Conceptual design and techno-economic assessment of coupled hydrothermal liquefaction and aqueous phase reforming of lignocellulosic residues

Journal of Environmental Chemical Engineering 11 (2023) 109076

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Conceptual design and techno-economic assessment of coupled hydrothermal liquefaction and aqueous phase reforming of lignocellulosic residues

Edoardo Tito [a], Giulia Zoppi [a], Giuseppe Pipitone [a,*], Edoardo Miliotti [b], Arturo Di Fraia [b], Andrea Maria Rizzo [b], Raffaele Pirone [a], David Chiaramonti [b,c], Samir Bensaid [a]

[a] Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Turin, Italy
[b] Renewable Energy Consortium for R&D (RE-CORD), Viale Kennedy 182, 50038, Scarperia e S. Piero, Florence, Italy
[c] Energy Department DENERG, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Turin, Italy

ARTICLE INFO

Keywords:
Aqueous phase reforming
Advanced biofuels
Biorefinery
Hydrothermal liquefaction
Renewable hydrogen
Techno-economic assessment

ABSTRACT

Hydrothermal liquefaction is a promising technology for producing renewable advanced biofuels. However, some weaknesses could undermine its large-scale application, such as the significant carbon loss in the aqueous phase (AP) and the necessity of biocrude upgrading. In order to deal with these challenges, in this work the techno-economic feasibility of coupling hydrothermal liquefaction (HTL) with aqueous phase reforming (APR) was evaluated. APR is a catalytic process able to convert water-dissolved oxygenates into a hydrogen-rich gas that can be used for biocrude upgrading. Two cases were proposed, based on different lignocellulosic feedstocks: corn stover (CS) and lignin-rich stream (LRS) from cellulosic ethanol production. HTL-APR plants operating with the same mass flow (3.6 t/h) at 10 wt% solid loading were herein evaluated, resulting in an input size of 20 MW (LRS) and 16.5 MW (CS). Based on experimental and literature data, the mass and energy balances were performed; subsequently, the main equipment was designed; finally, the capital and operating costs were evaluated. The analysis showed that the minimum selling prices for the biofuel (0% internal rate of return) were 1.23 (LRS) and 1.27 €/kg (CS). The heat exchangers accounted for most of the fixed capital investment, while electricity and feedstock had the highest impact on the operating costs. The implementation of APR was particularly profitable with CS, as it produced 107% of the hydrogen required for biocrude upgrading. In this case, APR was able to significantly reduce the H_2 production cost (1.5 €/kg) making it a competitive technology compared to conventional electrolysis.

1. Introduction

Growth in energy demand and concerns about greenhouse gas emissions have prompted the development of advanced biofuel processes, such as thermochemical conversion technologies, applied to lignocellulosic or residual biomass [1]. These processes include, among the others, gasification, hydrothermal liquefaction, pyrolysis, direct combustion, and supercritical fluid extraction [2].

Hydrothermal liquefaction (HTL), has several and unique characteristics [3]. Firstly, being in aqueous phase, it can be applied to wet feedstocks without energetically expensive drying pre-treatments. Furthermore, water at high temperature and pressure (sub- and supercritical conditions) significantly modifies its properties, reducing its polarity and increasing the H^+ concentration (due to the increased auto-ionization constant) [4]. As a result, water becomes an excellent solvent for solubilizing and decomposing biomass.

HTL has four different outputs. The main product is the biocrude, a viscous organic phase, having a moderately high heating value (ca. 30

Abbreviation: AC, activated carbon; APR, aqueous phase reforming; BTEX, benzene toluene ethylbenzene xylene; CEPCI, chemical engineering plant cost index; CHG, catalytic hydrothermal gasification; CS, corn stover; CtoG, carbon to gas; DCF, discounted cash flow; DB, dry basis; HT, hydrotreatment; HT FT, high temperature Fischer-Tropsch; HTG, hydrothermal gasification; HTL, hydrothermal liquefaction; IRR, internal rate of return; LLE, liquid-liquid extraction; LRS, Lignin-rich stream; MSP, minimum selling price; PSA, pressure swing adsorption; SR, steam reforming; TEA, techno-economic assessment; WACC, weighted average cost of capital; WB, wet basis; WGS, water gas shift; WHSV, weight hourly space velocity.

* Corresponding author.
E-mail address: giuseppe.pipitone@polito.it (G. Pipitone).

https://doi.org/10.1016/j.jece.2022.109076
Received 10 August 2022; Received in revised form 4 November 2022; Accepted 28 November 2022
Available online 30 November 2022

MJ/kg), but with a considerable residual oxygen content (ranging between 5 and 30 wt%) [5]. For this reason, the biocrude is commonly upgraded (i.e., hydrotreated) in order to remove oxygen and other heteroatoms. Doing so, several properties are improved (storage stability, corrosiveness, viscosity) and it can be used as a source of value-added chemicals [6] and/or as a liquid biofuel [7].

In addition to the biocrude, a gas, a solid (also known as char) and an aqueous phases (AP) are obtained. The gas is mainly constituted by CO_2, and only a minor fraction is represented by H_2 and CH_4, thus commonly resulting in a low heating value [8,9]. The char possesses distinct properties which differ according to the feedstock (moisture content, elemental composition, ash, surface area, etc.). It can be used for contaminant adsorption, soil enhancement and energy valorization [10].

The aqueous phase, whose dissolved organic compounds belong to several different classes of molecules (carboxylic acids, alcohols, ketones, etc.), can contain up to 45% of the feedstock carbon content [11]. This stream cannot be simply disposed of due to the associated costs and the environmental impacts of fresh water continuous supply, as well as the opportunity that the residual molecules exploitation offers.

The main challenges and opportunities of HTL-AP utilization, have recently been addressed by several authors in their review works [12–15]. Different options have been proposed (recirculation, anaerobic digestion, thermal gasification, etc.) [15,16]. Recycling of the AP from HTL has been proven to increase the biocrude yield thanks to the effect of dissolved organics [17,18]. However, this option is feasible when relatively low moisture feedstock is adopted. Hydrothermal gasification (HTG) of water soluble organics allows to produce hydrogen or methane-rich gas from HTL-AP [19], but the harsh reaction conditions and the problem of salt separation are the main drawbacks. Biochemical technologies, such as anaerobic digestion can also produce syngas but the complexity of the AP and the presence of microbial inhibitors represent the main issues hindering these processes [20].

Despite its potential for the exploitation of carbon-laden water fractions, none of these works took into account a novel way of valorizing the aqueous stream derived from hydrothermal liquefaction, i.e., aqueous phase reforming (APR) [21]. It is a catalytic reaction, carried out at mild operating conditions (225–270 °C and 30–60 bar) usually with noble metal catalysts (typically Pt). In these conditions, the dissolved oxygenated compounds, still in the liquid phase, can be converted into hydrogen (and carbon dioxide). Because of that, no vaporization of the aqueous phase is required, resulting in a higher energy efficiency of APR compared to conventional steam reforming (SR) of alkanes. In addition, the low temperature range promotes the water gas shift (WGS) reaction, so that hydrogen yield can be further increased in the same reactor without the necessity of different catalytic systems and multiple reactors [22]. Furthermore, CO content is minimized in the effluent gaseous stream [23]. APR studies commonly focused on the design of the optimum catalytic system, evaluating its performance over simple mono-component solutions [24]. On the other hand, fewer works were devoted to its application over synthetic or even actual mixtures, being closer to an industrially relevant environment [25]. As a matter of fact, strategic synergies can be evaluated when this process is found in combination with other technologies. For example, the hydrogen produced by APR can be then used for upgrading the HTL-derived biocrude by hydrogenation reactions [7]. The hydrogen requirement depends both on the intrinsic characteristics of the biocrude (mainly the heteroatom concentration) and on the catalyst and reaction conditions used in the upgrading step [26]. Since hydrogen is mainly produced by SR of natural gas, greener and renewable options are desirable. Moreover, the cost of hydrogen can have a strong impact for small-scale production facilities [27].

For all these reasons, the HTL-APR coupling is a valuable option to increase the carbon efficiency of the hydrothermal liquefaction, while providing an environmentally friendly source of hydrogen for the upgrading section. Techno-economic assessment (TEA) is a useful tool to investigate the economic viability of an innovative technology. Some works were performed on HTL and APR separately [27–34], but none of them evaluated possible synergies to be exploited, to the best of our knowledge.

In order to fill this gap, in this work the design and TEA of a combined HTL-APR plant was performed starting from two different feedstocks: corn stover (CS), representative of several lignocellulosic agricultural wastes; and a lignin-rich stream (LRS), being the by-product of a second generation bioethanol industrial plant [35]. In the second chapter the main units of the plant are described, as well as the methodology used to perform the economic analysis. In the subsequent section, the results are discussed starting from the mass and energy balances, followed by the design of the main units, and concluding with the economic evaluation. The calculations were based both on experimental data, mostly collected from previous works of the authors [36–38], and from the literature. Key performance indicators (minimum biofuel selling prices, hydrogen cost, etc.) are defined and compared for the different scenarios, while accounting for uncertainties thanks to a sensitivity analysis. Particularly, the lack of precise data with regards to the capital investment related to the low TRL of the examined process was examined, in order to avoid misleading results. This approach allowed to assess the feasibility of this novel integration and identify weaknesses that must be overcome before moving to commercial-scale implementation.

2. Methodology

The main processes involved in the plant are: i) HTL of a wet feedstock, ii) APR of the aqueous phase produced by HTL and iii) hydrotreatment of the biofuel. Two scenarios of HTL-APR coupling with different lignocellulosic feedstocks were studied in this work: corn stover (CS) and lignin-rich stream (LRS), whose characterization is reported in the Supplementary Materials (Table S1.1). The basic scheme of the process is represented in Fig. 1. The battery limit of the plant is from the feedstock pre-treatment to the biofuel production.

The capacity of the plant was chosen equal to 20 MW_{th} of LRS (based on its calorific value), corresponding to 12 t_{wb}/d of LRS (3.6 t_{db}/d) which is consistent with the size of the production of second generation bioethanol plants [39]. The same dry feedstock mass rate was considered for the second case (CS), which is equivalent to 16.5 MW_{th} (due to the different caloric value of the feedstock). This size is coherent with a 50-km radius of harvesting area, according to the average distribution of corn production in Europe [40] (corn/stover production equal to 1:1 [41]).

The model was developed in a Microsoft Excel© spreadsheet where mass and energy balances were performed based on results from experimental work of the author on LRS-HTL and APR; when own experimental data were not available, results from literature were used. Based on the balances, the design of the equipment was performed [42, 43]. The equipment of the gas purification and upgrading sections (heat exchangers, trim heater and hydrotreatment reactor) were not designed in detail, but their costs were evaluated based on correlations derived from the literature.

Hereafter, a brief description of the plant is reported. For a more in-depth description of the main units design, together with the performed calculations, the reader is referred to the Paragraph S2 in the Supplementary material. The preliminary process flow diagram is reported in Fig. S2.1., while the fundamental characteristics of the main equipment can be found in the equipment list (Table S2.2).

