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Spotlight statement: Screening for carbon value in a future bioeconomy through carbon oxidation states and statistical entropy

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SPOTLIGHT STATEMENT

Renewable carbon sources are essential for meeting global climate and resource goal, yet current decision-making processes for biomass valorisation remain hindered by their reliance on process-specific data, which is often unavailable for emerging technologies. This work introduces a state-based screening method using statistical entropy and carbon oxidation states with a direct link to minimum thermodynamic work required for this transformation. By revealing the trade-off between purification, energy requirements and value creation, this method provides an initial screening tool for guiding bioresource decision-making based on fundamental principles. This contributes to responsible resource use, climate mitigation, and innovation in sustainable industries, directly supporting UN SDGs 7 (Affordable and Clean Energy), 12 (Responsible Consumption and Production), and 13 (Climate Action).

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ARTICLE

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The growing need for renewable resources calls for novel decision-making methods that can guide the efficient exploitation and valorisation of biomass under conditions of limited process-specific data. This study introduces a novel state-based screening method for bioresource management that evaluates biomass conversion pathways using only compositional information, thereby avoiding reliance on data-intensive, kinetic, techno-economic or process-specific parameters. The framework is built on two state variables with a direct link to the thermodynamic minimum work required for this transformation: compositional entropy (*H*, capturing energy expenses to reduce molecular complexity) and carbon oxidation state (OS_C, capturing energy expenses for carbon reductions). Four biomass conversion processes were studied to evaluate the applicability of such framework: (i) reductive catalytic fractionation, (ii) gasification, (iii) pyrolysis, and (iv) combustion. These conversions were selected as they cover the entire range from reducing to oxidising the biomass. The findings indicate that *H* effectively captures compositional complexity, while OS_C reflects the energetic distance from reduced carbon products typical of the petrochemical value chain. The method reveals trade-offs between purification, energy requirements and value creation, thereby offering insights into the very fundamentals behind energy requirements and economic feasibility. The proposed framework therefore offers a practical screening tool for comparing potential end products from a given biomass feedstock when detailed process data are unavailable. This method helps identify transformations that are more likely to minimise thermodynamic work while preserving carbon value.

Introduction

Fossil-based products are the main driver of the current global economy[1,2]. Nevertheless, to achieve Net Zero Emissions by 2050[3,4], a transition towards using more renewable resources will be needed. This must be accomplished without further delay, as evidenced by unprecedented levels of CO_2 emissions recorded in 2022[5] and the 5% increase in heat-related CO_2 emissions by the chemical industry between 2017 and 2023[6]. Current commitments are thus inadequate to meet the 1.5 °C target[7]. Biomass is often shown as a promising renewable resource, ranging from biofuels to feedstock for the chemical industry[1]. Bioenergy is expected to account for 95% of the projected growth in the use of renewable fuels by 2030[6].

Lignocellulosic biomass is recognised as one of the most promising groups of renewable feedstocks available in large quantities. However, still a wide variety of compositional profiles can be identified within this group[8]. Furthermore, the feedstock can be employed in such a manner that a myriad of different end products can be produced, each with a different targeted composition[9]. The inherent complexity of biomass valorisation, stemming from the wide variety of feedstock-product combinations and the extensive array of conversion processes required to link them, renders the decision-making process highly challenging.

Erroneous decision-making can result in financial losses in R&D, which, in turn, can adversely impact competitiveness of biomass processing. Significant financial losses have been incurred by companies such as Abengoa (USA) and Beta Renewables (ITA). Both encountered technological challenges in the processing of lignocellulosic biomass to ethanol, ultimately leading to bankruptcy[10,11]. Furthermore, the Clariant's Sunliquid cellulosic ethanol plant (USA) experienced financial losses since starting their operations, until eventually filing for bankruptcy. Although no official statement has been issued regarding the specific losses incurred, it is probable that biomass supply and technological issues were the primary contributor[12].

