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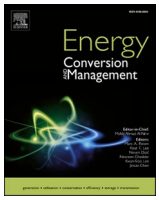

Flexible polygeneration of drop-in fuel and hydrogen from biomass: Advantages from process integration

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ABSTRACT

According to the latest report by the Intergovernmental Panel on Climate Change, significant effort is needed in the energy transition process to meet the milestones of the Paris Agreement. To this aim, the energy conversion of the biogenic carbon in biomass is a potent strategy to facilitate the energy transition. In recent years, scientific literature has evaluated, using numerical models, the process integration for the conversion of lignocellulosic biomass into high valuable energy carriers. In particular the combination of fast pyrolysis and gasification has been proposed. However, there is a lack of evaluation of the energy effectiveness of this combination. This work aims at quantifying the energy performance increase of converting lignocellulosic biomass into hydrogen, drop-in fuels, and syngas through the integration of pyrolysis, steam sorption enhanced gasification and hydrodeoxygenation processes, compared to a separated layout option where pyrolysis, hydrodeoxygenation, and sorption enhanced gasification processes occur in parallel. The processes have been evaluated using a mixed kinetic and equilibrium chemical modeling approach with the AspenPlus software. The results show that the integration of fast pyrolysis, hydrodeoxygenation, and sorption enhanced gasification leads to a significant increase in the energy performance of the convention route, increasing the energy yield between 19 % and 43 %, the efficiency between 26.7 % and 39.3 %, and the carbon conversion between 48.7 % and 73.1 %, depending on the operating conditions selected. The findings from this analysis not only demonstrate that the process integration of pyrolysis, hydrodeoxygenation and sorption enhanced gasification is effective, but also enhance the understanding of how such integration can significantly improve the conversion efficiency of lignocellulosic biomass into valuable energy carriers.

1. Introduction

Although the transition of the energy system to more sustainable and resilient solutions is ongoing, the speed and effectiveness of such transformation are still critical. The consequences of climate change are becoming increasingly concerning. In its last report [1], the Intergovernmental Panel on Climate Change (IPCC) mentioned that more ambitious efforts are needed compared to those already scheduled for the future. The energy transition trajectories must be rewritten to achieve more ambitious results in a short time. As an example of these concerns, the European Commission has revised the Renewable Energy Directive (RED) to its third version to achieve more ambitious goals [2]. The main goals of the 2030 directive are: reaching at least 42.5 % of the share of energy from renewable sources in the gross final consumption of energy; achieving at least 29 % of renewable fuels and renewable electricity supplied in the final energy consumption of energy in the transportation sector (or a reduction of the intensity of greenhouse gases of at least 14.5 %); and ensuring the combined share of advanced biofuels and biogas, and of renewable fuels of non-biological origin in the energy supplied to the transport sector, is at least 5.5 %.

According to this perspective, the conversion of biomass into valuable energy carriers has been recognized as a critical strategy for facilitating the energy transition. This is largely due to the biogenic origin of the biomass carbon, which substantially lowers the carbon footprint of the resulting energy carriers compared to fossil fuels. Within the scientific community, the production of energy carriers from biomass has been discussed and covered extensively through both experimental and numerical modeling studies. In numerical studies, one common objective is to develop accurate simulations of individual biomass conversion processes to achieve a high level of approximation of the actual chemical

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reactions occurring during biomass conversion. A primary focus on this topic is on the design optimization of the entire biomass conversion pathways. This entails identifying and manipulating key parameters that influence the efficiency and output of the conversion processes. Optimization efforts aim at enhancing the overall performance of biomass conversion systems, making them more viable and effective for large-scale implementation. Beyond the estimation or measurement of technical performance parameters, numerical modeling has is also been used to assess the energy and economic viability of biomass conversion processes.

In the recent years, the advantages of process integration and energy carriers polygeneration from biomass have been discussed in several papers. These studies analyzed different integrated approaches to demonstrate their effectiveness from both energy and environmental perspectives, highlighting the theoretical feasibility of the proposed pathways.

Prestipino et al. [3] analyzed the polygeneration of hydrogen, electricity, and heat from the gasification of wet biomass, specifically citrus peel. The outputs of the process included hydrogen flow, electrical power, and thermal power output derived from the valorization of syngas in an internal combustion engine. They found a maximum hydrogen yield of 40.1 kgH_2 per ton of dry biomass with an overall efficiency of 33 %. Butera et al. [4] studied an integrated system for the flexible polygeneration of methanol and electricity. The main components of the proposed pathway included a two-stage gasifier that provided syngas to a solid oxide fuel cell to produce hydrogen, and a methanol production reactor, which collected the outputs of the previous processes. The energy carrier outputs were flexible according to electricity grid price variations. The overall efficiency of the process ranged between 30% and 70%, depending on the configurations and operating points. The best performance was achieved when the plant operated for full methanol production; under these conditions, carbon conversion reached 92%. Poluzzi et al. [5] evaluated different layout systems for the production of power-biomass to methanol, where the biomass was converted into methanol, and the methanol production was enhanced by hydrogen production from an electrolyzer (which consumes electrical power, hence the term power-biomass to methanol). The processes involved steam gasification of biomass, reforming of the syngas, and methanol synthesis. The impact of adding the electrolyzer to enhance hydrogen production was also assessed. The advantage in terms of the levelized cost of methanol related to the addition of the electrolyzer was highly dependent on its capacity factor, while the capital cost impact was found to be less significant. The achieved global efficiency with that layout ranged from 62 % to 73.3 %, with a carbon conversion of up to 64 %. Peters et al. [6] analyzed the upgrade of lignocellulosic biomass to drop-in fuel through hydrodeoxygenation of bio-oil obtained via fast pyrolysis, using hydrogen produced by natural gas steam reforming, reaching a biomass-to-biofuel efficiency of 63.9 %. Baldelli et al. [7] evaluated the valorization of wet biomass residues by integrating anaerobic digestion and pyrolysis as pre-processes for a reforming reactor, where the gaseous and liquid products were converted into hydrogen. This combination allowed for a competitive hydrogen yield of 5.37 %, with hydrogen production from reforming distributed equally between biogas and pyrolysis products (44.5 % and 55.5 %, respectively). Zhao et al. [8] conducted a numerical analysis of introducing torrefaction as a pretreatment for steam gasification to produce hydrogen from food waste. They found that the integrated process achieved better energy performance (about 4 % higher overall efficiency, reaching 58.9%) and significantly better economic performance (44.5% higher net present value, 20.8% lower payback period, and 22.5% higher internal rate of return) compared to direct steam gasification. Yan et al. [9] proposed a complex integrated system for the polygeneration of electricity, ammonia, heat, and cooling from biomass. The process involved a solar-assisted biomass gasifier, a chemical looping ammonia generation reactor, a solid oxide fuel cell, a gas turbine, and a waste heat recovery unit. Solar integration significantly improved energy performance (increasing overall efficiency by 14% in cooling mode and 18.5% in heating mode, reaching about 61.5% and 57.8%), while ammonia production was up to 18.7 kg/h. Li et al. [10] analyzed an integrated process where the gasification of herbaceous biomass was thermally integrated with the pyrolysis of woody biomass. The scope of the integrated process was to produce electricity through a gas turbine fed by gaseous byproducts of pyrolysis and gasification, and hydrogen obtained by the steam reforming of bio-oil from the pyrolysis process. The system achieved a total efficiency of 51.2 % at operating conditions of 1265 °C and 18 bar for gasification and 520 °C and 1 bar for pyrolysis. Sensitivity analysis showed that increasing the pyrolysis temperature generally positively affected H_2 yield and power generation output, while increasing gasification temperature positively affected only the hydrogen yield. Safder et al. [11] evaluated an integrated multigeneration system for the production of methanol, hydrogen, and power from bagasse. The process involved the electricity generation from syngas obtained by the biomass gasification, which supplied the electrolyzer for the hydrogen production and the methanol production by the utilization of part of hydrogen produced and the carbon dioxide (CO_2) separated from flue gas, the overall efficiency of the process was of 78.13%.