2.1. Process description

2.1.1. Pre-treatment

HTL is fed by a lignin-rich/corn stover stream being a byproduct of a cellulosic ethanol plant and an agricultural residue, respectively. Due to the high water-content in the LRS case (70% moisture), the plant was

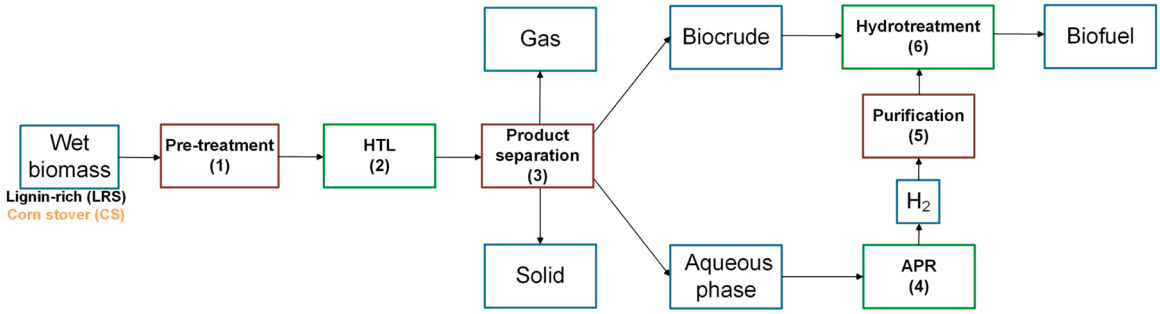

Fig. 1. Block flow diagram of the HTL-APR integrated plant. Block numbers in brackets are identifiers of plant sections.

assumed to be built next-door to the ethanol plant to avoid dewatering of the LRS matrix and high transport cost. The LRS is therefore temporarily stored, milled, and then mixed with recycled and make-up water.

The corn stover is instead harvested three months per year and is stocked to guarantee a continuous flow rate throughout the whole year. The longer time storage than LRS is possible assuming a higher biological stability guaranteed by the reduced amount of residual moisture (5.4 wt% [44]). Afterwards, corn stover is milled and mixed with water for the slurry formation. In order to provide a representative scenario of local biomass availability, the corn production in the province of Turin (Piedmont, Italy) was 522 kt in 2019 [45]. Since the ratio between corn production and stover is 1:1 [41], 522 kt of corn stover were present in Turin province. Therefore approximately 5% of production was needed to meet the plant target capacity, which is a reasonable size that does not pose particular problems in terms of biomass collection and transport logistics.

2.1.2. Hydrothermal liquefaction

The main reaction parameters for HTL reaction, as well as information on products distribution, are outlined in Table 1. Please note that with the term "biocrude" is hereafter defined the raw oil from HTL, while as "biofuel" is defined the upgraded product. For the LRS case, product distribution data were obtained from HTL experiments performed by the authors in a batch reactor at 350 °C for 10 min 10% of biomass to water ratio and no additives [37]. Since the gas phase was not characterized, its composition was based on typical literature values [34].

As far as corn stover is concerned, carbon distribution and aqueous phase composition (0.2 wt% methanol, 0.88 wt% acetic acid and 1.68 wt% glycolic acid) were calculated as average values of the experiments conducted by Panisko et al. with similar operating condition of the LRS case [11]. In order to obtain the distribution among each of the different phases, these information were derived Mathanker et al. [44], since they were not present in [11]. Gas composition was estimated equal to the LRS case, while ash distribution was based on mass balances performed with inorganic elements, as explained in paragraph 2.1.7. Further information on the biocrude and char properties obtained for the two scenarios can be found in Table S1.1.

2.1.3. Product separation

There are four different phases at the outlet of the HTL reactor, therefore an effective product separation is crucial to guarantee a high biofuel yield. In this work the proposed product separation consists of: high-temperature and pressure filtration (solid separation), flash separation (gas separation), and centrifugation (liquids separation). Among the by-products, the gas phase contains mainly CO_2 and has negligible calorific value (LHV= 0.27 MJ/kg); the solid is burnt to provide a portion of the heat required by the plant, while the aqueous phase is sent to the APR section.

Table 1
Main reaction conditions and assumptions of the LRS and CS scenarios.

DATA	LRS	Ref	CS	Ref
HTL DATA				
Temperature (°C)	350		350	
Pressure (bar)	200	[37]	200	[11]
Solid loading (wt%)	10%		10%	
Carbon distribution wt% (*db*)				
Biocrude	53%		49%	
Aqueous phase	16%	[37]	38%	[44]
Gas	15%		10%	
Solid	16%		4%	
APR DATA				
Temperature (°C)	270		270	
Pressure (bar)	60		60	Supp.
Catalyst	5%Pt/C	[38]	5%Pt/C	Mat.
WHSV (kg_C/kg_{cat} h)	0.28		0.40	Fig S3.1-A
Carbon to Gas (CtoG)	20%		48%	
kg H_2/kg C feed	0.037		0.084	
Gas composition vol% (*db*)				
H_2	62		68	Supp.
CO_2	28	[38]	28	Mat.
CH_4	9		4	Fig S3.1-B
C_2H_6	1		0	
HT DATA				
Temperature (°C)	400		400	
Pressure (bar)	104		104	
Catalyst	CoMo/alumina	[46]	CoMo/alumina	[46]
WHSV ($kg_{biocrude}/kg_{cat}$ h)	0.81		0.81	
Product distribution				
Biofuel yield[a]	74.4%		80.0%	
Water yield[a]	30.9%	[32, 46]	23.5%	[32,46]
Gas (C1-C6) yield[a]	2.9%		2.8%	
Hydrogen consumption				
H_2 to reactor (kg H_2/kg dry biocrude)	0.083		0.066	
H_2 consumed (kg H_2/kg dry biocrude)	0.042	[32, 46]	0.033	[32,46]
H_2 make-up (kg H_2/kg dry biocrude)	0.048		0.038	

[a] HT yields are defined as mass of each product (biofuel, water or gas) per mass of dry biocrude. Since H_2 is not considered in the definition, the products sum results higher than 100%.

2.1.4. Aqueous phase reforming

APR is performed in a catalytic (5 wt% Pt/C) fixed bed reactor which converts the carbon-laden water fraction into a gas phase rich in hydrogen by operating at 270 °C and 60 bar. The catalyst amount was calculated assuming the same weight hourly space velocity (WHSV) used in the laboratory scale tests. Its lifetime was assumed equal to 1 year, being this a conservative choice with respect to alternative hypothesis reported in literature [27].

Experimental APR results from the LRS-derived HTL aqueous phase were taken from previous tests performed by the authors [38]. In the CS-derived aqueous phase, APR performances were evaluated on a synthetic mixture whose composition is in agreement with the one from

Panisko et al. [11] and the results can be found in the Supplementary information (Fig S3.1-A,B). The APR results for LRS and CS are reported in Table 1.

2.1.5. Purification

Since the gas phase from APR is a mixture constituted by hydrogen, carbon dioxide, methane etc., it is necessary to separate the desired product from other impurities. For this reason, pressure swing adsorption (PSA) is adopted in this work, assuming for simplicity 100% of H_2 purity and 85% of H_2 recovery [27]. These assumptions are in accordance with the available literature which shows that PSA is from several decades the conventional technique to obtain high purity hydrogen, particularly at small scale [47]. This stream is used for hydrotreating the biocrude in the upgrading section, while the excess quantity (if any) is sold as coproduct.

2.1.6. Upgrading

The biocrude cannot be used as drop-in fuel due to the amount of heteroatoms (N, O, S), hence a subsequent upgrading step is required. For this purpose, it was decided to consider only the hydrotreatment step [34]. However, hydrotreatment (HT) technology is not yet well established for biocrude from HTL and, to the best of our knowledge, no works are known regarding HT of biocrude from LRS-HTL.

HT step converts biocrude into biofuel by catalytic (CoMo/alumina) hydrogenation with H_2 at 400 °C and 100 bar [46]. The relative hydrogen consumptions were calculated to be 0.042 (LRS) and 0.033 (CS) kg H_2/kg dry biocrude, these values took into account the H_2 consumed by side reactions and they were derived from extrapolation of data from the literature [32,46]. These hydrogen consumption resulted similar to those present in the literature [26,34,48]. Due to the low technology readiness level of the hydrotreatment step with regards to the biocrude upgrade, a sensitivity analysis was carried out by varying the amount of hydrogen required for the hydrotreatment. This choice allows to take into account the inherent uncertainties related with this technology.

The carbon yield of subproducts was adapted from [32,46]. In addition to biofuel, an off-gas containing the excess hydrogen is produced. This hydrogen must be separated and purified through PSA to recycle it at the inlet of the reactor. The residual off-gas (LHV=46.6 MJ/kg) is sent to the gas-burning furnace to recover its residual calorific value, while ammonia was assumed to be recovered mostly in the wastewater as reported from the literature [49]. Table 1 summarizes the yields of subproducts from dry biocrude are reported for both cases. The catalyst amount was calculated assuming a weight hourly space velocity (WHSV) equal to 0.81, as suggested by PNNL [46], and with a useful life of 2 years.

When APR was not able to fulfill the entire hydrogen need of the biocrude upgrading, the building of a hydrogen generation plant was simulated to provide the necessary missing quota. In the reference case, it was supposed that an alkaline electrolysis system was implemented [50]. Since the hydrogen production technology has a significant impact on the final fuel selling price, an alternative process was considered for the sake of comparison, i.e., steam reforming of natural gas. In order to carry out its design, technical parameters based on commercial plants were used, and the catalyst was assumed to have a 5-years life [46]. The followed methodoloy, i.e., designing an on-site hydrogen generation plant rather than considering hydrogen as an operative cost, is commonly performed in literature for similar systems [51–54]. In fact, it takes into account the decentralized nature of biorefineries, which would lead to high costs for transportation and delivery if hydrogen derives from a centralized plant. In addition, it allows for a more precise estimation of the hydrogen price than average data available in databank, thanks to its sensitivity to the plant size.

2.1.7. Aqueous phase recycling

Due to the consistent amount of water required, wastewater at the outlet of the APR was recycled to dilute inlet feedstocks. This recycling improves the sustainability and cost-effectiveness of the process by reducing the supply of fresh water and the disposal of wastewater. For the LRS case, the effect of the recycling was tested through preliminary batch experiments (Paragraph S5 Supplementary Materials). In the LRS case, the three main inorganic elements were Na, K and Ca, probably in the form of carbonates.

For the CS case, the main inorganic elements present in the aqueous phase (Na, K) were evaluated from Panisko et al. [11]; the inorganic distribution to biocrude and char was assumed to be equal to the one of LRS. The hypothesis is based on the findings of Toufiq Reza et al., which observed that most of the ash content in corn stover can be found in its lignin fraction [55]. In both cases, a large amount of inorganic compounds remains in the aqueous phase and a purge is therefore necessary to avoid their build-up. APR tests were carried out with water containing up to 3000 ppm of Na and no deactivation was observed. To evaluate the purge ratio, it was assumed that the recirculation didn't change the inorganic distribution between the phases. As the purge ratio varied, it was possible to calculate the amount of inorganics present in the recycling loop. The amount of recycled water was hence evaluated to not exceed the 3000 ppm of inorganics at the inlet of the APR reactor.