Currently, decision-making relies on process-based assessments, primarily techno-economic analysis (TEA) and life cycle assessment (LCA), focussing on specific processes, conversions, life-cycle stages, and contexts. The predominant parameter influencing these decisions is energy, either as a utility cost within TEA or as the largest contributor to global

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warming potential (GWP) impact within LCA. Due to the process specific character of these assessments, a complete data inventory is essential, requiring extensive expertise, time, and data. However, obtaining this complete data inventory is challenging for novel technologies at low technology readiness levels (TRLs) suffering from unavailable or scattered data. New studies often lack in comparability, owing to the absence of both general functional units and system boundaries. The confidentiality of laboratory data with no standardised reporting protocols further limits the accessibility and reliability of the already scarce data. Moreover, the inherent uncertainties in process-based assessments of existing processes are compounded. For instance, the necessity to scale lab data and the reliance on assumptions regarding the operability of the future plan further exacerbate these uncertainties[13]. This demonstrates that long-term screening of diverse pathways against a continuously changing economic and technological background is nearly impossible, which highlights the need for new and complementary methods.

Regarding the valorisation of lignocellulosic biomass, the focus is primarily on two main fundamental processes: decreasing biomass complexity and chemically transforming the biomass to the end product. In other words, the process entails the purification of the targeted compounds diluted within the biomass resource, resulting in a more concentrated product stream, apt for functional material synthesis. Concurrently, this chemical transformation process often involves a change in the oxidation state of the compounds. Reduced carbon is closer to typical petrochemical products. Because of historic dominance of fossil feedstocks, such reduced materials are more competitive and therefore a better match requiring fewer energy intensive transformation steps. This stems from the discrepancy in the oxidation state of current fossil-based materials versus that of biomass.

We hypothesise that the energy requirements for the fundamental processes of lignocellulosic biomass valorisation can be estimated and interpreted by a state-based screening method based on two state variables, namely statistical entropy and carbon oxidation states. Shifting away from the current deterministic process-based assessments enables decision support independent of the path taken reducing time, cost, and data required to do so. The method aims to identify the path of least energy, or in this context the path of least thermodynamic resistance.

The first state variable, statistical entropy H, originates from information theory (Shannon entropy), which essentially is a more generalised concept to Boltzmann's entropy (S), removing the temperature/energy dependent factor (Boltzmann constant). Instead of quantifying the disorder of physical microstates, the uncertainty on information within various probability distributions is quantified, allowing to capture complexity[14]. Within this novel method, concentrations are considered as probabilities. A low entropy indicates a concentrated stream (low complexity), while a high entropy signifies a diluted or complex stream. Since concentrating a stream, i.e., the reduction of its complexity, requires energy, a correlation between statistical entropy and energy must exist.

Statistical entropy thus has the potential to serve as a proxy for energy requirements related to concentrating resources to a more purified end product.

The second proposed state variable, carbon oxidation state OS_C, is indicative of the energy expenses required to match often oxidized resources with traditionally reduced functional molecules[15]. It is therefore a metric that captures thermodynamic distance between biomass-derived carbon and reduced petrochemical-like products within the context of biomass upgrading, fundamentally not susceptible to market fluctuations[16]. The oxidation state of carbon is widely acknowledged to be one of the most crucial metrics in the context of current circular economy initiatives[17]. Carbon oxidation states can vary from its most oxidised (+IV in CO_2) to its most reduced state (-IV in CH_4)[18]. It has been established that a reduced carbon atom possesses a greater electron density, thus rendering it more susceptible to covalent bond formation. Reduced carbons have a higher chemical energy level with CH_4 being the most energy-rich hydrocarbon. In contrast, more oxidised carbons are in an energy sink and have limited potential in releasing energy. This means that using oxidised carbon as a building block requires a large energy input[19,20]. Furthermore, when targeting typical petrochemical-derived end products, carbon in its reduced form (i.e., alkanes, alkenes, aromatics, alcohols) is closer to such products, requiring fewer process steps compared to more oxidised compounds[20]. At the other extreme, CO_2 is highly stable and chemically inert, requiring strong activation for further transformations[21]. OS_C is not a universal proxy for reactivity or value, but a directional metric for upgrading effort.

As both state variables are rooted in thermodynamics, their energetic requirements or thermodynamic work can be quantified. Lowering the entropy, i.e., concentrating the biomass stream is directly proportional to the Gibbs free energy of mixing[22]. Whereas, changing the oxidation state of carbon from its most reduced to most oxidised form costs -891 kJ/mol[23] with a near-linear relationship per oxidation state unit[24].

Though thermodynamic work alone tells only a part of the story. A key innovation of the present work is the establishment of a unified thermodynamic reference state. Methane (CH_4, H = 0, OS_C = -4) is proposed as reference. It is the most reduced, pure form of carbon relevant for biomass valorisation, introducing the distance-to-methane metric D_{CH4}. This metric integrates H and OS_C into a single quality metric while penalising for the production of CO_2.