The combination of pyrolysis and subsequent char gasification of lignocellulosic biomass has been deeply investigated in the context of process integration studies. Generally, these articles focused on the fast pyrolysis process as the core of the upgrading pathway [12]. Raw bio-oil was the major output; however, due to its poor energy and chemical properties, upgrading was needed for its use as a bio-fuel, usually requiring a stream of hydrogen. Rezaei and Mehrpooya [13] performed an analysis of the heat integration process based on pyrolysis, steam gasification, steam reforming, and bio-oil upgrading, using various types of wood biomass feedstock. They found that the optimal configuration for heat integration led to reductions in heat and cold duty by up to 75.02% and 47.80%, respectively, compared to the baseline, achieving an overall efficiency of 65.8% for the optimized process. Detchusananard et al. [14] performed an economic analysis of integrating pyrolysis and steam gasification processes. A parametric study was conducted to determine the critical operating parameters. The optimal values for maximizing energy carrier production were found to be a steam-to-biochar mass ratio of 2.7, a gasifier temperature of 900 °C, and a steam-to-syngas mass ratio of 3. The economic analysis yielded good results, with a payback period of about 6 years and an internal rate of return of 22%. In a recent work [15], the authors proposed a new design for a pyrolysis bio-oil upgrading plant. This design incorporates a method initially suggested by Di Carlo et al. in various studies [16-18], involving in-situ CO_2 capture through the absorption of CO_2 using calcium oxide (CaO) as a sorbent. The studies by Di Carlo evaluated different aspects of the sorbent process, such as the development and validation of a numerical method for describing the sorbent capacity decline by characterizing particle grain size [16], while in Di Carlo et al. [17] a 2D Computational Fluid-Dynamic (CFD) model of a pilot-scale reactor was developed and validated using experimental data from the literature. Additionally, in Di Nardo et al. [18] a CFD model was provided to support the experimental activities of a pilot-scale reactor, estimating numerically how the operative conditions could affect the reactor's behavior. This method, known as the steam Sorption Enhanced Gasification (SEG) process, was used by the authors to produce the hydrogen required for upgrading bio-oil in the Hydrodeoxygenation (HDO) section. The system overall produces hydrogen, drop-in fuels, and syngas. The results were evaluated at several pyrolysis temperatures, and the optimal operative conditions of the SEG reactor were determined. In all analyzed configurations, hydrogen production was more than sufficient to feed the bio-oil upgrading processes; moreover, net hydrogen production was obtained in all operative conditions. The efficiency achieved varied between 64% and 74%, and the energy yields of the different energy carriers depended significantly on the operative conditions. Lower pyrolysis temperatures promoted hydrogen

Table 1
Bibliography analysis synthesis.

Processes involved	Biomass – Outputs		Goals	Major findings	References
Gasification	Citrus Peel	Hydrogen, Electricity, Heat	Demonstrate the energy self-sufficiency of the process for hydrogen production.	Achieved energy self-sufficiency with and energy yield 40 $kg_{H2}/ton_{Biomass}$ at a Steam to Biomass ratio of 1.25	[3]
Pyrolysis, Gasification, Solid Oxide Cells, Methanol synthesis	Woody Biomass	Methanol, Electricity	Techno-economic analysis of a flexible methanol production facility for storage and electricity production.	Economic results were highly dependent on electricity price scenarios, and high investment costs significantly impacted economic feasibility.	[4]
Sorption Enhanced Gasification, Reforming, Electrolyzer, Methanol synthesis	Woody Biomass	Methanol	Techno-economic assessment of the conversion of several plant layouts.	The levelized cost of methanol was highly dependent on electrolyzer capacity factor.	[5]
Pyrolysis, Reforming, Bio-Oil Upgrading	Woody Biomass	Drop-in Fuel, Syngas	Evaluate the energy conversion of lignocellulosic biomass using hydrogen from steam reforming of natural gas.	The steam reforming section was critical for the performance of the conversion.	[6]
Anaerobic digestion, Pyrolysis, Reforming	Quinoa Residues, Wastewater Sludge	Hydrogen, Syngas	Evaluate the integration of anaerobic digestion and pyrolysis as reforming pre-process for wet biomass.	Achieved a hydrogen yield of 5.37 $\%_{mass}$, with both pre-processes equally contributing to hydrogen production.	[7]
Torrefaction, Steam gasification	Food waste	Hydrogen	Quantify the energy and economic effects of integrating torrefaction and steam gasification for hydrogen production.	The integrated process had better energy performance (58.9 % efficiency, 11 % H_2 yield) and better economic performance.	[8]
Gasification, Ammonia synthesis, Solid Oxide Cells.	unspecified	Ammonia, Electricity, Heat, Cool.	Evaluate a polygeneration system for the energy valorization of biomass.	The integrated process achieved overall efficiency between 57.8 %-61.5 % and an ammonia yield up to 5.2 %.	[9]
Gasification Pyrolysis Reforming	Herbaceous biomass, Woody biomass.	Electricity, Hydrogen	Evaluate the process integration of gasification of herbaceous biomass and pyrolysis of woody biomass.	The integrated process achieved an overall efficiency of 51.2 % and a notable hydrogen yield	[10]
Gasification, Electrolyzer, Methanol synthesys	Bagasse	Electricity, Hydrogen, Methanol.	Evaluated the process integration of gasification of bagasse and eletrolyzer to produce carbon–neutral hydrogen and methanol.	Integrated process reached an overall efficiency of 78.13 %.	[11]
Pyrolysis, Steam Gasification, Steam Reforming, Bio-Oil Upgrading	Wood biomass	Hydrogen, Drop-in, Syngas	Evaluate the energy conversion of lignocellulosic biomass using hydrogen from steam reforming of syngas.	Identified hybrid poplar as the best feedstock; plant optimization achieved through thermal integration.	[13]
Pyrolysis, Steam Gasification, Bio-Oil Upgrading	Wood Biomass	Hydrogen, Drop-in, Syngas	Techno-economic assessment of conversion plants integrating pyrolysis and steam gasification processes.	Determined the best operating conditions with a payback period of 5.98 years.	[14]
Pyrolysis, Sorption Enhanced Gasification, Bio-Oil Upgrading	Wood Biomass	Hydrogen, Drop-in, Syngas	Evaluate the energy conversion of lignocellulosic biomass using hydrogen from Sorption Enhanced Gasification.	Achieved net hydrogen production and determined the best operating conditions.	[15]