Besides inorganic compounds, a build-up of organic was also present, especially acetic acid [56]. Therefore, its presence can be considered as an "inert" carbon. To this end, the amount of carbon soluble in the aqueous phase coming out of the APR reactor was assumed to be inert through HTL and APR. Knowing the purge ratio, was possible to know the amount of "inert" carbon present inside the recycling loop. The amount of fresh water needed to dilute the feedstock was calculated accordingly to the purge ratio.

2.2. Economic assessment

2.2.1. Capital costs

The aim of the work was to compare the two scenarios and calculate the minimum fuel selling price and the production cost of hydrogen from APR. Due to the low TRL of the hypothesized plant, uncertainties in the estimations should be carefully taken into account. For this reason, the deterministic results obtained in this section were further discussed in the sensitivity analysis, where the values of the main variables were modified in the range suggested by the technical literature to examine their relative influence on the economic indicators.

The economic analysis was performed considering preliminary estimates, which have a typically accuracy of ± 30%, in accordance with the Association for the Advancement of Cost Estimating International (AACE International) [57]. Fixed capital investment was based on the grassroots costs evaluated by the module costing technique described in [58]. Grassroots costs are related to the construction of a new facility and include direct and indirect costs, contingency, fee and auxiliary facilities costs. The module cost technique relates plant costs to the purchased cost of each piece of equipment, based on Guthrie method [59]. If correlations for bare module cost were not present in [58], these were taken from [59] or from extrapolation from other sources; details are reported in Supplementary S4. Due to the pandemic situation, the costs were discounted to 2019 through the CEPCI factors ($CEPCI_{1968}$ =112; $CEPCI_{2001}$ =397; $CEPCI_{2019}$ =608) and converted in euros (USD/EUR=1.11).

2.2.2. Operating costs

Operating costs were evaluated based on unit costs shown in Table 2. Apart from the feedstock cost, the other items were assumed equal in both simulations.

Feedstocks costs were assumed to be 60 €/t for lignin-rich stream and 75 €/t for corn stover, as found in literature [60,61]. Costs for electric power and natural gas were average values present in the EU market in 2019. Regarding the APR catalyst, Sladkovskiy et al. reported the possibility to neglect the cost of Pt due to its possible recover at the end of its

Table 2
Data for the material & utilities costs.

Item	Unit	Price	Ref.
LRS feedstock (*db*)	€/t	60	[60]
CS feedstock (*db*)	€/t	75	[61]
Electric power	€/kWh	0.09	[62]
Natural gas	€/Nm^3	0.35	[63]
Cooling power	€/MWh	0.9	[64]
Make up water	€/t	3.5	[53]
Wastewater disposal	€/kg COD	0.064	[51]
APR catalyst	€/kg	45	[27]
HT catalyst	€/kg	28	[46]
SR catalyst	€/t H_2	6.54	[46]
H_2 selling price	€/kg H_2	5	[65]

lifetime [27]. For the evaluation of the overall operating cost, the labor and maintenance costs were added to the material & utilities cost. Labor cost was assumed to be equal to 56100 €/y per worker and the number of operators was calculated based on the Turton method [58], to which other workers were added (supervisor, logistic, amminstration etc). Maintenance was assumed equal to 5% of the sum of fixed capital investment and startup cost every year.

2.2.3. Minimum selling price

The objective of the work is to define the minimum selling price (MSP) of the biofuel; this was carried out using the "Discounted Cash Flow" (DCF) method. The depreciation and plant life were fixed to 20 years and the main set parameters are reported in Table 3. Maintenance cost takes into account both ordinary and extraordinary maintenance due to the long plant life.

Please note that the figures evaluated in the twenty-year projection profile are real values. It means that they were kept constant throughout the entire life plant, without considering possible variations dependent on inflation trends.

As regards the return on invested capital, two hypotheses were considered:

- Contribution of the necessary equity by a public operator, non-profit making, in pursuit of environmental objectives with generation of positive non-economic externalities (IRR=0%).
- Contribution of the equity by a private operator, pursuing profit objectives (IRR = 10%).

Two MSPs values were hence herein evaluated, differentiated by internal rate of return (IRR). The use of a MSP with an IRR= 0% (hereafter referred to as MSP$^{0\%}$) was justified by the fact that the specificity of the energy sector and the need for public incentives for the ongoing ecological transition may consider the assumption of public support to the initiative. On the other hand, MSP with an IRR= 10% (hereafter referred to as MSP$^{10\%}$) is usually used as reference parameter to evaluate biofuel profitability [30,52,54,61,66–68]. Based on this, the MSP$^{0\%}$ was calculated to assess the profitability of the plant and to perform the sensitivity analysis. The MSP$^{10\%}$ was instead evaluated to be consistent with the literature and to allow for comparison with other TEAs based on technology differences rather than different economic management assumptions.

Table 3
Economic set parameters.

Parameter	Value
Startup cost	5% of fixed capital investment
Working Hours	8000 h/y
Depreciation time	20 y
Starting ratio equity/debt ratio	75%/25%
Income tax rate	33%
Internal rate of return (IRR)	0–10%

The production of hydrogen used for the biocrude upgrade via APR is one of the actual benefits of the coupling of these two processes. Therefore, it is worthy to evaluate the hydrogen production cost by this technology. Since the two sections are thermally integrated, it was not possible quantifying it only considering the APR section. Hence, it was quantified by difference, i.e., subtracting to the global costs of the integrated HTL-APR plant the contribution of a virtual plant in which the APR section is not implemented. The hydrogen production cost was then evaluated as ratio of the difference in costs to the amount of hydrogen that APR can produce with the integrated plant (Eq. (1)). When electrolysis was necessary (LRS scenario), its costs were not taken into account for a safe comparison.

$$H_2 production\ \ cost_{APR} = \frac{\sum costs_{HTL+APR} - \sum costs_{HTL}}{H_2 mass\ \ production(APR)} \quad (1)$$

2.2.4. Sensitivity analysis

At the end, a sensitivity analysis was conducted to study the effects of some fundamental parameters (operative costs, hydrotreatment step parameters, investment, plant life, catalyst cost and nominal size) on the biofuel cost. Furthermore, scenarios with different sources of H_2 (SR plant or alkaline electrolyzer) were analyzed for comparison with the HTL-APR coupling.

Table 4 reports the variations used for the sensitivity analysis. The determination of the feedstocks price is intrinsically complicated by the fact that a market for lignin and corn stover has not yet been established. For this reason, the effect of a change in the cost of LRS and CS was investigated by varying it in a wide range (± 50%). As regard electricity and natural gas cost variations, the minimum and maximum costs from EU countries in 2019 were taken as ranges for the sensitivity.

To assess the impact deriving from the uncertainties in the hydrotreatment step, the amount of hydrogen required for the upgrading and the biofuel yield were varied. The range for the H_2 required was considered between the lowest and highest values found in the literature for lignocellulosic feedstocks (26–40 g/kg dry biocrude [26,48]). The HT-biofuel yield was changed within ± 5%, in accordance with common procedures carried out in similar TEA [48].

The MSP variation was assessed for different plant life, plant size and different total and hydrotreatment-related investment cost. Total investment costs were varied within ± 30%, according to the accuracy of the used method [57], while HT investment costs were modified on a wider range (± 50%) due to the higher uncertainties. In addition, the influence of catalyst cost on the minimum fuel selling price was assessed, considering a 52–153 €/kg range [69]. The upper value was derived from the work of Baral et al., correcting by the lower metal loading used herein (5%) with respect to the reference (10%). This analysis was carried out to take into account the impact of limitations in the noble metal catalyst recovery ability on the economic profitability of the plant.

The impact on the MSP was also assessed in case a 20% solid loading in the inlet slurry. The carbon distribution and elemental composition of the products, as well as the APR reaction parameters, were maintained equal to the 10% solid loading case. This assumption was in agreement

Table 4
Variations used for the sensitivity analysis.

Item	Min	Max	Unit
Feedstock price	-50%	+ 50%	%
Electricity price	54	144	€/MWh
Gas natural price	0.23	0.61	€/Nm^3
APR catalyst price	–	153	€/kg
H_2 consumption	26	40	g/kg biocrude
Biofuel yield	-5%	+ 5%	%
Plant life	15	30	y
Plant size	10	40	MW_{th}
Total investment cost	-30%	+ 30%	%
HT investment cost	-50%	+ 50%	%
Solid loading	–	20%	wt%

with experimental tests performed by the authors (LRS case) and a previous work by Zhu et al. [34] (CS case). In order to take into account the differences in the slurry rheological properties, pumps and heat exchangers for the 20% solid loading case were sized assuming an increase in the slurry viscosity of 10 000 times compared to that of water (used for the 10% case). This assumption was based on slurry viscosity range from PNNL [70].

As one of the key aspects of this work concerns the production of hydrogen needed for upgrading, the economic impact of replacing the H_2 derived from the APR section was evaluated. Steam reforming and electrolysis were the two H_2-producing technologies compared with APR, since they represent respectively the most established way and the most investigated decarbonized option.

3. Results and discussion

3.1. Mass balance

Table 5 and Fig. 2 show the main inputs and outputs of the plant.

As regards the production of biocrude, the two cases had a mass yield (dry biocrude/dry feedstock) of 39.0 wt% (LRS) and 29.0 wt% (CS); the biofuel yields after upgrading were 29.1% (LRS) and 23.4% (CS). The H_2 yield of the HTL-APR integrated plant was lower with LRS (0.039 Nm^3/kg dry LRS) than with CS (0.131 Nm^3/kg dry CS). The difference was due to the higher organic concentration in the AP for the CS case and to the presence of compounds with higher H_2 productivity.

In addition, due to the higher oxygen content and mass flow of the biocrude, the H_2 required for upgrading was greater with LRS than with CS. It follows that, in the LRS case APR was able to provide only 19% of the H_2 required for hydrotreatment, while for CS the HTL-APR coupling was particularly advantageous in that it resulted in a surplus of hydrogen (107% of the H_2 required) that was assumed to be sold as coproduct.

A higher char yield was obtained using LRS, compared with CS, and this stream was not valued as coproduct but instead was energetically exploited in situ.

Wastewater purge ratios resulted equal to 0.29 (LRS) and 0.32 (CS). In this way, the amount of inert carbon at APR outlet were 34.8 g C/L (LRS) and 26.7 g C/L (CS) while inorganic compounds remained below 3000 ppm. The amount of water required to dilute the slurry was mainly derived from the purging, promoting the sustainability of the process. The demand for fresh water was limited to 3.3% (LRS) and 30.1% (CS) of the overall water demand.

Table 5
Main input and output streams.

