The syngas produced by the enriched air gasification is sent to a conditioning line for tar conditioning and to a gas turbine coupled with an ORC circuit for electricity generation. Electricity is used mainly for green hydrogen production but is enough to cover the self-consumptions of the whole plant (except optional B3 and nutrients recovery, not included in the calculations). The utilization of a gas turbine requires to use a clean syngas, without trace of condensable hydrocarbons, completely dried and compressed. The tar conversion is obtained by using a plasma cracker using an oxygen-steam ionized stream to promote, in a very fast sequence of reactions, cracking, partial oxidation and hydrocarbons reforming. The tar conversion allows to increase the syngas yield and its calorific value. After the tar conversion, the syngas is sent to a heat recovery system that allows the parallel cooling of syngas and heating of diathermic oil; the cooled syngas is sent to a double-stage scrubber for removal of alkali and acids and finally to a drier for removal of any trace of water. The conditioned syngas is sent to a gas compressor and fed to the gas turbine; this latter will use natural gas as additional fuel to ensure stable electricity production. The flue gas from gas turbine, at 400°C, will be used for additional electricity production in an ORC production.

2.2.6 Electrolysis

The electrolysis process allows the production of hydrogen from water obtained in section (III) of the plant. This process uses electricity to obtain a dissociation of the water molecules into the H^+ and OH^- ions, which, by reacting respectively with the anode and cathode, produce molecules of hydrogen H_2 and oxygen O_2.
The main electrolyzer technologies that exist today whit with an appreciable diffusion are:

1) AEC (alkaline electrolytic cell), operating at low temperatures and pressures.
2) PEM, proton exchange membranes, operating at low temperatures and high pressures, in which protons pass through a special membrane

3) AEM (Anion Exchange Membrane), operating at low temperatures and high pressures, in which anions pass through a special membrane
4) SOEC (Solid Oxide Electrolysis Cells), operating at high temperatures (700-800°C).

The AEC type was chosen as the technology to be adopted for Electrolysis, as it is the most widespread, dominating with 61% of the installed capacity of hydrogen production in 2020 (IEA, "Global Hydrogen Review", 2021).

3. The mass and energy balance

3.1 The block diagram

The block diagram of the model is reported in figure 2. Each unit process is represented by a block where input and output lines represent mass flows.
The import data is the biowaste that is already mixed with the desired amount of water to carry out the HTC process under the cited operating conditions. The HTC process converts the solid fraction of the biowaste into hydrochar and a small fraction of gas containing more than 95% of carbon dioxide; the leachate is rich in nutrients and contains dissolved carbon. Hydrochar flow is removed with a fraction of water since the remaining part, about 60-70%, is left evaporating before the hydrochar discharge.
The water content in the hydrochar extracted from the HTC reactor is removed mechanically in the dewatering stage with a good efficacy since hydrochar is hydrous phobic. The biofuel preparation consists in an agglomeration system heated with the hot oil (300°C) obtained by the heat recovery system (note that auxiliaries are not shown). The water content is controlled and maintained below 15%.
The biofuel is fed to the bubbling fluidized bed gasifier together with an oxygen-air mixture in a ratio suitable to reach an equivalence ratio of 0.20-0.25. The resulting syngas is sent to the conditioning and energy recovery from which electricity, heat and ashes are obtained as outputs.
The electricity produced is used to power the electrolysis section that uses 1MW for producing hydrogen with an efficiency of 65%. The electrolysis also uses a small portion of the water recovered from the HTC reactor after a process consisting in a slow evaporation-condensation of the steam and a reverse osmosis applied only to the stream of water to be sent to electrolyzer.
The evaporation is realized by using the accumulated sensible heat in the water during the HTC process and it is realized in such a way to minimize the transportation of nutrients and fines. Operating in this way allows to have a leachate with high content in nutrients and dissolved organic carbon DOC from the dewatering section that is possibly used as fertilizer or for nutrients recovery while the evaporated (and condensate) water retrieved from the top is enough dilute to be treated in a conventional waste-water treatment plant WWTP.
In this model the WWTP is the origin plant of biowaste (sludge) so that the water returns to the water body after depuration.

3.2 The model assumptions

The mass and energy balances reported in figure 1 are the results of a series of sub-models applied to each block/unit process; the solving of the resulting equations requires a database that is in part derived by experimental campaign and in part from assumptions based on literature.
In the following the main assumptions for the main unit processes are reported.

Table 2: Biowaste characterization

Ash content (as produced)	6%
Carbon content (dry basis)	33%

Table 3: HTC process parameters

Gas production / dry solids yield	15%
Hydrochar / dry solids yield	70%
Evaporated water fraction	70%
Power heat request: kW	19493
Reaction time, h:	6
Heating time, h:	0.5

Table 4: Dewatering

Dewatering efficacy	80%
Loss of ashes/solids in water	10%

Table 5: Drying and granulation

Dried water efficiency	60%
Power heat request: kW	213

Table 6: Water condensation

Cooling transfer efficiency	70%
Power cooling request: kW	5767

Table 7: Electrolysis

Hydrogen yield efficiency (energy), %	65%
Power electrical request: kW	1000

Table 8: BFB gasification and energy production

%C	0.35
%H	0.05
Oxygen demand, kg/h	155
Air demand, kg/h	598
Chemical energy content of syngas, kW	11182
LHV hydrochar, MJ/kg	26.00
LHV syngas, MJ/kg	20.80
Electricity efficiency conversion, %	35%
Heat recovery, %	50%
Electricity produced, kW	3913.69
Heat produced, kW	5590.99