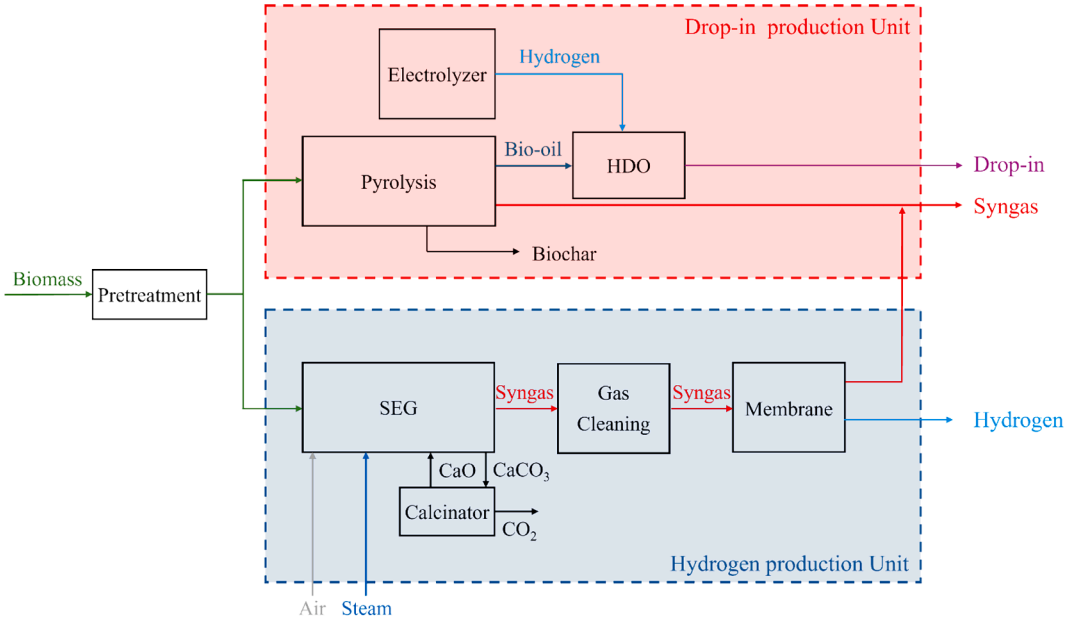

Fig. 1. Graphical representation of the separated layout.

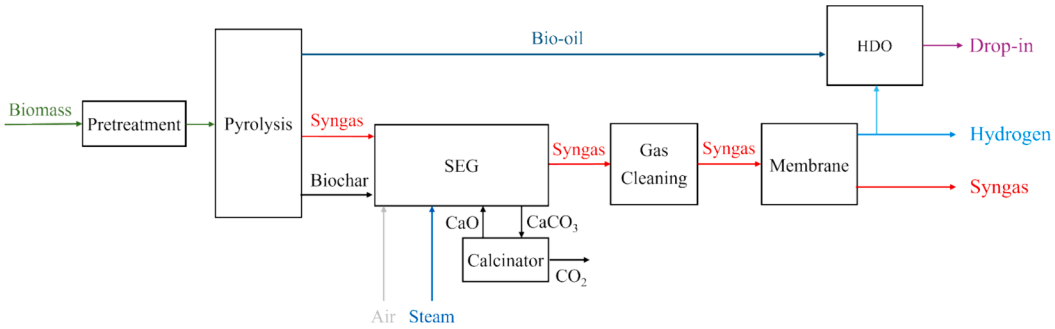

Fig. 2. Graphical representation of the integrated layout.

production, while higher temperatures in the range of 350–400 °C were recommended to support drop-in fuel production. To better illustrate the literature review presented in this work, Table 1 summarizes the main information of the studies described above. For each article, the processes involved, the biomass utilized, the main outputs of the systems, the goals of the articles, and their major findings are collected.

As shown in the above literature review, there is a high interest in evaluating the feasibility and performance of integrated biomass conversion systems. However, there has been limited systemic and detailed investigation into the integrated thermochemical system to understand the effectiveness of their combination compared to biomass upgrading through separate processes. Therefore, this work aims at analyzing, comparing, and quantifying the energy performance of converting lignocellulosic biomass into hydrogen, drop-in fuels, and syngas through the integration of pyrolysis, SEG, and HDO, as opposed to a separated layout where pyrolysis + HDO and SEG processes occur in parallel. This aims to clarify the advantages obtainable from process integration.

In this work, two layouts are proposed and discussed. The separated layout is composed of two units: the first, dedicated to drop-in production, includes a pyrolysis reactor and an HDO section for bio-oil upgrading. Due to the hydrogen demand in the HDO section, an electrolyzer is added to this unit. The second unit is dedicated to hydrogen and syngas production and comprises the SEG and a membrane reactor for hydrogen separation. The comparison between the separated and integrated process layouts is carried out by analyzing the energy performance of the two layouts per unit biomass fed (1 kg). Additionally, a sensitivity analysis is conducted on the biomass input distribution across the two units of the separated layout to determine the influence of this parameter in comparison to the integrated layout.

2. Methods

The layouts analyzed share the same processes, differing mainly because, in the separated layout, processes occur in parallel, whereas in the integrated layout, they are sequential. In the separated layout, raw biomass is fed into the system, pretreated, and then directed to two different units of the plant. Part of the biomass goes to the drop-in production unit and undergoes fast pyrolysis. The resulting bio-oil is subsequently upgraded in the HDO section to produce drop-in fuels. In this layout, the hydrogen required for the HDO is supplied by an electrolyzer. The left biomass fraction is sent to the hydrogen production unit, where it is processed in the SEG unit, yielding an enriched hydrogen syngas stream. This hydrogen is then separated from the syngas using a membrane. Fig. 1 provides a graphical representation of the separated layout.