	LRS	CS
Main input (kg/h)		
Feedstock (*wb*)[a]	12000	3805
Feedstock (*db*)[a]	3600	3600
Make-up water	780	9706
Relevant internal streams (kg/h)		
Water from recycling	23220	22489
HTL inlet	36000	36000
H_2 required for HT	67	40
H_2 produced from APR	13	43
H_2 missing quota	55	0
Main output (kg/h)		
Biocrude (*db*)	1406	1050
Biofuel (*db*)	1047	841
H_2 surplus	0	3
Solid char	619	171
Wastewater	10169	11091

[a] feedstock of the plant (corn stover or lignin-rich stream).

3.2. Energy balance

The block diagram in Fig. 3 shows the energy streams for both cases.

Several heat exchangers allow the partial recovery of thermal power from the HTL products stream, saving 11.9 MW_{th} (LRS) and 12.6 MW_{th} (CS). After the economizers, the remaining heat is provided by diathermic oil from the furnace. The char combustion in the furnace, allowed to save 3.2 MW_{th} (LRS) and 0.8 MW_{th} (CS). The heat required for the APR section is completely provided by the economizer, able to preheat the feed and to cool down the liquid product, and by the thermal integration with the HTL section. Before gas separation and after compression of the product gas (purification section) further heat must be removed. For the LRS plant, an additional amount of heat from the electrolyzer shall be removed (1.1 MW_{th}). The upgrading section required 0.2 MW_{th} to heat up the biocrude for hydrotreatment that it is partially provided by the off-gas sent to the furnace, leading to a positive thermal balance of the upgrading section.

The overall energy consumptions are shown in Table 6. The overall required thermal power was similar between the two cases (41 GWh/y for LRS and 40 GWh/y for CS); however, due to a lower production of char and off-gas from upgrading, the net thermal demand provided with natural gas was higher with CS. Cooling power did not differ strongly between the two cases while the discrepancy between the electricity consumption was mainly due to the energy cost (26 GWh/y) of the electrolyzer.

3.3. Economic analysis

In Table 7 the main sections identified in the biorefinery are summarized along with the main unit operations. In order to evaluate the economic feasibility of the proposed integrated plant, the main equipment were designed to determine their cost.

The overall costs are summarized in Table 8. The details of capital and operating costs are detailed below.

3.3.1. Capital costs

Fixed capital investments were equal to 26.8 M€ and 22.2 M€, for LRS and CS case, respectively. The distributions of these costs between the sections of the plant are reported in Fig. 4; in Fig. S6.1 the breakdown of costs between equipment is reported.

The HTL section was the most expensive of the plant due to the high number of heat exchangers operating at high pressure (LRS: 24%; CS: 29% of the overall fixed capital cost), to the hose pump P-201 (LRS: 8.1%; CS: 9.7%) and, secondly to the HTL reactor (LRS: 5.4%; CS: 6.5%). APR was also quite demanding from the economic point of view (LRS: 15%; CS: 16% of the overall cost) and its impact mainly derived from the heat exchangers (LRS: 7.2%; CS: 6.2%) and the APR reactor (LRS: 4.1%; CS: 6.0%). Biomass pre-treatment had almost no impact on costs, as well as the product separation section.

Cost differences between the LRS and the CS case were mainly due to the purification and upgrading sections: 30% of the fixed capital investment for the LRS case were allocated to the upgrading section because of the electrolyzer (16% of the overall cost), which is needed to supply the missing hydrogen. On the other hand, in the CS case the purification section cost was almost double of the LRS case due to the higher amount of hydrogen produced from APR.

3.3.2. Operating costs

Operating costs accounted for 8.2 M€/y and 6.7 M€/y for the LRS and the CS case, respectively. As can be seen from Fig. 5, one of the two highest costs was related to the purchase of the feedstock. In the LRS case, the highest cost was due to electricity, especially related to the electrolyzer. Maintenance had the same impact in both cases (17% of the overall operating costs) while labor had the same cost but different share. In the CS case natural gas accounted for 13%, due to the higher energy input required, and water make-up accounted for 4%, due to the

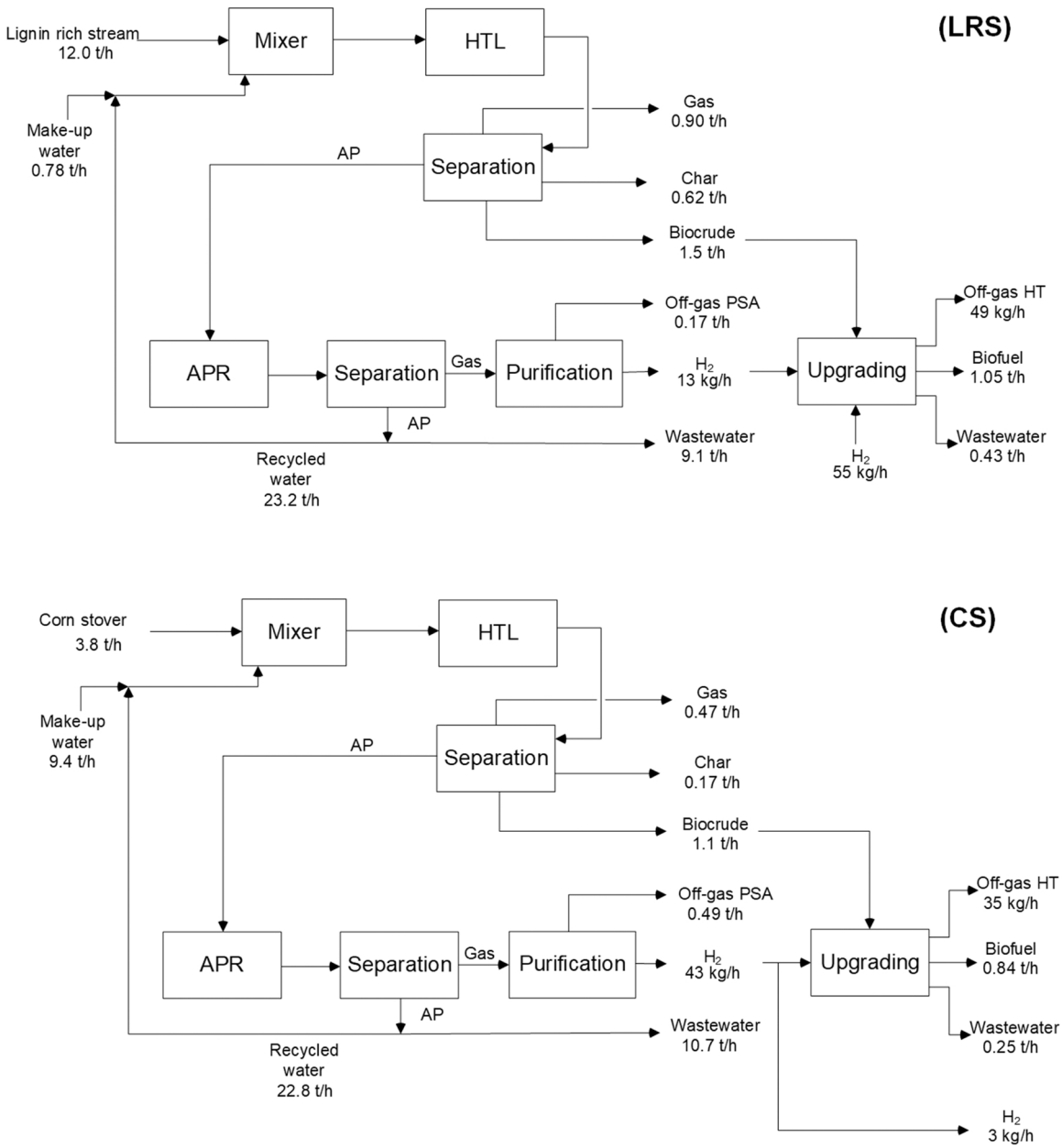

Fig. 2. Mass flows for the LRS case (above) and the CS case (below).

low moisture of the feedstock. Wastewater disposal was modest in both cases (6%), while catalysts and cooling power costs had very low impacts.

Within the CS case, the credit from the sale of the produced hydrogen was subtracted from the material & utilities costs, resulting in a slightly lower net cost (6.6 M€/y).

3.3.3. *Minimum selling prices and economic indicators*

The resulting $MSPs^{0\%}$ of the biofuels were 1.23 €/kg (LRS) and 1.27 €/kg (CS) and, assuming a distillation cut similar to diesel (LHV=43 MJ/kg), the gasoline equivalent prices were equal to 3.43 €/GGE (LRS) and 3.54 €/GGE (CS). The $MSPs^{10\%}$ were 1.57 €/kg (4.40 €/GGE) and 1.63 €/kg (4.54 €/GGE) for the LRS case and the CS case, respectively, which are in the range of existing TEAs. For comparison with the present work, the MSPs of other biofuels in the literature are given in Table S7.1.

In Table 8 the main economic parameters are reported.

The H_2 production costs were estimated at 7.7 €/kg (LRS) and 1.5 €/kg (CS). The costs attributable to the APR section were mostly dependent on the amount of aqueous stream to be treated, which was approximately the same for both cases. Hence, the higher profitability of the CS case was ascribed to its higher H_2 production rate. APR competitiveness therefore strongly depends on the carbon concentration and H_2 productivity of the organic compounds present in the aqueous phase.

Compared to the literature, both these values are significantly lower than the hydrogen produced by APR of sorbitol syrup (11.7 €/kg) [27], which was heavily penalized by the high cost of the feedstock that constituted up to 91.8% of the overall costs. In this work, APR was instead carried out on a low value stream. In addition, the HTL-APR coupling also allowed the reduction of the COD of the HTL water, resulting in lower disposal costs and higher profitability. Khodabandehloo et al. also assessed the economic performance of APR from a by-product of glycerol stream from biodiesel production [28]. Glycerol was assumed to have a residual value of 45 €/kg, and the resulting H_2 production cost was estimated to be 6.7 €/kg. Although slightly lower than the LRS case, this value is much higher than in the CS case.