The introduction of these metrics quantifies the thermodynamic potential of investigated processes correlated but not equal to the market value of the commoditised products. Diamond (OS_C = 0) is extremely valuable and has a low reactivity, compared to the more modest, however, constantly varying, market value of methane. The claim of this framework is not to fully estimate the market value, but rather to quantify its thermodynamic potential: a product that is thermodynamically far from functional reduced materials requires additional energy investments, and thus additional costs.

To support the hypothesis that statistical entropy and carbon oxidation state can serve as state variables for screening the carbon value, we investigated a case study comparing valorisation of poplar through four different conversion pathways: (i) reductive catalytic fractionation, (ii) gasification, (iii) pyrolysis, and (iv) combustion. Initially, the evolution of entropy and carbon oxidation states for transforming the biomass to the different end products are determined. Next, the thermodynamic work needed for these transformations quantified. Finally, a TEA is conducted independently based on Aspen Plus and literature on process flowsheet simulations. The results of both studies are then compared to verify their consistency, and predicative and interpretive value.

Methods

Rationale

For four conversion pathways that were investigated ((i) reductive catalytic fractionation, (ii) gasification, (iii) pyrolysis, and (iv) combustion), a state-based screening and process-based assessment is conducted comparatively. The state-based screening method demands solely compositional data concerning the feedstock and end products, thereby facilitating the calculation of changes in statistical entropy and carbon oxidation state from beginning to end state. Conversely, the process-based assessment requires a process model comprising full mass and energy balance, in conjunction with the anticipated CAPEX and OPEX. These parameters are the inputs required to determine the cumulative energy demand (CED, total amount of energy required throughout the process) and the selected economic parameter MSP (minimum selling price). The outputs of both assessments are then compared in order to establish whether an analysis based on statistical entropy and carbon oxidation states would yield the similar decision results as one based on CED (cumulative energy demand) and on economics (TEA). Fig. 1 provides a graphical representation of the general methodology.

Biomass feedstock

Poplar wood is selected as a hardwood feedstock for each of the investigated conversion processes, with the compositional data represented in Table 1.

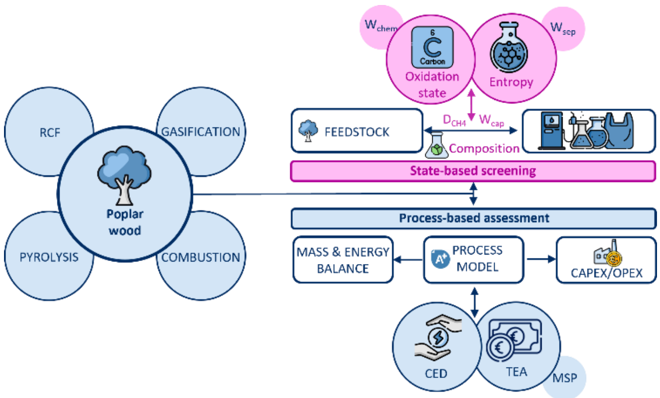

Fig. 1– Graphical representation research methodology

Table 1 Lignocellulosic biomass composition of poplar wood[26]

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Component	Content w% d.b.	Content w%
Cellulose	46.4	37.1
Xylan	13.4	10.7
Arabinan	0.2	0.2
Mannan	3.7	3.0
Galactan	1.4	1.1
Sucrose	0.1	0.1
Lignin	28.5	22.8
Acetate	3.5	2.8
Extractives	1.6	1.3
Ash	1.1	0.9
Water	0.0	20.0
Other [a]	0.1	0.1

[a] Not included in the simulation as no exact composition can be determined

A comprehensive table outlining the chemical components of poplar wood is provided in the ESI (see Table S1). In contrast to the majority of studies, such as that of Humbird et al.[25], which concentrate on the valorisation of the carbohydrate fraction whilst considering the lignin fraction as a waste, we particularly focus on lignin as a complex feedstock component to be valorised. It is acknowledged that potential lignin fractionation reactions may occur, resulting in the formation of lignin derived monomers, dimers, and oligomers. We added additional chemicals to the models to represent the lignin derivatives, some of which were available in the Aspen Plus database. However, 3-syringyl-1-propanol, 4-propylsyringol, dihydroconiferyl alcohol, syringaresinol, guaiacyl dimer, and syringyl oligomer were added manually by chemical structure. The oligomer derived from guaiacyl was not included due to the fact that the available estimations from the database were insufficient to run a simulation. Figure S1 of the ESI visually represents the solubilized lignin derivatives of S- and G-subunits. Hardwoods have little to no H-subunits which can therefore be excluded[8].