In the integrated layout, downstream of the pretreatment, the whole biomass fraction feeds the pyrolysis reactor. The resulting bio-oil is then directed to the HDO reactors to produce drop-in fuels, while the biochar and syngas are processed in the SEG unit. The enriched hydrogen syngas produced is then separated in the membrane reactor to extract a pure hydrogen stream. In this layout, the hydrogen demand for the HDO section is met internally by the production process. In fact, under all

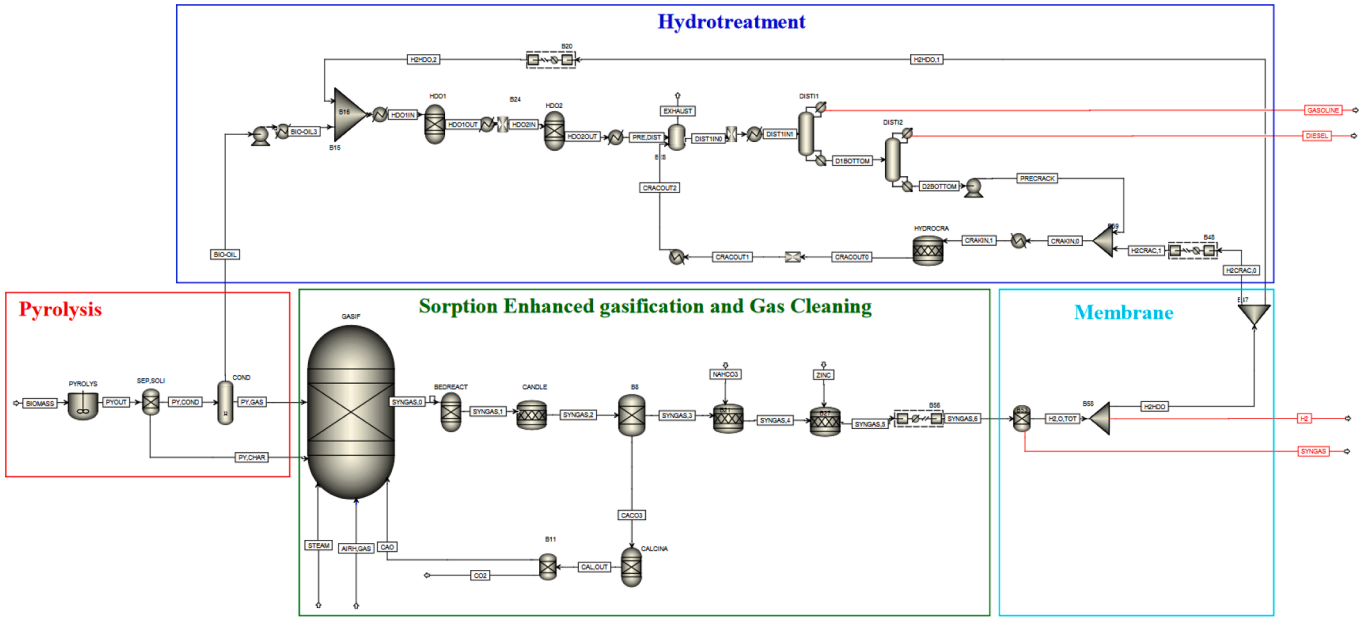

Fig. 3. Aspen Plus flowsheet of the integrated layout.

Table 2
SEG operative conditions by varying the Pyrolysis Temperature.

	T_{Pyro}	$T_{Gasification}$	CaO/Char	Steam/Char
Integrated Layout	300 °C	650 °C	1.5	0.8
	350 °C	650 °C	1.5	1.2
	400 °C	650 °C	1.5	1.6
Separated Layout	300 °C	650 °C	1.5	0.6
	350 °C	650 °C	1.5	0.6
	400 °C	650 °C	1.5	0.6

operating conditions evaluated, hydrogen production sufficiently exceeds the demand, resulting in a net output of hydrogen from the layout. Fig. 2 provides a graphical representation of the integrated layout.

2.1. Modeling

The performances of the different layouts are evaluated by a mixed kinetic and equilibrium chemical modeling approach in the AspenPlus software [19]. In the following a concise summary of the process sections is provided, while for a more detailed description of the numerical modelling the reader is referred to previous work [15]. Fig. 3 depicts a flowsheet of the proposed integrated layout. Fast Pyrolysis occurs at temperatures of 300 °C, 350 °C, and 400 °C under atmospheric pressure. Outputs include a liquid stream for the HDO section and biochar used as feedstock for the SEG. The pyrolysis section is modeled using a cascade of lumped kinetic chemical reactions based on real and pseudo-species components, following the approach proposed by Ranzi et al. [20,21]. Products are bio-oil, syngas, and biochar. Sorption Enhanced Gasification (SEG) converts biochar (integrated layout) or raw biomass (separated layout) into hydrogen-rich syngas. In situ CO_2 adsorption using CaO enhances the water–gas shift reaction, increasing hydrogen production in the output syngas. SEG modeling employs an equilibrium approach typical for this application. After gasification, syngas undergoes a cleaning process and hydrogen separation using a membrane reactor. Bio-Oil Upgrading (HDO Section) is necessary to enhance the bio-oil's properties. A two-step HDO process is evaluated, with reactors operating at 170 bar and 250 °C, and 140 bar and 370 °C respectively. Post-upgrading, products undergo cascade distillation to produce valuable outputs such as gasoline-like and diesel-like fuels. Hydrocracking breaks down heavier compounds from distillation, returning them as input to the distillation section.

2.2. The Sorption Enhanced gasification operative conditions

The comparison of the integrated and separated layouts is performed keeping constant the operating conditions of the different reactors. Three pyrolysis temperatures have been assessed: 300, 350, and 400 °C. The gasification temperature is kept constant at 650 °C, which is a typical value for the SEG with CaO sorbent [16–18,22–25], while its Steam/Char and CaO/Char ratios are selected to maximize the efficiency of the SEG process. In fact, the optimal values of these ratios are related to the elemental composition of the SEG feedstock. In the separated layout, the SEG feedstock is always the raw biomass, while in the integrated layout the SEG feedstock is the biochar, whose elemental composition depends on the pyrolysis temperature. Table 2 summarizes the SEG condition as a function of the pyrolysis temperature of the layouts.

2.3. The key performance indicators

Three different Key Performance Indicators (KPIs) are selected to analyze the performance of the integrated and separated layouts, which are: energy yield, overall energy efficiency, and carbon conversion.

The energy yield of an energy carrier is the ratio between the chemical energy of a specific energy carrier produced by the process for weight unit of biomass. Its formulation is reported in Equation (1). The energy yield estimates the effectiveness of the process to convert the biomass into the desired energy carrier.

$$EnergyYield_i = \frac{m_{out,i} \bullet LHV_{out,i}}{m_{biomass}} \quad (1)$$

Where:

- $m_{out,i}$: is the mass flow of the energy product-i;
- $LHV_{out,i}$: is the Low Heating Value of the energy product-i;
- $m_{biomass}$: is the mass flow of the biomass;

The overall energy efficiency ($\eta_{overall}$) allows to account also for the energy request by the process. It is calculated as the ratio of the sum of the chemical energy content in the produced energy carriers and the energy input of the systems, which is the sum of energy demand of the processes and the chemical energy content of the input biomass. Its formulation is reported in Equation (2).

$$\eta_{overall} = \frac{\sum_{out,i}^{m} LHV_{out,i}}{m_{biomass} LHV_{biomass} + \sum^{P} w_i} \quad (2)$$

Where:

- $m_{out,i}$: is the mass flow of the energy product-i;
- $LHV_{out,i}$: is the Low Heating Value of the energy product-i;
- $m_{biomass}$: is the mass flow of the biomass;
- $LHV_{biomass}$: is the Low Heating Value of the biomass;
- Pw_i: is the power consumption of the process-i.