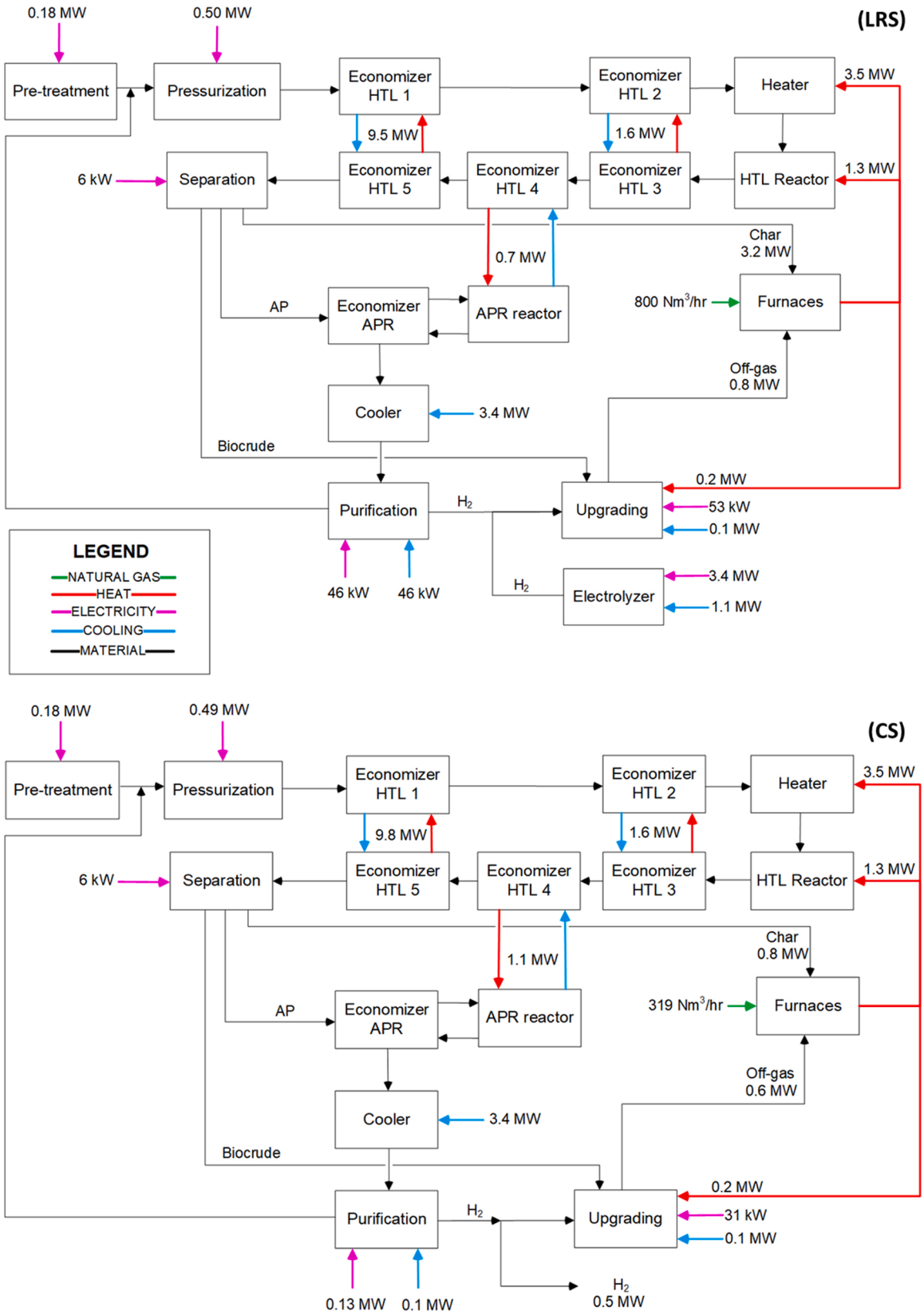

Fig. 3. Block diagram and energy streams for the LRS case (above) and the CS case (below).

Table 6
Electric and thermal yearly inputs of the plant.

	LRS	CS
Electric power (GWh)	34.0	7.1
Cooling power (GWh)	33.9	29.9
Natural gas (GWh)	7.1	28.3

Table 7
Plant sections and unit operations.

Section number	Section name	Unit operations
1	Biomass pre-treatment	Storage, Mixing, Milling
2	Hydrothermal liquefaction	Heating, HTL reaction, Cooling
3	Product separation	Flash evaporation, Filtration, Centrifugation
4	Aqueous phase reforming	Heating, APR reaction, Flash
5	Purification	Compression, Cooling, PSA
6	Upgrading	Hydrotreatment, H_2 production, Electrolyzer[a]

[a] Implemented only for the LRS case.

Table 8
Economic parameters and main indicators for LRS and CS case.

	LRS	CS
Fixed capital investment (M€)	26.8	22.2
Start-up cost (M€)	1.3	1.1
Total investment cost (M€)	28.2	23.3
Maintenance cost (M€/y)	1.4	1.2
Material cost (raw material, catalyst, water) (M€/y)	2.5	3.0
Utilities cost (M€/y)	3.3	1.5
General cost (M€/y)	0.6	0.6
Labor cost (M€/y)	1.0	1.0
H_2 credit (M€/y)	0	0.12
$MSP^{0\%}$ (€/kg)	1.23	1.27
$MSP^{10\%}$ (€/kg)	1.57	1.62

The cost of producing hydrogen from steam reforming (SR) and electrolysis was also calculated as benchmark. These values were obtained by means of correlations, reported in the Supplementary paragraph S4, based on the flow rates required by the two cases. The resulting costs were 2.7–2.9 €/kg for SR and 6.4–6.5 €/kg for electrolysis, which fell within the ranges known for these two technologies: 1.3–3.6 €/kg for steam methane reforming [71] and 3–9 €/kg for electrolysis using different electricity sources [72]. Although the hydrogen requirement in this work fell within the lower operability limit of the typical SR plant, the use of a centralized upgrading plant, where biocrudes are collected from multiple HTL plants, could be economically beneficial if SR is adopted. On the other hand, with APR this lower limit does not exist and hence this technology can be a valid solution for HTL plants with in-situ upgrading. The comparison with other technologies for hydrogen production will be investigated in detail in paragraph 3.3.4.

3.3.4. Sensitivity analysis

The $MSPs^{0\%}$ variations, related to the parameter described in the methodology paragraph, are reported in Fig. 6. As can be seen from the figure, the main factor affecting both cases was plant size: a reduction to 10 MW in nominal capacity would lead to a large increase in MSP (+21% LRS, +26% CS). On the other hand, an opposite increase to 30 MW would lead to a less pronounced decrease (−6.8% LRS, −9.5% CS). However, a bigger plant would require adequate biomass availability. The second most impacting on the $MSP^{0\%}$ of the LRS-derived biofuel was the electricity price (−12%/+17%). This is attributable to the high amount of electricity required by electrolysis; therefore, the dependence on electricity is not to be traced directly to the HTL-APR integration, but to the missing quota of hydrogen that APR was not able to provide. In fact, an HTL-APR plant capable of being self-sufficient in the production of hydrogen limits the strong influence that electricity has on the selling price of the biofuel. This is corroborated by the lower MSP variations observed for electricity price variation for the CS-case (−3.1%/+4.4%).

The increase of solid loading to 20 wt% led to a reduction in the capital and operating costs in both cases, resulting in a significant decrease of 9.6% (LRS) and 11% (CS) in both $MSPs^{0\%}$. This is attributable to the fact that with a double solid loading the flow rate of the biofuel produced is kept constant while the mass flow to be treated is halved. However, with state-of-the-art technology it is difficult to pump slurry with 20% of solid [73]. This problem is strictly linked to the biomass feature and is currently receiving great attention in order to evaluate, on the different types of substrates, the optimal solution (pre-treatments, basic additives, biocrude recycling). This result confirmed a commendable improvement of the economic performance of a plant operating at a higher solid concentration, but further investigations are necessary to support its technical feasibility.

Feedstock price variation changed the LRS-$MSP^{0\%}$ within ± 8.3% while changed the CS-$MSP^{0\%}$ within ± 13%; despite it was important in both cases, the variation was particularly evident for the CS case because of the high share of the feedstock in the operating costs. Also, the impact of the cost of natural gas was higher with the CS case than in the LRS case because of the almost thermal self-sufficiency of the latter. Natural gas

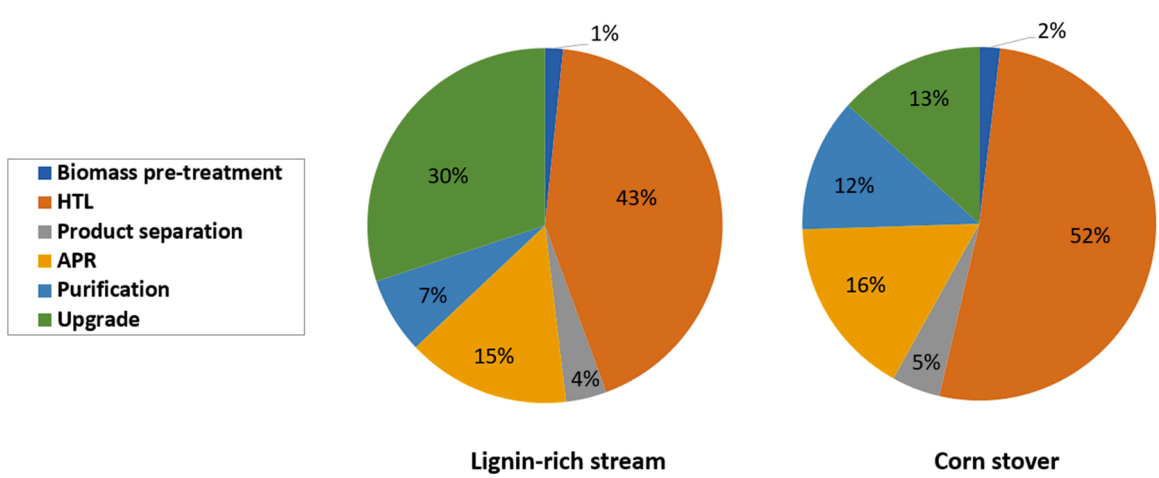

Fig. 4. Grassroot costs breakdown between sections, with LRS case (left) and CS case (right).

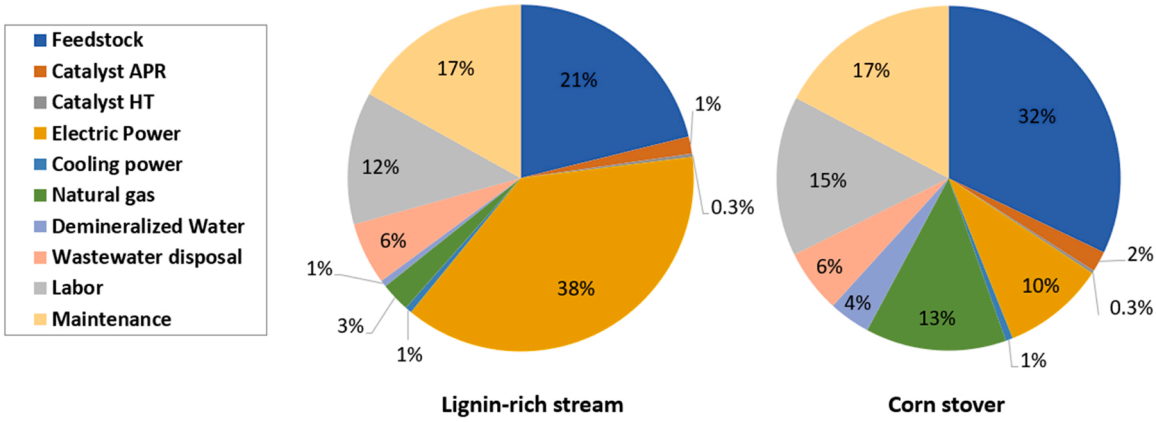

Fig. 5. Operating costs, with LRS case (left) and CS case (right).

Fig. 6. $MSP^{0\%}$ changes as consequence of the sensitivity analysis performed for the lignin-rich stream (above) and corn stover (below) scenario.

cost variation had the smallest impact among all the parameters studied for the LRS case (−0.7%/+1.6%) while was the fifth most impacting parameter for the CS case (−3.5%/+7.6%). Catalyst cost increase led to very low variations (+3.0% LRS, +5.1% CS), especially when referring to the high value used for sensitivity.