Statistical entropy analysis (SEA)

In accordance with Shannon's definition of entropy (Appendix B1 of the ESI), and Rechberger and Brunner's expansion to statistical entropy analysis for material flows[14,27], the compositional entropy of a material flow can be calculated (1), with statistical entropy H_j of material flow j with a concentration c_{ij} of compound i containing a total of N compounds. By using mass fractions to represent the concentrations, the complexity of biomass flows and end products can be quantified. This enables the selection of the pathway with the lowest entropy difference or least thermodynamic resistance, thus providing a proxy for the lowest amount of energy associated with purification or refining.

$$H_j = -\sum_{i=1}^{N} c_{ij} \log_2 c_{ij} \qquad (1)$$

In the context of the composition of lignocellulosic biomass, the calculated statistical entropy is referred to as compositional entropy. The concentrations are defined on a molecular level, representing all compounds within the biomass going to the monomers from which cellulose, hemicellulose, and lignin are built and can be found in Appendix B3 of the ESI. It is imperative to use the highest available compositional resolution because it influenced the H-baseline with the following preferred hierarchy: measured composition (e.g., GC-MS), literature compositions, and representative compounds as last resort. To determine the entropy change of a conversion process *X*, we calculate the entropy of both the input streams of the process (biomass and reagents) and output streams (product, by-products, and waste). As these processes can have multiple inputs and outputs, the entropy for each stream H_j must be quantified relative to the stream size according to equation (2) for the input and (3) for the output. The entropy of the input streams $\mathrm{H}_{X,IN}$, which contain *M* different streams, is calculated by multiplying the entropy of each individual input stream $\mathrm{H}_{j,IN}$ by its mass $m_{j,IN}$ relative to the total mass of the process m_{tot}. The calculation of the entropy of the *P* output streams $\mathrm{H}_{X,OUT}$ is analogous. This facilitates the calculation of the entropy difference, denoted as $\Delta\mathrm{H}_X$, as illustrated in equation (4).

$$\mathrm{H}_{X,IN} = -\sum_{j=1}^{M} \frac{m_{j,IN}}{m_{tot}} \mathrm{H}_{j,IN} \quad (2)$$

$$\mathrm{H}_{X,OUT} = -\sum_{j=1}^{P} \frac{m_{j,OUT}}{m_{tot}} \mathrm{H}_{j,OUT} \quad (3)$$

$$\Delta\mathrm{H}_X = \mathrm{H}_{X,OUT} - \mathrm{H}_{X,IN} \quad (4)$$

Carbon Oxidation State (OS_C)

Carbon oxidation states OS_C can be calculated using the known oxidation states of the non-carbon compounds $OS_{x\neq C}$, where *x* represents the non-carbon atoms (H (+I) and O (-II)), and the number of non-carbon and carbon atoms ($N_{x\neq C}$ and N_C, respectively), according to equation (5)[18,28]. We consider exclusively those compounds containing carbon, as the non-carbon compounds have a carbon oxidation state of 0, in other words they do not affect the assessment of carbon-based molecular products.

$$OS_C = \frac{\sum_{x\neq C} N_{x\neq C} \times OS_{x\neq C}}{-N_C} \quad (5)$$

Determining the average carbon oxidation state in a mixture requires four distinct steps. Firstly, it is necessary to ascertain the composition of the stream. Secondly, the quantity of carbon, hydrogen, and oxygen in each component of the stream is to be known. Subsequently, for each of the compounds in the stream their mole fraction is multiplied by their accompanying number of the carbon, hydrogen, and oxygen atoms. As with the statistical entropy calculations, the data requirement is limited to this compositional information only. Finally, it is possible to calculate the carbon oxidation state in a materials flow *j* ($OS_{C,j}$) by adapting equation (5) to equation (6) to represent the presence of multiple chemical compounds *i* in the stream with molar concentration n_{ij}.

$$OS_{C,j} = \frac{\sum_{x\neq C} N_{x\neq C,} n_{ij} \times OS_{x\neq C}}{-N_C n_{ij}} \quad (6)$$

As with the concept of compositional entropy, the difference over a conversion process *X* can be determined. This indicates how the carbon oxidation state evolves during the conversion process. Equation (1), (2), (3), and (4), which were utilised in the calculation of the compositional entropy, are now expressed in terms of carbon oxidations states (Appendix B2 of the ESI). Contrary to the entropy definition, the carbon oxidation state $\Delta OS_{C,X}$ is weighted by the number of carbon atoms the stream contains relative to the total number of carbon atoms in the system.