Since biomass is a biogenic source of carbon, is carbon neutral (excluding the related indirect emissions), and then it is important to evaluate the carbon conversion of the overall process. In fact, Carbon Conversion, also known as carbon efficiency or carbon conversion efficiency, is an important KPI in order to evaluate the effectiveness of the overall process to collect the biogenic carbon in the energy carriers and thus utilizing the biomass as a sustainable source of carbon. Carbon conversion is calculated, according to Equation (3), as the ratio between the carbon mass flow in the outlet energy product and the inlet carbon mass flow in the input biomass. It is worth mentioning that the carbon content in inert species (such as the CO_2 in the syngas) is not taken into account in the calculation of the carbon conversion.

$$CarbonConversion = \frac{\sum m_{C,i}}{m_{C,biomass}} \quad (3)$$

Where:

- $m_{C,i}$: is the Carbon mass flow of the energy product-i;
- $m_{C,biomass}$: is the Carbon mass flow of the biomass.

2.4. Sensitivity analysis

Since the biomass distribution between the two units of the separated layout significantly affects overall performance, and so does the comparison with the integrated layout, a sensitivity analysis is carried out to thoroughly analyze different operating conditions. Initially, an equal distribution (50%/50%) of biomass feeding flow between the two units of the separated layout is considered. Subsequently, the biomass distribution among the two units is varied in increments of 20 %, starting from total biomass allocation to the drop-in production unit (labeled as 0 %Gas-100 %Pyro) to total allocation to the hydrogen production unit (labeled as 100 %Gas-0 %Pyro). In total, six different operating scenarios have been analyzed, denoted according to their biomass distribution using the format "x%Gas-y%Pyro." Here, x% represents the

Table 3
Mass fraction of the main process at different pyrolysis temperatures related to the input biomass.

Pyrolysis output				
Operative Condition	No Pyro	300 °C	350 °C	400 °C
Char	N/A	59.9 %	33.9 %	24.8 %
Gas	N/A	15.3 %	24.1 %	31.8 %
Oil	N/A	24.8 %	42.0 %	43.4 %
SEG input				
Operative Condition	No Pyro	300 °C	350 °C	400 °C
Char/Biomass	100.0 %	59.9 %	33.9 %	24.8 %
H_2O	60.0 %	47.9 %	40.7 %	39.7 %
CaO	150.0 %	89.9 %	50.8 %	37.2 %
SEG Output				
Operative Condition	No Pyro	300 °C	350 °C	400 °C
$H_{2;\ total}$	8.5 %	7.0 %	4.8 %	4.6 %
$H_{2;\ HDO}$	0.0 %	1.5 %	2.5 %	2.6 %
$H_{2;\ net}$	8.5 %	5.5 %	2.3 %	2.0 %
Syngas	150.4 %	122.7 %	107.1 %	104.0 %

Table 4
Elemental composition of the seg feedstock at different operative conditions.

	Elemental Composition of Char/Biomass			
Operative Condition	No Pyro	300 °C	350 °C	400 °C
C	51.0 %	55.5 %	65.8 %	69.5 %
H	6.0 %	5.0 %	4.5 %	4.4 %
O	43.0 %	39.5 %	29.7 %	26.2 %

fraction of biomass processed in the hydrogen production unit, and y% represents the fraction processed in the drop-in production unit.

3. Results and discussion

The results are presented in three main sections. In the first part, the comparison of the separated and integrated process approaches is performed, with equal distribution assumed between the production units in the separated approach. Following, a sensitivity analysis on the biomass fractioning between the two production units is discussed. Lastly, a comparison between the integrated process and results available in the literature is described.

3.1. Comparison between integrated and separated approach – Biomass balanced distribution

All analyses have been carried out under three different operating conditions, as detailed in the Methods section. In the separated layout, the hydrogen production unit is unaffected by changes in pyrolysis temperatures, maintaining a constant hydrogen yield across all operational conditions. This consistency arises as the SEG process, in cahrge of hydrogen production, operates consistently under each pyrolysis temperature condition, processing the same biomass flow rate, as reported in Table 2. Conversely, in the drop-in production unit of the separated layout, significant variability in energy outputs is observed by changing pyrolysis temperatures. In the integrated layout, as previously mentioned, variations in pyrolysis temperature directly affect the optimal operational conditions of the SEG process, as detailed in Table 2. Table 3 illustrates the primary mass flows within the different layouts, expressed as percentages relative to the input biomass. Increasing the pyrolysis temperature reduces in fact the biochar fraction and increases the fractions of bio-oil and syngas. Particularly noteworthy is the sharp increase in bio-oil production between pyrolysis temperatures of 300–350 °C, followed by a plateau at 350–400 °C. Moreover, an increasing pyrolysis temperature leads to higher carbon content in the char. For instance, while raw biomass has an approximate carbon mass fraction of 51%, the biochar reaches 70% at a pyrolysis temperature of 400 °C, as shown in Table 4. Lastly, it is observed that the hydrogen demand in the HDO section increases with higher pyrolysis temperatures. This increase is directly linked to the bio-oil mass, as discussed further in subsequent sections.

Tables 5 and 6 summarize the energy requirements for both layouts. As previously mentioned, the processes in both layouts are identical, including an electrolyzer in the drop-in production unit of the separated layout. The specific energy consumption of the electrolyzer is assumed to be 50 kWh/kg of hydrogen, as referenced in [32], and the total energy demand accounts for the hydrogen requirements of the HDO section under each operational condition. Table 5 shows that the energy demand of the electrolyzer increases notably between pyrolysis temperatures of 300 °C and 350 °C, stabilizing between 350 °C and 400 °C, and following the trend of bio-oil yield. As the hydrogen demand for the entire bio-oil upgrading process is approximately 6% by mass of the bio-oil, an increase in bio-oil production directly impacts the hydrogen demand in the HDO section. Both layouts have identical pretreatment energy demands, calculated according to [26], as the comparisons are carried out with the same amount of input biomass. The energy consumptions of other processes are derived from the numerical model and detailed in Tables 5 and 6. Upon analyzing the energy consumption data, it is evident that, except for the case of a 300 °C pyrolysis temperature where it is higher by about 20 %, the integrated layout generally exhibits lower energy consumption compared to the separated layout. Specifically, reductions in energy consumption of approximately 12 % and 19 % are observed for pyrolysis temperatures of 350 °C and 400 °C, respectively, in the integrated layout compared to the separated layout under the same operational conditions. In fact, In the integrated layout, the energy consumption of SEG decreases significantly as the pyrolysis temperature increases. Compared to the SEG energy consumption in the separated layout at a pyrolysis temperature of 300 °C, the integrated layout shows a 32 % higher demand. However, at higher pyrolysis temperatures the SEG energy consumption has a reduction of about 11% and 25% with respect to the separated layout with at the same pyrolysis temperature respectively at 350 °C and 400 °C. On the other hand, energy consumption in the drop-in section increases notably, primarily due to the consumption of the electrolyzer. When focusing solely on the energy demand of the pyrolysis and HDO processes, the integrated layout initially exhibits higher energy expenses compared to the separated layout, due to handling a greater biomass amount. In the separated layout, however, the energy costs associated with hydrogen production for drop-in fuels are covered by the electrolyzer. Once these energy expenses are factored in, the separated process becomes more energy-intensive than the integrated one for the overall demand of the drop-

Table 5
Specific energy demand ($MJ/kg_{biomass}$) of the separated layout by process.