The hydrogen requirement for the hydrotreatment step for the LRS-

derived biocrude was higher than values reported in the literature. In addition, the value of 26 g/kg, chosen as the minimum value for sensitivity, was lower than the required stoichiometric value (31 g/kg): the latter was therefore used as the minimum value for sensitivity. The decrease in hydrogen requirement led to a consistent decrease in $MSP^{0\%}$ (−7.9%) for the LRS case. On the other hand, the variation in hydrogen consumption for the CS case led to a lower variation in $MSP^{0\%}$ (−3.2%/+3.9%). However, for the upper limit value of the analysis (40 g/kg), it was necessary to introduce the electrolyzer to produce the 12% of the hydrogen required that APR was no more able to produce.

In both cases HT biofuel yield variations (± 5%) led to MSP variations (−4.7/+5.2%) proportional to the increase/decrease of biofuel produced.

Among the uncertainties for investment costs and plant life, the total investment cost has the biggest impact: ± 30% variation led to ± 8.1% (LRS) and ± 8.2% (CS) change in the $MSPs^{0\%}$. Different assumptions for the plant life also impact the $MSPs^{0\%}$ (−5.0%/+5.3% for LRS and −5.1%/+5.3% for CS) while ± 50% variations of the HT investment cost had very low effect on the $MSPs^{0\%}$.

In order to evaluate the competitiveness of the APR implementation, different plant configurations for the hydrogen supply are described in Fig. 7, along with the $MSP^{0\%}$ variations with respect to the base configuration.

Looking at the LRS case, an external hydrogen source was always required because APR can produce only 19% of the hydrogen needed for upgrading. Compared to the production of the remaining 81% via electrolysis (Fig. 7A), the use of SR was economically very advantageous (Fig. 7C) as the $MSP^{0\%}$ was reduced by 18%. The resulting $MSPs^{0\%}$ in configuration E (only electrolyzer) and D (only reforming) turned out to be lower than with APR. The economic advantage of using SR and electrolyzer instead of APR derives from their lower H_2 production cost.

For the CS case, the integrated HTL-APR plant (Fig. 7B) was able to produce 107% of the hydrogen required by the upgrading section. In this case, the replacement of the APR section with electrolyzer (Fig. 7E) or SR (Fig. 7D) led to an increase of $MSP^{0\%}$ (+18% and +3.5%, respectively). These results confirmed the lower H_2 production cost through HTL-APR (1.5 €/kg) compared to the other technologies. The economic performance of the HTL-APR plant was further improved by the fact that a surplus of hydrogen can be sold, thus increasing the revenue.

$MSPs^{0\%}$ for the LRS-derived biofuels were much lower than the CS-derived ones if conventional H_2-producing technologies were used: 1.21 vs 1.49 €/kg with electrolysis and 0.95 vs 1.31 €/kg with steam reforming. This was mostly due to the higher biofuel productivity with LRS, despite LRS-derived biocrude was more oxygenated and hence required higher upgrading expenses. However, the difference between $MSPs^{0\%}$ of the two cases with the integrated HTL-APR plants (case A and B) was almost levelled; this was due to the high H_2 productivity (107% of the hydrogen required) through APR of the residual aqueous phase from HTL of CS. For this reason, while HTL plants are more profitable with feedstocks or operating conditions which allows higher biocrude yield and quality, good carbon yield in the aqueous phase and good hydrogen yield (kg H_2/kg C feed) are required to make the HTL-APR

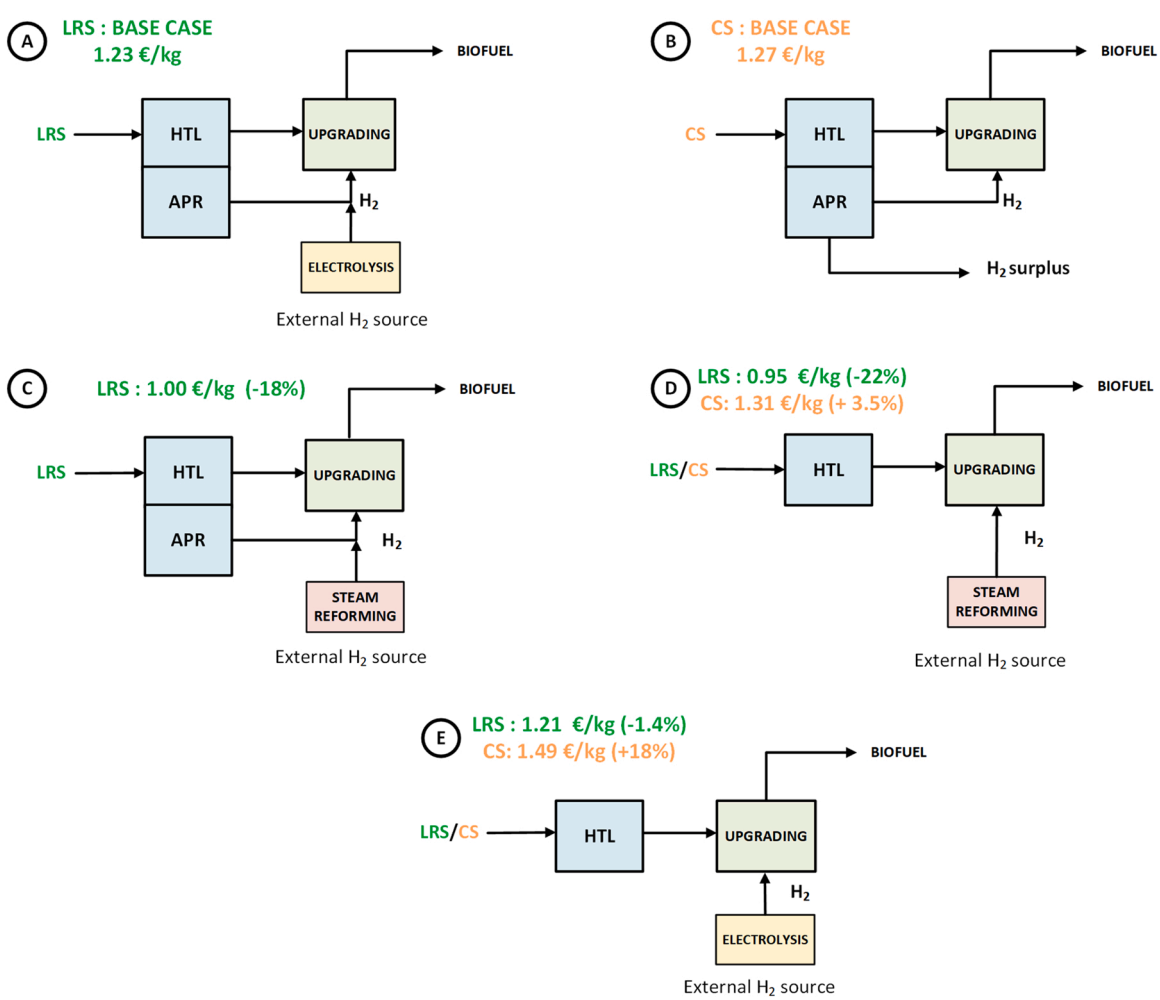

Fig. 7. plant configurations for hydrogen supply. A) APR+electrolysis, B) APR alone, C) APR+SR, D) SR alone, E) Electrolysis alone, F) No upgrading. The percentage values refer to the variation of the $MSP^{0\%}$ of the considered configuration compared to the respective base case (A for LRS and B for CS).

integration attractive.

4. Conclusion

This study investigated the conceptual design and a novel techno-economic assessment of an HTL-APR integrated plant. Hydrothermal liquefaction has been confirmed as an appropriate technology for producing advanced biofuels, while APR has shown great potential to be coupled with it.

Two different feedstocks were compared, maintaining the same mass flow rate and 10 wt% of solid loading: a lignin-rich stream (LRS, 20 MW input) and corn stover (CS, 16.5 MW input).

The design was carefully customized to increase the carbon recovery and energy efficiency by valorizing the by-products. In order to do this, it was important to overcome technical issues, such as the separation section.

The economic assessment evaluated the capital and operating costs resulting in a minimum selling price with IRR 0% (IRR 10%) of 1.27 (1.62) €/kg for CS and 1.23 (1.57) €/kg for LRS. A sensitivity analysis was performed to understand how the main operating cost items impacted the MSP. For both cases, this was consistently affected by the feedstock cost variation: ± 8.3% for LRS, ± 13% for CS. Variations to the electricity price significantly influenced the MSP of the LRS-derived biofuel, mainly due to the high electricity demand for electrolysis. Instead, for the CS case, total investment costs uncertainties and natural gas cost variations had a consistent impact. A first economic assessment for a 20% solid loading plant was made, resulting in a MSP reduction of 10–11%.

Finally, various scenarios showed that the addition of an APR section to the HTL plant has great potential, especially for the corn stover case. In fact, the hydrogen production costs were 7.7 €/kg (LRS) and 1.5 €/kg (CS). The compellingly low value of the latter was attributed to APR, being able to produce 107% of the hydrogen required for biocrude upgrading. This indicates that APR can be a useful process for producing greener hydrogen, but its effectiveness is strongly related to the feedstock. In fact, LRS and CS showed different compositions of biocrude (lower hydrogen demand for CS-derived biocrude) and hydrogen productivity from the aqueous phase. It is worth noting that these results should be confirmed in an industrially relevant environment. In fact, while a real water stream from lignin-rich HTL was used for the assessment, it will be necessary evaluating the APR performance also in the case of real water fractions from corn stover HTL and taking advantage of more robust design data availability (such as for the biocrude upgrade step).

To conclude, the proposed biorefinery shows great potential for the production of biofuels from lignocellulosic residue, reducing the need for fossil hydrogen thanks to the striking balance between HTL and APR.

CRediT authorship contribution statement

Edoardo Tito: Data curation, Formal analysis, Investigation, Methodology, Writing – review & editing. **Giulia Zoppi**: Data curation, Formal analysis, Investigation, Methodology, Writing – review & editing. **Giuseppe Pipitone**: Data curation, Methodology, Supervision, Writing – review & editing. **Edoardo Miliotti**: Data curation, Formal analysis, Writing – review & editing. **Arturo di Fraia**: Data curation, Formal analysis, Writing – review & editing. **Andrea Maria Rizzo**: Investigation, Methodology, Project administration, Supervision, Writing – review & editing. **Raffaele Pirone**: Conceptualization, Formal analysis, Investigation, Methodology, Validation, Writing – review & editing. **David Chiaramonti**: Conceptualization, Project administration, Resources, Writing – review & editing. **Samir Bensaid**: Conceptualization, Project administration, Supervision, Writing – review & editing.

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.

Data availability

Data will be made available on request.

Acknowledgment

The project leading to this research has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement N° 764675.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2022.109076.