Energy equivalence of state variables

To calibrate both state variables, H and OS_C, into a single value as proxy for its energy requirement for transitioning from the biomass resource to the different end products, each of the individual state variables needs to be linked to their respective energy requirement.

The energetic work of H required for purifying or separating the biomass W_{sep} is theoretically grounded in the thermodynamic work for separating an ideal mixture. Concentrating the biomass stream could therefore be assumed proportional to the Gibbs free energy of mixing[22]. The thermodynamic minimum separation work W_{sep} is calculated using equation (7) with constants R = 8.314 J/mol, T = 473 K (a mid-process temperature), and ln(2) to transition from the natural logarithm in Gibbs energy for mixing to the $\log_2$ in compositional entropy.

The energetic work of OS_C required for chemically transforming W_{chem} the biomass is grounded in the Gibbs free energy of oxidation or reduction reactions of carbon-containing compounds (equation (8)). Complete oxidation of carbon from its most reduced (CH_4, OS_C = -4) to most oxidised (CO_2, OS_C =+4) form yields -891 kJ/mol[23]. A near-linear relationship between this energy and oxidation state units[24] resulting in approximately -111 kJ/mol$_C$.

Adding the separation and chemical work results in the thermodynamic minimum work W_{min} required for transforming the biomass to the end products (equation (9)). This work is a strict lower bound on process energy demand for transforming the biomass into its end product. Comparing the W_{min} to the CED can serve as a thermodynamic efficiency metric. However, to add together the work based on both state variables, the work needs to be converted to the same unit, in which W_{sep} is multiplied with the molar flow n of the investigated stream while W_{chem} needs to be multiplied by the molar flow of carbon atoms n_C.

$$W_{sep} = -RT.\ln 2 \,.\, \Delta H.\, n \quad (7)$$

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$$W_{chem} = -111\, kJ/mol_C \,.\, \Delta OS_C . n_C \quad (8)$$

$$W_{min} = W_{sep} + W_{chem} \quad (9)$$

To quantify whether the biomass transition is towards a more desired state, a unified thermodynamic reference state is introduced, the distance-to-methane D_{CH4}. Methane is selected as it satisfies $\mathrm{H} = 0$ (pure stream) and OS_C = -4 (most reduced state). This defines the origin of the two-dimensional screening space (H, OS_C). Similar to the thermodynamic minimum work, the distance-to-methane is the result of two parameters, D_{sep} and D_{chem}. For each product the distance is calculated according to equations (10) and (11) resulting in (12). The entropy H_j and carbon oxidation state $OS_{C,j}$ term express how far they are from the reference state. $D_{sep,j}$ ranges from 0 for pure streams with increasing compositional entropy. $D_{chem,j}$ ranges from 0 for methane to 890 kJ/mol_C for CO_2 (OS_C = +4). This way the production of CO_2 is automatically penalised.

$$D_{sep,j} = -RT.\ln 2\,.\,(0 - \mathrm{H}_j).\, n_j \quad (10)$$

$$D_{chem,j} = -111\, kJ/mol_C \,.\,(-4 - OS_{C,j}).\, n_{C,j} \quad (11)$$

$$D_{CH4,j} = D_{sep,j} - D_{chem,j} \quad (12)$$

Comparing the distance-to-methane of the feedstock against the end products of each investigated process indicates its success in moving carbon in a desirable direction. This net thermodynamic work captured by the process W_{cap} (equation (13)) indicates whether the output is closer to (positive W_{cap}) or further from (negative W_{cap}) methane and thus provides an objective, price independent measure of valorisation quality.

$$W_{cap} = D_{CH4,feed} + \sum_{j=1} D_{CH4,j,out} \quad (13)$$

Process modelling

Reductive catalytic fractionation (RCF). The RCF process is a lignin-first process in which the lignin is fractionated from the carbohydrates and depolymerised simultaneously. This approach prevents the formation of recalcitrant lignin structures, thus allowing further valorisation possibilities for the lignin besides combustion[29,30]. The final product resulting from this stage is a lignin oil consisting of lignin-derived monomers, dimers, and oligomers.