Table 2 reports the main data regarding the biowaste composition, highlighting that those sludges have a very low ash content when compared with other biowaste and biomasses. The carbon present in the biowaste is mineralized during the HTC process by producing a limited amount of carbon dioxide in the gas phase (Table 3) and of dissolved carbon in the water phase. Only 15% of gas is produced during HTC (Table 3) and the carbon in this phase is about 27%. Once the reaction is completed, the outlet valve at the reactor top is slowly opened so reducing the pressure inside the reactor and promoting evaporation of water. The evaporation ends when the temperature reaches the boiling value at about 1 bar and, at this stage, about 70% of water is removed under form of steam (Table 3); the rest is a high-rich in nutrients liquid phase at the reactor bottom sent to mechanical dewatering (Table 4) and WWTP. The solid fraction from dewatering is pelletized and dried to form a stable granule (Table 5). The steam is filtered and condensed (Table 6) to form a distillate; only a part of the distillate is further cleaned by reverse osmosis to feed the electrolysis process (Table 7). The granulated biofuel is converted into syngas by means of a BFBG (Table 8) so allowing the production of energy for the self-sustaining of the whole plant.

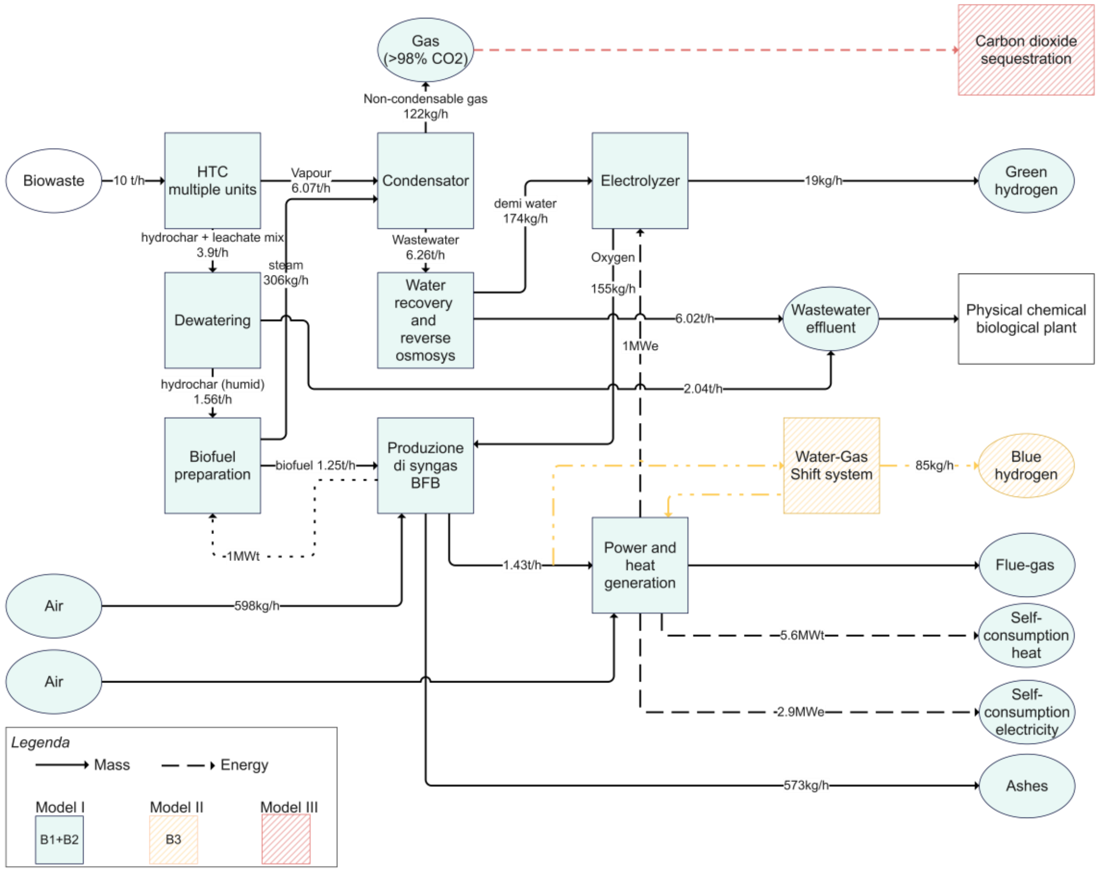

Figure 1: Block diagram of the model (only Model 1 is quantified and considered in the calculations)

4. Conclusions

The conceptual model of a synergistic system that allows the production of green hydrogen by using “circular” electricity and recovered water has been assessed by developing a mathematical model. The H_2 production is energy intensive but also requires a massive fraction of freshwater in a ratio water/hydrogen that is 9:1 [kg]. The model has been built by writing the mass balances over the system boundaries of the main unit processes composing the sub-systems of the whole model. A hybrid experimental-state-of-art database of yields, efficiencies, compositions, chemical reactions, etc, has been used to solve the equations. The evaluation of the energy needs of the main unit processes and the energy produced has also been reported to demonstrate the self-sustaining of the overall model.
The results of the model indicate that:
1. the biowaste containing a low fraction of solids in a water medium can be conveniently transformed into granulated hydro-char by using hydrothermal carbonization in a system operated batchwise with three / four turn-keys per day.
2. the hydro-char can be transformed into a bio-fuel having a good calorific value after proper densification and moisture reduction.
3. the gasification with enriched air obtained by using the oxygen produced as a by-product from the electrolysis of water can produce enough heat and electricity to sustain the whole plant.
4. the green hydrogen can be therefore produced by using demineralized water ad the electricity coming from the biowaste so realizing a real circularity of the integration between “waste management” and “commodity production”.

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