References

[1] L. Zhang, C. (Charles) Xu, P. Champagne, Overview of recent advances in thermo-chemical conversion of biomass, Energy Convers. Manag 51 (2010) 969–982, https://doi.org/10.1016/j.enconman.2009.11.038.
[2] A. Dimitriadis, S. Bezergianni, Hydrothermal liquefaction of various biomass and waste feedstocks for biocrude production: A state of the art review, Renew. Sustain. Energy Rev. 68 (2017) 113–125, https://doi.org/10.1016/j.rser.2016.09.120.
[3] L. Grande, I. Pedroarena, S.A. Korili, A. Gil, Hydrothermal liquefaction of biomass as one of the most promising alternatives for the synthesis of advanced liquid biofuels: A review, Mater. (Basel) 14 (2021), https://doi.org/10.3390/ma14185286.
[4] D. Castello, T.H. Pedersen, L.A. Rosendahl, Continuous hydrothermal liquefaction of biomass: A critical review, Energies 11 (2018), https://doi.org/10.3390/en11113165.
[5] J. Lu, J. Watson, Z. Liu, Y. Wu, Elemental migration and transformation during hydrothermal liquefaction of biomass, J. Hazard. Mater. 423 (2022), 126961, https://doi.org/10.1016/j.jhazmat.2021.126961.
[6] C. Rutten, A. Ramírez, J. Posada Duque, Hydrotreating and hydrothermal treatment of alkaline lignin as technological valorization options for future biorefinery concepts: a review, J. Chem. Technol. Biotechnol. 92 (2017) 257–270, https://doi.org/10.1002/jctb.5103.
[7] J.A. Ramirez, R.J. Brown, T.J. Rainey, A review of hydrothermal liquefaction biocrude properties and prospects for upgrading to transportation fuels, Energies 8 (2015) 6765–6794, https://doi.org/10.3390/en8076765.
[8] S.S. Toor, L. Rosendahl, M.P. Nielsen, M. Glasius, A. Rudolf, S.B. Iversen, Continuous production of bio-oil by catalytic liquefaction from wet distiller's grain with solubles (WDGS) from bio-ethanol production, Biomass-.-. Bioenergy 36 (2012) 327–332, https://doi.org/10.1016/j.biombioe.2011.10.044.
[9] R.B. Madsen, P.S. Christensen, K. Houlberg, E. Lappa, A.J. Mørup, M. Klemmer, E. M. Olsen, M.M. Jensen, J. Becker, B.B. Iversen, M. Glasius, Analysis of organic gas phase compounds formed by hydrothermal liquefaction of Dried Distillers Grains with Solubles, Bioresour. Technol. 192 (2015) 826–830, https://doi.org/10.1016/j.biortech.2015.05.095.
[10] A. Mathanker, S. Das, D. Pudasainee, M. Khan, A. Kumar, R. Gupta, A review of hydrothermal liquefaction of biomass for biofuels production with a special focus on the effect of process parameters, co-solvents and extraction solvents, Energies 14 (2021) 4916, https://doi.org/10.3390/en14164916.
[11] E. Panisko, T. Wietsma, T. Lemmon, K. Albrecht, D. Howe, Characterization of the aqueous fractions from hydrotreatment and hydrothermal liquefaction of lignocellulosic feedstocks, Biomass Bioenergy 74 (2015) 162–171, https://doi.org/10.1016/j.biombioe.2015.01.011.
[12] L. Leng, W. Zhang, S. Leng, J. Chen, L. Yang, H. Li, S. Jiang, H. Huang, Bioenergy recovery from wastewater produced by hydrothermal processing biomass: Progress, challenges, and opportunities, Sci. Total Environ. 748 (2020), 142383, https://doi.org/10.1016/j.scitotenv.2020.142383.
[13] A. Swetha, S. Shrivigneshwar, K. Panchamoorthy, R. Sivaramakrishnan, R. Shanmuganathan, J. Arun, Review on hydrothermal liquefaction aqueous phase as a valuable resource for biofuels, bio-hydrogen and valuable bio-chemicals recovery, Chemosphere 283 (2021), 131248, https://doi.org/10.1016/j.chemosphere.2021.131248.
[14] P. Sundarrajan, K.P. Gopinath, J. Arun, K. Gracepavithra, A.A. Joseph, S. Manasa, Insights into valuing the aqueous phase derived from hydrothermal liquefaction, Renew. Sustain. Energy Rev. 144 (2021), 111019, https://doi.org/10.1016/j.rser.2021.111019.
[15] J. Watson, T. Wang, B. Si, W.T. Chen, A. Aierzhati, Y. Zhang, Valorization of hydrothermal liquefaction aqueous phase: pathways towards commercial viability,