The two predominant product streams within the RCF process are the lignin-derived product stream, and a carbohydrate-rich stream containing cellulose and hemicellulose which serve as a feedstock for ethanol production. In order to achieve the desired outcome, three important parameters must be given full consideration: namely, the solvent (pure solvents or a mixture of alcohols and water in which an acid of base can be added), the reducing agent (H_2, hydrogen from the solvent or extracted from hemicellulose), and the biomass feedstock. The composition of the final product is primarily influenced by the biomass feedstock, with the variety of lignocellulosic composition impacting the quantity of lignin-derived product and its distribution[26,31].

The studied RCF process is based on the work of Bartling et al. (2021)[26], with poplar wood as the feedstock, H_2 as the reducing agent, methanol/water as the solvent, and a 15% Ni/C catalyst. A total of four output streams are considered: an RCF oil as the product, a carbohydrate-rich stream as by-product, and offgas and wastewater as two waste streams. Moreover, the study by Melaina et al.[32] was utilised to incorporate hydrogen recovery into the simulation. A process flowsheet and more details about the Aspen Plus simulations are provided in Appendix C of the ESI.

Gasification. Gasification is the process of thermally degrading biomass in a limited oxygen environment, from which syngas is derived as a final product[33,34]. The process can be subdivided into four distinct stages: drying, pyrolysis, oxidation, and reduction. It is imperative to implement a drying step to reduce the biomass moisture content[35]. In the subsequent stage of the process, the biomass is pyrolyzed at an elevated temperature in an oxygen-free environment. This process results in the release of volatile components, including CO, CO_2, H_2, and CH_4, in addition to char, ash, and water. The stream is then oxidised, which results in the generation of a mixture comprising CO, CO_2, H_2, and H_2O. Finally, a reduction process occurs, in which, in the absence of oxygen, the main product is syngas (a mixture of CO and H_2). This syngas can serve as a resource in the chemical industry after being upgraded with a Fischer-Tropsch process to either fuels or chemicals[33].

The studied gasification process is based on the NREL report by Spath et al.[36], as well as the work of Diaz Gonzalez et al.[37], with poplar wood as the feedstock and dry air as the gasification medium in the absence of a catalyst. Four distinct output streams are syngas (product stream), wastewater, offgas, and ash. Syngas could undergo further reaction through Fischer-Tropsch synthesis, resulting in the formation of a fuel mixture. This mixture can then be subjected to further separation, yielding various fractions, including natural gas, LPG, gasoline, kerosine, diesel, heavy fuels, and residual oils.

Appendix D of the ESI contains a process flowsheet and more details about the Aspen Plus simulations for the gasification process.

Pyrolysis. Pyrolysis, like gasification, is a thermal degradation process. However, it occurs in the (complete) absence of oxygen with the aim of producing pyrolysis oil[38-40]. The pyrolysis process can be subdivided into three distinct stages: a drying process, the actual conversion process, and product separation. Pyrolysis yields three main products: gases, liquids, and solids, requiring separation[39]. The gases have the potential to be recycled as process feed or to provide heat. The solids (char) can also provide heat through combustion, and the liquids (bio-oil/pyrolysis oil) can undergo further upgrading to either chemicals or fuels. Upgrading bio-oil requires additional workup steps, known as hydroprocessing. This term encompasses a combination of hydrotreating and hydrocracking[41,42]. These additional steps lie beyond the scope of this research, consequently, bio-oil is considered as the end product.

In this study, no Aspen Plus simulation was developed. The input data for the assessments was solely based on the NREL reports of Ringer et al.[39] and Wright et al.[41], which included a detailed process description, an Aspen Plus simulation, mass balances, and TEA. Where literature data and the investigated conversion process did not exactly match, some assumptions were made (e.g., bio-oil yields), as described in detail in the ESI (Appendix E).

Combustion. Combustion is defined as a thermal degradation process that with an excess of oxygen while producing combustion gas[43,44]. During biomass combustion, heat is generated that can be utilised to generate power and electricity. A frequently implemented industrial combustion process involves the utilisation of a combined heat and power (CHP) plant[45]. CHP processes require pretreatment, which involves grinding down the biomass to the size of sawdust. The heat generated during subsequent combustion is then utilised to create steam from water. During the process of combusting biomass exhaust (which contains CO_2, excess air and H_2O vapours) and ashes are generated.