	Pretreatment	Hydrogen Unit		Drop-in Unit				Overall layout
	Pretreatment	SEG	Hydrogen production	Pyrolysis	HDO	Electrolyzer	Drop-in production	Total
T_{Pyro} = 300 °C	0.5	3.6	3.6	0.3	0.7	1.3	2.4	6.2
T_{Pyro} = 350 °C	0.5	3.6	3.6	0.5	1.2	2.32	3.9	8.0
T_{Pyro} = 400 °C	0.5	3.6	3.6	0.55	1.2	2.3	4.0	8.1

Table 6
Specific energy demand ($MJ/kg_{biomass}$) of integrated layout by process, in brackets are reported percentual comparison with respect to separated layout.

	Pretreatment	SEG	Pyrolysis	HDO	Drop-in Production	Total
$T_{Pyro} = 300\ °C$	0.5	4.7 (+32 %)	0.6	1.5	2.1 (−11 %)	7.4 (+19.7%)
$T_{Pyro} = 350\ °C$	0.5	3.2 (−11 %)	0.9	2.4	3.3 (−15.5 %)	7.0 (-12.4%)
$T_{Pyro} = 400\ °C$	0.5	2.7 (−25 %)	1.0	2.3	3.3 (−16.5 %)	6.6 (-19.1%)

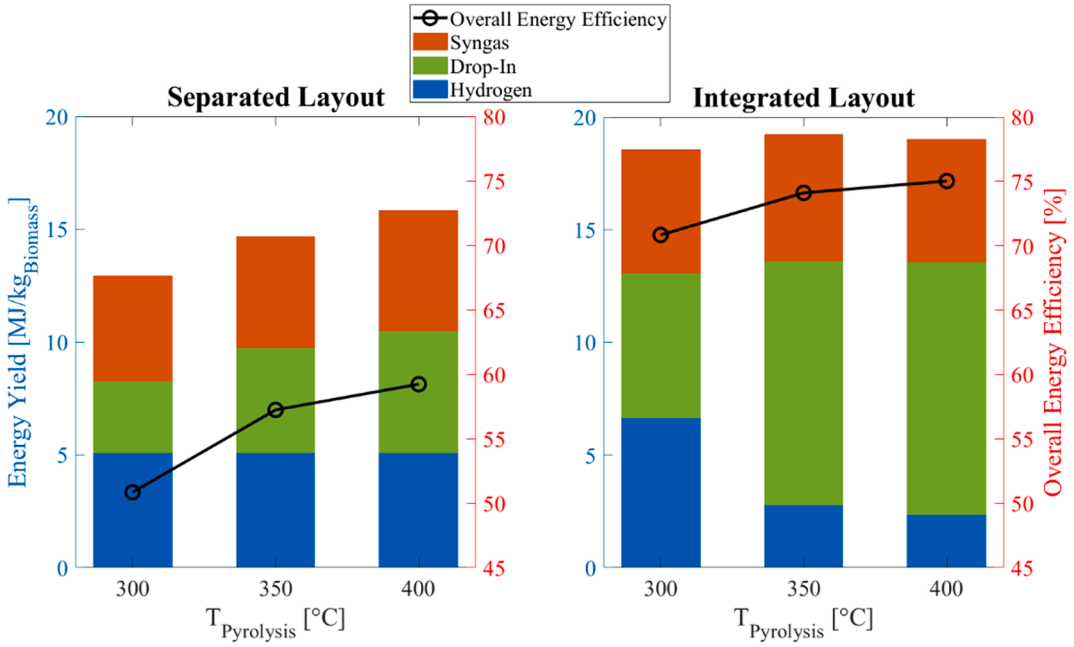

Fig. 4. Comparison of the energy parameters of the integrated and separated layouts.

in production section. The specific energy demand of the integrated drop-in production section is in fact lower by approximately 11%, 15.5%, and 16.5% at pyrolysis temperatures of 300 °C, 350 °C, and 400 °C, respectively, compared to the separated drop-in production unit. Observing the overall results, it is evident that the decrease in energy demand for SEG in the integrated layout, coupled with the increase in energy demand for the electrolyzer in the separated layout, leads to a generally higher energy requirement in the separated layout as the pyrolysis temperature rises.

Fig. 4 presents the energy analysis results for both the separated and integrated layouts across different pyrolysis temperatures. The bars represent the energy yield of various energy carriers, while the black lines depict the overall energy efficiency. In the separated layout (left side of Fig. 4), the total energy yield increases significantly with higher pyrolysis temperatures. There is a notable rise of 13% and 16% at pyrolysis temperatures of 350 °C and 400 °C, respectively, compared to the baseline of 300 °C. Specifically, the energy yield of hydrogen remains consistent across different conditions due to consistent processing in the hydrogen production unit. The syngas energy yield also increases with temperature, showing gains of about 6 % and 15 % at 350 °C and 400 °C, respectively. The most substantial increase is observed in drop-in fuel energy yield, which ramps-up by approximately 69 % from 300 °C to 350 °C, with further growth at 400 °C, resulting in an overall increase of 75%. On the right side of Fig. 4, representing the integrated layout, several observations can be made. The total energy yield shows more stability across different pyrolysis temperatures, with a minor peak at 350 °C. However, the hydrogen production in this layout decreases significantly, dropping by 58% and 65% at 350 °C and 400 °C, respectively, to be compared with 300 °C. This reduction is primarily due to increased hydrogen demand for the higher bio-oil production in the HDO process, requiring 70% more hydrogen at 350 °C and 75 % more at 400 °C compared to 300 °C. Additionally, hydrogen output from the SEG process is decreased by increasing pyrolysis temperatures, by 31 % and 35 % at 350 °C and 400 °C, respectively. Similar to the separated layout, the energy yield from syngas remains relatively stable across different conditions in the integrated layout. The energy yield from drop-in fuels also shows significant variations with pyrolysis temperature, mirroring the increase in bio-oil yield. In summary, with same distribution of biomass between the two production units into the separated layout, the integrated layout consistently shows a higher total energy yield across all the discussed conditions. The difference diminishes as pyrolysis temperature increases. At 300 °C, the integrated layout outperforms the separated layout by 43 %, narrowing to 19% at 400 °C. This decrease is primarily due to steady hydrogen production in the separated layout and, to a lesser extent, increased energy yield from pyrolysis syngas. Conversely, in the integrated layout, hydrogen energy yield decreases while syngas energy yield remains stable. Fig. 4 also illustrates the overall energy efficiency for both layouts, indicated by the black solid lines. Efficiency increases with higher pyrolysis temperatures for both layouts, with more pronounced gains in the separated layout (13 % and 16 % at 350 °C and 400 °C, respectively) compared to the integrated layout (5 % and 6 % at the same temperatures). These differences can be attributed to variations in energy yield outcomes between the layouts.