Prog. Energy Combust. Sci. 77 (2020), 100819, https://doi.org/10.1016/j.pecs.2019.100819.
[16] R.B. Madsen, P. Biller, M.M. Jensen, J. Becker, B.B. Iversen, M. Glasius, Predicting the Chemical Composition of Aqueous Phase from Hydrothermal Liquefaction of Model Compounds and Biomasses, Energy Fuels 30 (2016) 10470–10483, https://doi.org/10.1021/acs.energyfuels.6b02007.
[17] Z. Zhu, L. Rosendahl, S.S. Toor, D. Yu, G. Chen, Hydrothermal liquefaction of barley straw to bio-crude oil: Effects of reaction temperature and aqueous phase recirculation, Appl. Energy 137 (2015) 183–192, https://doi.org/10.1016/j.apenergy.2014.10.005.
[18] P. Biller, R.B. Madsen, M. Klemmer, J. Becker, B.B. Iversen, M. Glasius, Effect of hydrothermal liquefaction aqueous phase recycling on bio- crude yields and composition, Bioresour. Technol. 220 (2016) 190–199, https://doi.org/10.1016/j.biortech.2016.08.053.
[19] R. Cherad, J.A. Onwudili, P. Biller, P.T. Williams, A.B. Ross, Hydrogen production from the catalytic supercritical water gasification of process water generated from hydrothermal liquefaction of microalgae, Fuel 166 (2016) 24–28, https://doi.org/10.1016/j.fuel.2015.10.088.
[20] R. Posmanik, R.A. Labatut, A.H. Kim, J.G. Usack, J.W. Tester, L.T. Angenent, Coupling hydrothermal liquefaction and anaerobic digestion for energy valorization from model biomass feedstocks, Bioresour. Technol. 233 (2017) 134–143, https://doi.org/10.1016/j.biortech.2017.02.095.
[21] A. Di Fraia, E. Miliotti, A.M. Rizzo, G. Zoppi, G. Pipitone, R. Pirone, L. Rosi, D. Chiaramonti, S. Bensaid, Coupling Hydrothermal Liquefaction and Aqueous Phase Reforming for integrated production of biocrude and renewable H2, AIChE J. (2022), https://doi.org/10.1002/aic.17652.
[22] I. Coronado, M. Stekrova, M. Reinikainen, P. Simell, L. Lefferts, J. Lehtonen, A review of catalytic aqueous-phase reforming of oxygenated hydrocarbons derived from biorefinery water fractions, Int. J. Hydrog. Energy 41 (2016) 11003–11032, https://doi.org/10.1016/j.ijhydene.2016.05.032.
[23] R.R. Davda, J.W. Shabaker, G.W. Huber, R.D. Cortright, J.A. Dumesic, A review of catalytic issues and process conditions for renewable hydrogen and alkanes by aqueous-phase reforming of oxygenated hydrocarbons over supported metal catalysts, Appl. Catal. B Environ. 56 (2005) 171–186, https://doi.org/10.1016/j.apcatb.2004.04.027.
[24] G. Pipitone, G. Zoppi, R. Pirone, S. Bensaid, A critical review on catalyst design for aqueous phase reforming, Int. J. Hydrog. Energy 47 (2022) 151–180, https://doi.org/10.1016/j.ijhydene.2021.09.206.
[25] G. Zoppi, G. Pipitone, R. Pirone, S. Bensaid, Aqueous phase reforming process for the valorization of wastewater streams: Application to different industrial scenarios, Catal. Today 387 (2022) 224–236, https://doi.org/10.1016/j.cattod.2021.06.002.
[26] D. Castello, M.S. Haider, L.A. Rosendahl, Catalytic upgrading of hydrothermal liquefaction biocrudes: Different challenges for different feedstocks, Renew. Energy 141 (2019) 420–430, https://doi.org/10.1016/j.renene.2019.04.003.
[27] D.A. Sladkovskiy, L.I. Godina, K.V. Semikin, E.V. Sladkovskaya, D.A. Smirnova, D. Y. Murzin, Process design and techno-economical analysis of hydrogen production by aqueous phase reforming of sorbitol, Chem. Eng. Res. Des. 134 (2018) 104–116, https://doi.org/10.1016/j.cherd.2018.03.041.
[28] M. Khodabandehloo, A. Larimi, F. Khorasheh, Comparative process modeling and techno-economic evaluation of renewable hydrogen production by glycerol reforming in aqueous and gaseous phases, Energy Convers. Manag 225 (2020), 113483, https://doi.org/10.1016/j.enconman.2020.113483.
[29] G. Haarlemmer, M. Briand, A. Roubaud, J. Roussely, M. Déniel, Economic evaluation of a hydrothermal liquefaction process, Detritus 3 (2018) 84–92, https://doi.org/10.31025/2611-4135/2018.13695.
[30] X. Gu, L. Yu, N. Pang, J.S. Martinez-Fernandez, X. Fu, S. Chen, Comparative techno-economic analysis of algal biofuel production via hydrothermal liquefaction: One stage versus two stages, Appl. Energy 259 (2020), 114115, https://doi.org/10.1016/j.apenergy.2019.114115.
[31] A. Aierzhati, J. Watson, B. Si, M. Stablein, T. Wang, Y. Zhang, Development of a mobile, pilot scale hydrothermal liquefaction reactor: Food waste conversion product analysis and techno-economic assessment, Energy Convers. Manag. X 10 (2021), 100076, https://doi.org/10.1016/j.ecmx.2021.100076.
[32] I. Tews, Y. Zhu, C.V. Drennan, D. Elliott, L.J. Snowden-Swan, K. Onarheim, Y. Solantausta, D. Beckman, Biomass direct liquefaction options: technoeconomic and life cycle assessment, Pac. Northwest Natl. Lab (2014) 62. 〈https://www.osti.gov/biblio/1184983〉.
[33] L.A. Pedersen, Thomas Helmer, Hansen, Nick Høy, Pérez, Oscar Miralles, Cabezas, Daniel Esteban Villamar, Rosendahl, Renewable hydrocarbon fuels from hydrothermal liquefaction: A techno-economic analysis, Biofuels, Bioprod, Biorefining 12 (2018) 213–223, https://doi.org/10.1002/bbb.
[34] Y. Zhu, M.J. Biddy, S.B. Jones, D.C. Elliott, A.J. Schmidt, Techno-economic analysis of liquid fuel production from woody biomass via hydrothermal liquefaction (HTL) and upgrading, Appl. Energy 129 (2014) 384–394, https://doi.org/10.1016/j.apenergy.2014.03.053.
[35] R. Solimene, A. Cammarota, R. Chirone, P. Leoni, N. Rossi, P. Salatino, Devolatilization and fragmentation of solid lignin-rich residues from bioethanol production in lab-scale fluidized bed reactors, Chem. Eng. Trans. 50 (2016) 79–84, https://doi.org/10.3303/CET1650014.
[36] S. Dell'Orco, E. Miliotti, G. Lotti, A.M. Rizzo, L. Rosi, D. Chiaramonti, Hydrothermal depolymerization of biorefinery lignin-rich streams: Influence of reaction conditions and catalytic additives on the organic monomers yields in biocrude and aqueous phase, Energies 13 (2020), https://doi.org/10.3390/en13051241.
[37] E. Miliotti, S. Dell'Orco, G. Lotti, A.M. Rizzo, L. Rosi, D. Chiaramonti, Lignocellulosic ethanol biorefinery: Valorization of lignin-rich stream through hydrothermal liquefaction, Energies 12 (2019), https://doi.org/10.3390/en12040723.
[38] G. Pipitone, G. Zoppi, S. Bocchini, A.M. Rizzo, D. Chiaramonti, R. Pirone, S. Bensaid, Aqueous phase reforming of the residual waters derived from lignin-rich hydrothermal liquefaction: investigation of representative organic compounds and actual biorefinery streams, Catal. Today 345 (2020) 237–250, https://doi.org/10.1016/j.cattod.2019.09.040.
[39] D. Chiaramonti, A. Giovannini, S. Pescarolo, R. Nistri, 2° Generation Bioethanol The world ' s largest demo plant ready to be transferred all over the world - A Handbook - Part II, 2013.
[40] Foreign Agricultural Service, Europe: Corn production (2010–2014 Average), (n.d.).
[41] S. Menardo, G. Airoldi, V. Cacciatore, P. Balsari, Potential biogas and methane yield of maize stover fractions and evaluation of some possible stover harvest chains, Biosyst. Eng. 129 (2015) 352–359, https://doi.org/10.1016/j.biosystemseng.2014.11.010.
[42] R.H. Perry, D.W. Green, Perry's Engineers' Handbook, 1997.
[43] D.Q. Kern, Process Heat Transfer, McGraw-Hill,, 1965, https://doi.org/10.1016/B978-0-12-373588-1.X5000-1.
[44] A. Mathanker, D. Pudasainee, A. Kumar, R. Gupta, Hydrothermal liquefaction of lignocellulosic biomass feedstock to produce biofuels: Parametric study and products characterization, Fuel 271 (2020), 117534, https://doi.org/10.1016/j.fuel.2020.117534.
[45] Table 02.18 Superficie coltivata e produzione di cereali in Piemonte per provincia - Anno 2019, (n.d.).
[46] L.J. Snowden-Swan, Y. Zhu, M.D. Bearden, T.E. Seiple, S.B. Jones, A.J. Schmidt, J. M. Billing, R.T. Hallen, T.R. Hart, J. Liu, K.O. Albrecht, S.P. Fox, G.D. Maupin, D. C. Elliott, Conceptual Biorefinery Design and Research Targeted for 2022: Hydrothermal Liquefaction Processing of Wet Waste to Fuels, Pnnl 27186 (2017) 1–40.
[47] L. Lin, Y. Tian, W. Su, Y. Luo, C. Chen, L. Jiang, Techno-economic analysis and comprehensive optimization of an on-site hydrogen refuelling station system using ammonia: hybrid hydrogen purification with both high H2 purity and high recovery, Sustain, Energy Fuels 4 (2020) 3006–3017, https://doi.org/10.1039/c9se01111k.
[48] J.R. Collett, J.M. Billing, P.A. Meyer, A.J. Schmidt, A.B. Remington, E.R. Hawley, B.A. Hofstad, E.A. Panisko, Z. Dai, T.R. Hart, D.M. Santosa, J.K. Magnuson, R. T. Hallen, S.B. Jones, Renewable diesel via hydrothermal liquefaction of oleaginous yeast and residual lignin from bioconversion of corn stover, Appl. Energy 233– 234 (2019) 840–853, https://doi.org/10.1016/j.apenergy.2018.09.115.
[49] S. Jones, Y. Zhu, D. Anderson, R.T. Hallen, D.C. Elliott, Process design and economics for the conversion of algal biomass to hydrocarbons: whole algae hydrothermal liquefaction and upgrading, Pnnl (2014) 1–69. 〈http://www.pnnl.gov/main/publications/external/technical_reports/PNNL-23227.pdf〉.
[50] M. Sánchez, E. Amores, D. Abad, L. Rodríguez, C. Clemente-Jul, Aspen Plus model of an alkaline electrolysis system for hydrogen production, Int. J. Hydrog. Energy 45 (2020) 3916–3929, https://doi.org/10.1016/j.ijhydene.2019.12.027.
[51] Y. Zhu, K.O. Albrecht, D.C. Elliott, R.T. Hallen, S.B. Jones, Development of hydrothermal liquefaction and upgrading technologies for lipid-extracted algae conversion to liquid fuels, Algal Res 2 (2013) 455–464, https://doi.org/10.1016/j.algal.2013.07.003.
[52] Y. Zhu, S.B. Jones, A.J. Schmidt, K.O. Albrecht, S.J. Edmundson, D.B. Anderson, Techno-economic analysis of alternative aqueous phase treatment methods for microalgae hydrothermal liquefaction and biocrude upgrading system, Algal Res 39 (2019), 101467, https://doi.org/10.1016/j.algal.2019.101467.
[53] M. Magdeldin, T. Kohl, M. Järvinen, Techno-economic assessment of the by-products contribution from non-catalytic hydrothermal liquefaction of lignocellulose residues, Energy 137 (2017) 679–695, https://doi.org/10.1016/j.energy.2017.06.166.
[54] T.R. Brown, R. Thilakaratne, R.C. Brown, G. Hu, Techno-economic analysis of biomass to transportation fuels and electricity via fast pyrolysis and hydroprocessing, Fuel 106 (2013) 463–469, https://doi.org/10.1016/j.fuel.2012.11.029.
[55] M.T. Reza, R. Emerson, M.H. Uddin, G. Gresham, C.J. Coronella, Ash reduction of corn stover by mild hydrothermal preprocessing, Biomass-.-. Convers. Biorefinery 5 (2015) 21–31, https://doi.org/10.1007/s13399-014-0122-x.
[56] G. Pipitone, G. Zoppi, S. Ansaloni, S. Bocchini, F.A. Deorsola, R. Pirone, S. Bensaid, Towards the sustainable hydrogen production by catalytic conversion of C-laden biorefinery aqueous streams, Chem. Eng. J. 377 (2019), https://doi.org/10.1016/j.cej.2018.12.137.
[57] G. Towler, R.K. Sinnott, Chemical Engineering Design - Principles, Practice and Economics of Plant and Process Design (2nd Edition), 2013.
[58] R. Turton, R.C. Bailie, W.B. Whiting, J.A. Shaeiwitz, D. Bhattacharyya. Analysis, synthesis, and design of chemical processes, 4th edition.,, Pearson,, 2012, https://doi.org/10.5860/choice.36-0974.
[59] K.M. Guthrie, Capital cost estimating, 1969.
[60] L.T. Funkenbusch, M.E. Mullins, L. Vamling, T. Belkhieri, Technoeconomic assessment of hydrothermal liquefaction oil from lignin with catalytic upgrading for renewable fuel and chemical production, 2019: 1–12. https://doi.org/10.1002/wene.319.
[61] R.M. Swanson, A. Platon, J.A. Satrio, R.C. Brown, Techno-economic analysis of biomass-to-liquids production based on gasification, Fuel 89 (2010) S11–S19, https://doi.org/10.1016/j.fuel.2010.07.027.

[62] B. Alves, Prices of electricity for industries with a consumption of 20,000 to 70,000 MWh in the European Union from 2008 to 2020, Statista, 2021. ⟨https://www.statista.com/statistics/1046683/industry-electricity-prices-european-union-eu-28/⟩ (accessed December 31, 2021).
[63] N. Sönnichsen, Industrial natural gas prices in the European Union from 2008 to 2020, by consumption, Statista, 2021. ⟨https://www.statista.com/statistics/1047070/natural-gas-price-european-union/⟩ (accessed December 31, 2021).
[64] S. Masoumi, A.K. Dalai, Biomass and Bioenergy Techno-economic and life cycle analysis of biofuel production via hydrothermal liquefaction of microalgae in a methanol-water system and catalytic hydrotreatment using hydrochar as a catalyst support, Biomass-.-. Bioenergy 151 (2021), 106168, https://doi.org/10.1016/j.biombioe.2021.106168.
[65] E.B. Agyekum, C. Nutakor, A.M. Agwa, S. Kamel, A Critical Review of Renewable Hydrogen Production Methods: Factors Affecting Their Scale-Up and Its Role in Future Energy Generation, Membr. (Basel) 12 (2022), https://doi.org/10.3390/membranes12020173.
[66] Y. Nie, X.T. Bi, Techno-economic assessment of transportation biofuels from hydrothermal liquefaction of forest residues in British Columbia, Energy 153 (2018) 464–475, https://doi.org/10.1016/j.energy.2018.04.057.
[67] M.M. Wright, D.E. Daugaard, J.A. Satrio, R.C. Brown, Techno-economic analysis of biomass fast pyrolysis to transportation fuels, Fuel 89 (2010) S2–S10, https://doi.org/10.1016/j.fuel.2010.07.029.
[68] J.A. Ramirez, T.J. Rainey, Comparative techno-economic analysis of biofuel production through gasi fi cation, thermal liquefaction and pyrolysis of sugarcane bagasse, J. Clean. Prod. 229 (2019) 513–527, https://doi.org/10.1016/j.jclepro.2019.05.017.
[69] N.R. Baral, M. Yang, B.G. Harvey, B.A. Simmons, A. Mukhopadhyay, T.S. Lee, C. D. Scown, Production Cost and Carbon Footprint of Biomass-Derived Dimethylcyclooctane as a High-Performance Jet Fuel Blendstock, ACS Sustain. Chem. Eng. 9 (2021) 11872–11882, https://doi.org/10.1021/acssuschemeng.1c03772.
[70] D. Knorr, J. Lukas, P. Schoen, Production of advanced biofuels via liquefaction, Hydrothermal Liq. React. Des. 303 (2013). ⟨www.nrel.gov/publications⟩.
[71] R. Yukesh Kannah, S. Kavitha, Preethi, O. Parthiba Karthikeyan, G. Kumar, N. V. Dai-Viet, J. Rajesh Banu, Techno-economic assessment of various hydrogen production methods – A review, Bioresour. Technol. 319 (2021), 124175, https://doi.org/10.1016/j.biortech.2020.124175.
[72] Hydrogen Production Costs 2021, 2021. ⟨https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/1011506/Hydrogen_Production_Costs_2021.pdf⟩ (accessed December 31, 2021).
[73] I.M. Dărăban, L.A. Rosendahl, T.H. Pedersen, S.B. Iversen, Pretreatment methods to obtain pumpable high solid loading wood-water slurries for continuous hydrothermal liquefaction systems, Biomass Bioenergy 81 (2015) 437–443, https://doi.org/10.1016/j.biombioe.2015.07.004.