The required data for the TEA was based on the studies of Alizadeh et al.[45] and Sadaka and Johnson[44]. A comprehensive description of the combustion process and a detailed list of the assumptions made is provided in the ESI (Appendix F).

Techno-economic analysis (TEA)

A TEA is conducted to evaluate the economic feasibility of each of the conversion pathways of poplar wood[46,47]. The same feedstock, location, and general assumptions were applied for the four studied conversion pathways.

Market Study. In the context of this particular TEA, Belgium is regarded as the location, which consequently results in a tax rate of 25% for the biorefinery. The project lifetime is set at 20 years, starting in 2021, with an annual operating time of 8,000 hours, a discount rate of 15%, and a linear depreciation rate of 10 years, aligning with the assumptions of Tschulkow et al.[48] and Brienza et al.[49], who both examined the economic performance of valorising the lignin fraction of lignocellulosic biomass. Furthermore, the plants were assumed to have a capacity of 2000 dry metric tons of poplar per day, with the biomass composition represented in Table 1.

Mass and energy balances. To obtain the required mass and energy balance data, we created or consulted process flowsheet simulations. The process flowsheet for the four conversion pathways under investigation are illustrated in the designated section of the ESI (Appendix C-E). Aspen Plus (V12.2) was utilised to simulate the process for RCF and gasification. For the remaining two conversion pathways (i.e. pyrolysis and combustion), mass and energy balances were retrieved from literature. Depending on the process, mass balances can be obtained from experimental data and used as an input for Aspen Plus, or alternatively from reaction modelling, and from the resulting models energy balances and equipment cost can be determined. Finally, for the conversion pathways for which an Aspen Plus simulation was built, the Aspen Energy Analyser (AEA) was utilised to create a heat exchanger network (HEN) to optimise generated heat within the process.

Although heat integration is not a direct component of a TEA, it exerts a significant impact on the obtained results, decreasing utility costs. Nevertheless, it must be noted that this integration incurs additional capital expenditures, which in turn increase the overall costs. Consequently, a trade-off must be made to ascertain whether this heat integration is beneficial. In the creation of a HEN most of the default assumptions were maintained, although the ROR (rate of return), plant lifetime, and yearly operating hours which brought in line with the general TEA assumptions, respectively 15%, 20 years, and 8000 h/year.

Process economics. The minimum selling price (MSP) of the end product (i.e., the price of the end product that leads to an NPV (net present value) of 0, considering the predefined assumptions) is calculated as the economic indicator to be compared to the current market price of the product.

The calculation of both operational expenditures (OPEX) and capital expenditures (CAPEX) is based on assumptions derived from the book by Sinnot and Towler (2020)[47]. Aspen Process Economic Analyser is utilised to determine equipment costs for each unit operation within the simulation. In instances where no simulation data is available, literature is consulted as substitute.

Adjustments to the time (reference year 2021) for the equipment costs were conducted using the chemical engineering plant cost index (CEPCI)[50]. Changes in equipment size were adjusted using scaling factors, while changes in time for materials and utilities were adjusted using producer price indices (PPI)[51,52]. Finally, changes in currency were accounted for by using the exchange rate in 2021[53].

A comprehensive summary of all assumptions and equations essential for calculating the economic parameters is presented in the ESI (see Appendix B4). This overview encompasses the equations necessary to adjust for time, size, and currency.

Interpretation. The results obtained are interpreted by comparing the calculated economic parameters (MSP) to current market prices or estimates thereof. A sensitivity analysis is undertaken to identify key impacts on the selected economic indicator (MSP). A total of eight parameters are taken into consideration: fixed capital investment (FCI), OPEX, discount rate, feedstock price, chemical costs, catalyst cost (if applicable), utility cost, and by-product selling price (if applicable). The selected parameters were subjected to a 10% increase and decrease, allowing for the identification of key influential parameters for the MSP. It is acknowledged that the conversion processes are not yet implemented on a commercial scale, besides combustion, and as a consequence, some uncertainties are inherent to the results. Learning effects are not considered in the TEA.

Results and discussion

Compositional entropy H and Carbon oxidation states OS_C

The entropy and oxidation state calculations for each of the investigated case studies are reported in the ESI (ESI Novel state-based screening method H and OSC.xlsx).