Specifically, the energy yield in the separated layout shows significant growth, whereas in the integrated layout, it remains relatively

Table 7
Comparison of carbon conversion.

Operative condition	Separated layout	Integrated layout
$T_{Pyro} = 300\ °C$	30.6 %	45.5 %
$T_{Pyro} = 350\ °C$	40.1 %	69.4 %
$T_{Pyro} = 400\ °C$	42.6 %	70.5 %

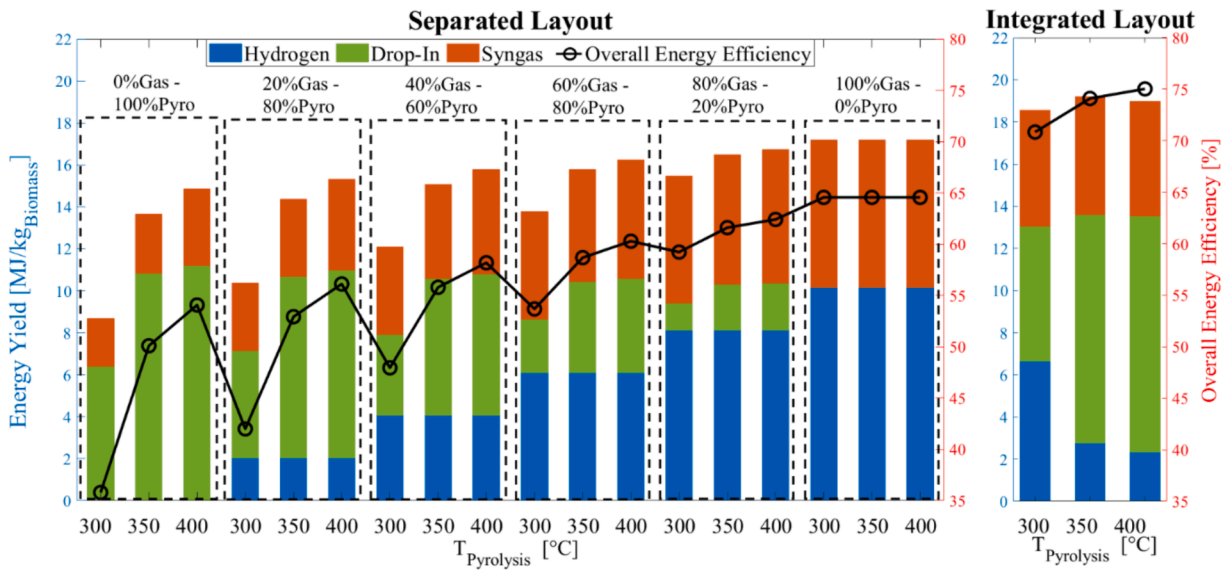

Fig. 5. Comparison of the energy parameters of the layouts at different biomass repartition.

constant across different operating conditions. The less substantial efficiency improvement in the integrated layout is primarily due to the reduction in energy demand. Overall, the integrated layout demonstrates higher efficiency, exceeding the separated layout by more than 39.3% at a 300 °C pyrolysis temperature and over 26.7% at 400 °C, whenever compared under the same operating conditions.

Table 7 presents the results for the last key performance indicator (KPI) used for the analysis, carbon conversion. Notably, both layouts exhibit their lowest performance at a pyrolysis temperature of 300 °C, while reaching a stable plateau at temperatures of 350–400 °C. This stabilization is attributed to the increased production of drop-in fuels at these higher pyrolysis temperatures. Data clearly show that the integrated layout consistently outperforms the separated layout across all the conditions analyzed. Specifically, carbon conversion rates for the separated layout never exceed 45 %, whereas the integrated layout consistently achieves rates above this value. The comparative results in each operating condition reveal significant increases in carbon conversion for the integrated layout: 48.7%, 73.1%, and 65.5% at pyrolysis temperatures of 300 °C, 350 °C, and 400 °C, respectively, compared to the separated layout under the same pyrolysis conditions.

The difference in carbon conversion between the two processes can primarily be attributed to the lack of utilization effectiveness of the biochar in the separated process for energy valorization. While carbon sequestration in char is recognized as a carbon-negative footprint strategy and is valued for its high carbon stability, its role in carbon mitigation [27] and its utility in various material applications like soil improvement, activated carbon production, and as a catalyst for tar removal [28–30], do not influence the energy analysis focus of this study. Therefore, in the context of evaluating energy efficiency and carbon conversion, the integrated layout capability of better utilizing carbon sources results in markedly higher efficiency, highlighting its advantages over the separated process in terms of comprehensive energy and carbon management.

3.2. Sensitivity analysis

As mentioned in the Methods section, the discussions of results thus far have assumed an equal distribution of biomass between the two units of the separated layout. However, the biomass fractioning between the hydrogen and drop-in production units in the separated layout significantly impacts its performance, requiring a detailed sensitivity analysis. Fig. 5 clears out the effects of variable biomass distributions within the separated layout, detailing results from six different biomass fractions ranging from 100 % in the drop-in production unit (labelled as 0 %Gas – 100 %Pyro) to 100 % in the hydrogen production unit (labelled as 100 % Gas – 0 %Pyro), with increments of 20 %. The right side of Fig. 5 provides a comparative analysis with the integrated layout. The bar charts reports the energy yield and the solid black line the overall efficiency of each pyrolysis temperature and each biomass fractioning. The left blue Y-axis reports the amount of the Energy Yield of the energy outputs, the right red Y-axis reports the overall Energy Efficiency of the process layout. The analysis of Fig. 5 reveals that increasing the biomass share directed to the hydrogen production unit results into a higher energy yield and efficiency. This outcome is primarily due to the lack of utilization of biochar as a feedstock in the drop-in production unit, which results into a considerable loss of energy yield potential. This is particularly evident when analyzing the performance across different pyrolysis temperatures; higher temperatures, which yield less biochar, also

Table 8
Results of the sensitivity analysis on biomass repartition on carbon conversion.

	Separated Layout						Integrated Layout
	0 %Gas – 100 % Pyro	20 %Gas – 80 % Pyro	40 %Gas – 60 % Pyro	60 %Gas – 40 % Pyro	80 %Gas – 20 % Pyro	100 %Gas – 0 % Pyro	Integrated Layout
T_{Pyro} = 300 °C	31.9%	31.4%	30.8%	30.8%	29.7%	29.2%	45.5 %
T_{Pyro} = 350 °C	51.1%	46.7%	42.3%	42.3%	33.5%	29.2%	69.4 %
T_{Pyro} = 400 °C	56.0%	50.7%	45.3%	45.3%	34.5%	29.2%	70.5 %

Table 9
Literature comparison.

Outputs	Efficiency	Energy yield	Carbon Conversion	References
Hydrogen, Drop-in, Syngas	64 % – 75 %	H_2: 6.6–2.3 MJ/$kg_{biomass}$ Drop-in: 6.4–11.2 MJ/$kg_{biomass}$ Syngas: 5.5 MJ/$kg_{biomass}$	45.5 %-70.5 %	[15]- this work
Hydrogen, Electricity, Heat	33 %	4.8 MJ/$kg_{biomass}$	/	[3]
Methanol, Electricity	30 % –70 %,	Methanol: 0–23.6 MJ/$kg_{biomass}$ Electricity: 0–6.8 MJ/$kg_{biomass}$	0 %-92.3 %	[4]
Methanol	62 % – 73.3 %	Methanol: 8.9–14.7 MJ/$kg_{biomass}$	40.3 %-64.4 %	[5]
Drop-in Fuel Syngas	63.9 %	Drop-in: 6.7 MJ/$kg_{biomass}$	/	[6]
Hydrogen, Syngas	18.91 %	Hydrogen: 6.4 MJ/$kg_{biomass}$	/	[7]
Hydrogen	58.9 %	Hydrogen: 13.2 MJ/$kg_{biomass}$	/	[8]
Ammonia, Electricity, Heat, Cool.	57.85 %-61.53 %	Ammonia: 0.98 MJ/$kg_{biomass}$	/	[9]
Electricity, Hydrogen	51.2 %	Hydrogen: 6.09 MJ/$kg_{biomass}$	/	[10]
Electricity, Hydrogen, Methanol.	78.13 %	Hydrogen: 2.77 MJ/$kg_{biomass}$ Metanol: 1.15 MJ/$kg_{biomass}$	/	[11]
Hydrogen, Drop-in, Syngas	65.8 %	/	/	[13]
Hydrogen, Drop-in, Syngas	/	H_2: 0.85 MJ/$kg_{biomass}$ Drop-in: 5.9 MJ/$kg_{biomass}$ Syngas: 0.5 MJ/$kg_{biomass}$	/	[14]

show improved performance in terms of both energy yield and efficiency. For example, in the 0 %Gas–100 %Pyro configuration, the 400 °C pyrolysis temperature scenario achieves a 65 % higher energy yield and 45 % higher efficiency compared to the same biomass distribution at 300 °C. Despite these findings, the overarching conclusion from Fig. 5 is that the integrated layouts consistently outperform all biomass fractioning scenarios within the separated layouts across each operational condition. Even when a high proportion of biomass is allocated to hydrogen production in the separated process, inefficiencies are still evident.

Inefficiencies in fact include the poor conversion of carbon content in the biomass, where it is converted only into syngas, and there is no further conversion into drop-in fuels. Thus, the integrated layout demonstrates superior overall performance, optimizing the use of biomass and effectively managing carbon conversion more efficiently than any configuration within the separated layout. In Table 8, the carbon conversion results for different configurations from the sensitivity analysis are detailed. Interestingly, better performance is observed when a higher proportion of biomass is allocated to the drop-in production unit. This improvement, which is in contrast to the energy analysis just discussed, is associated with the effective valorization of carbon into liquid fuel within this unit, highlighting the efficiency of converting biomass carbon content into valuable outputs. Despite these findings, the carbon conversion rates in the separated layout is substantially lower than those achieved in the integrated layout. Specifically, the separated layout carbon conversion is 29.9%, 26.4%, and 20.6% less efficient than the integrated layout at the pyrolysis temperatures of 300 °C, 350 °C, and 400 °C, respectively. This significant discrepancy highlights the integrated layout superior capability to optimizing carbon utilization across all perating conditions, effectively outperforming the separated layout irrespective of the biomass distribution strategy applied in the sensitivity analysis. This reinforces the integrated layout strengths in achieving higher overall efficiency and sustainability in biomass conversion processes.

3.3. Comparison of the proposed approach with state-of-the-art literature review

After comparing the integrated and separated processes, a further comparison was conducted to evaluate the integrated layout's performance in terms of efficiency, energy yield, and carbon conversion against findings from literature reviews, highlighting the validity of the proposed design. The summarized results are presented in Table 9.

The integrated process demonstrates balanced performance across all key performance indicators (KPIs). It stands out for its competitive efficiencies and wide-ranging carbon conversion capabilities observed in other configurations. The variability in energy yield among different outputs within the integrated process reflects targeted optimization of process parameters tailored to each product, thereby maximizing overall efficiency and utility. The consistent performance of the integrated setup highlights its robustness and adaption capabilities.

4. Conclusions

In this study, the integration of fast pyrolysis, Sorption Enhanced Gasification (SEG), and Hydrodeoxygenation process (HDO) was thoroughly examined to assess its impact on enhancing the energy performance of converting lignocellulosic biomass into hydrogen, drop-in fuels, and syngas. Using Aspen Plus software, numerical comparisons contrasted two operational layouts: a separated layout where pyrolysis + HDO and SEG processes operated independently, and an integrated layout where these processes were cascaded.

The key conclusions drawn from this study are as follows:

- The integrated layout demonstrated a notable decrease in energy demand as the pyrolysis temperature increased (up to an 19.1 % reduction at 400 °C), primarily driven by a significant reduction (up to 25 % reduction at 400 °C) in SEG process energy demand at higher temperatures. Conversely, the separated layout exhibited an opposite trend with increasing energy demand.
- Integration of SEG with fast pyrolysis + HDO consistently improved total energy yield (between 19 % and 43 %) and overall plant efficiency (between 26.7 % and 39.3 %) compared to the separated layout. This underscores the synergistic benefits of integrating these processes.
- The integrated layout achieved higher levels of carbon conversion (between 48.7 % and 73.1% with the respect to the separated process at the same operative conditions). This inefficiency of the separated layout stemmed from the lack of valorization of biochar in the drop-in production unit and the absence of drop-in fuel production in the hydrogen production unit. Integration in the integrated layout effectively addressed these inefficiencies, enhancing carbon conversion rates.
- Analysis of biomass distribution within the separated layout units revealed that the primary factor contributing to its lower energy performance was the underutilization of biochar, significantly limiting its effectiveness compared to the integrated approach.

These findings highlight the effectiveness of integrating pyrolysis, HDO, and SEG processes in enhancing the efficiency of converting lignocellulosic biomass into valuable energy products. Future research

will extend this analysis by applying Life Cycle Assessment (LCA) methodologies to further elucidating the integration benefits and developing comprehensive design tools for thermochemical plants based on multi-dimensional sustainability criteria aimed at valorizing residual biomass more effectively.

CRediT authorship contribution statement

Lorenzo Bartolucci: Writing – review & editing, Supervision, Methodology, Conceptualization. **Stefano Cordiner:** Writing – review & editing, Resources, Conceptualization. **Emanuele De Maina:** Writing – original draft, Software, Methodology, Investigation, Formal analysis, Data curation. **Vincenzo Mulone:** Writing – review & editing, Resources, Conceptualization.

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.

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