Reductive catalytic fractionation (RCF). The RCF process is characterised by a negligible entropy change of -0.02 (Fig. 2a). This is logical and can be attributed to the manner in which the compositional entropy of the biomass is defined, namely by its monomers and for lignin, by its monomers, dimers and oligomers. Owing to the inherent complexity of lignin, it is more realistic to hypothesize that complete depolymerisation is not achieved. The negligible entropy change is attributable to the occurring fractionation. Limited reactions occur, with only H_2 acting as a reducing agent, which does not result in a significant alteration to the complexity of the mixture and, consequently, the entropy. RCF is essentially a fractionation process, not a simplification process. The complexity of the input biomass is redistributed across rather than reduced. The other two inputs, methanol and water are utilised solely as solvents and do not react; therefore, their addition does not influence the entropy change of the system. Nevertheless, the solvent composition does need to be included in the entropy calculations, as it is possible that a fraction of the solvent will react. A clear difference in entropy evolution emerges when specific fractions obtained from fractionating the biomass are considered. Each of the individual streams undergoes a decrease in entropy, thus experiencing a process of purification, except for the product stream (+0.85) which increases. This is due to the intrinsic complexity of the lignin fraction. The removal of other less complex compounds in larger quantities (e.g. glucose) results in a complex mixture. In contrast, the by-product (carbohydrate-rich pulp) undergoes a purification, resulting in an entropy reduction. Where the overall $\Delta\mathrm{H}$ of -0.20 gives the impression that the RCF process is entropically neutral, the $\Delta\mathrm{H}$ of the individual streams reveal the separation steps that occur, it is just internally compensated. The overall $\Delta\mathrm{H}$ masks the internal complexity redistribution.

Regarding the carbon oxidation state (Fig. 2e), the more complex lignin oil product stream exhibits a decrease in ΔOS_C (-0.29), thus rendering it slightly closer to the desired reduced state. All the other product streams show a decease as well. This confirms the reducing character of the RCF process. Upon examining the process in its entirety, a small increase has been observed (+0.07) caused by the addition of methanol (OS_C = -2.00) as an input. Solely considering the feedstock to all the outputs show a decrease of -0.27. The net chemical transformation is almost negligible, confirming the findings of $\Delta\mathrm{H}$ which identifies the occurrence of a fractionation rather than a reaction.

Gasification. In contrast to the RCF process, gasification exhibits a distinct entropy change ($\Delta\mathrm{H}$ = -0.85, Fig. 2b). The negative value indicates a decrease, or overall purification. In addition to the fractionation of the biomass, several severe reactions occur, resulting in the formation of three main fractions: a gaseous, liquid, and solid fraction. The process of breaking down the complex biomass into a less complex mixture of gasses (e.g., CO, CO_2, H_2, etc) thus results in a lower compositional entropy. As illustrated, the gasification process also results in an entropy decrease in each of the outgoing streams individually. It is only when the produced syngas is subjected to further reaction to generate a mixture of fuels (with a composition ranging from C_2 to C_{60}, Appendix D7 of the ESI) that the entropy once again increases. Further separation of different fractions would evidently decrease the entropy.

The significant reduction of entropy has a flipside. While a decrease in H was observed, an increase in oxidation state over the entire process (+2.93) and to syngas (+2.28) were observed (Fig. 2f). Even though a more purified stream is obtained, the process is moving carbon away from the reduced, high-value state at a large scale. This finding serves to reinforce the hypothesis that OS_C is a significant supplementary parameter for the decision-making process in bioprocessing systems. From an OS_C perspective, the generation of a mixture of fuels through the Fischer-Tropsch synthesis would be advantageous in achieving the desired decrease (-0.29) though overall still an increase is found caused by the production of fluegas (ΔOS_C = 0.92). Nevertheless, in the quest for low-entropy functional materials this path is not efficient, given the entropy increase.

It should be noted, however, that the FT-process is an upgrading process and therefore follows the gasification process. Thus, complexity is first decreased, while the value is destroyed and then recreated simultaneously. This will have implications for the energy requirements which is visualised through the $\Delta\mathrm{H}$ and ΔOS_C trajectory without any process modelling.

Pyrolysis. Biomass pyrolysis results in a change in entropy (Fig. 2c), although the extent of this change strongly depends on the level of detail in which the bio-oil compositional data is available. The bio-oil composition is often identified by using representatives, capturing an entire diverse group of different compounds[39,41] resulting in an oversimplification of the composition of the bio-oil as shown in Appendix E5 of the ESI. This oversimplification causes an artificial entropy decrease with -0.27 (Appendix E5). However, literature reports bio-oil

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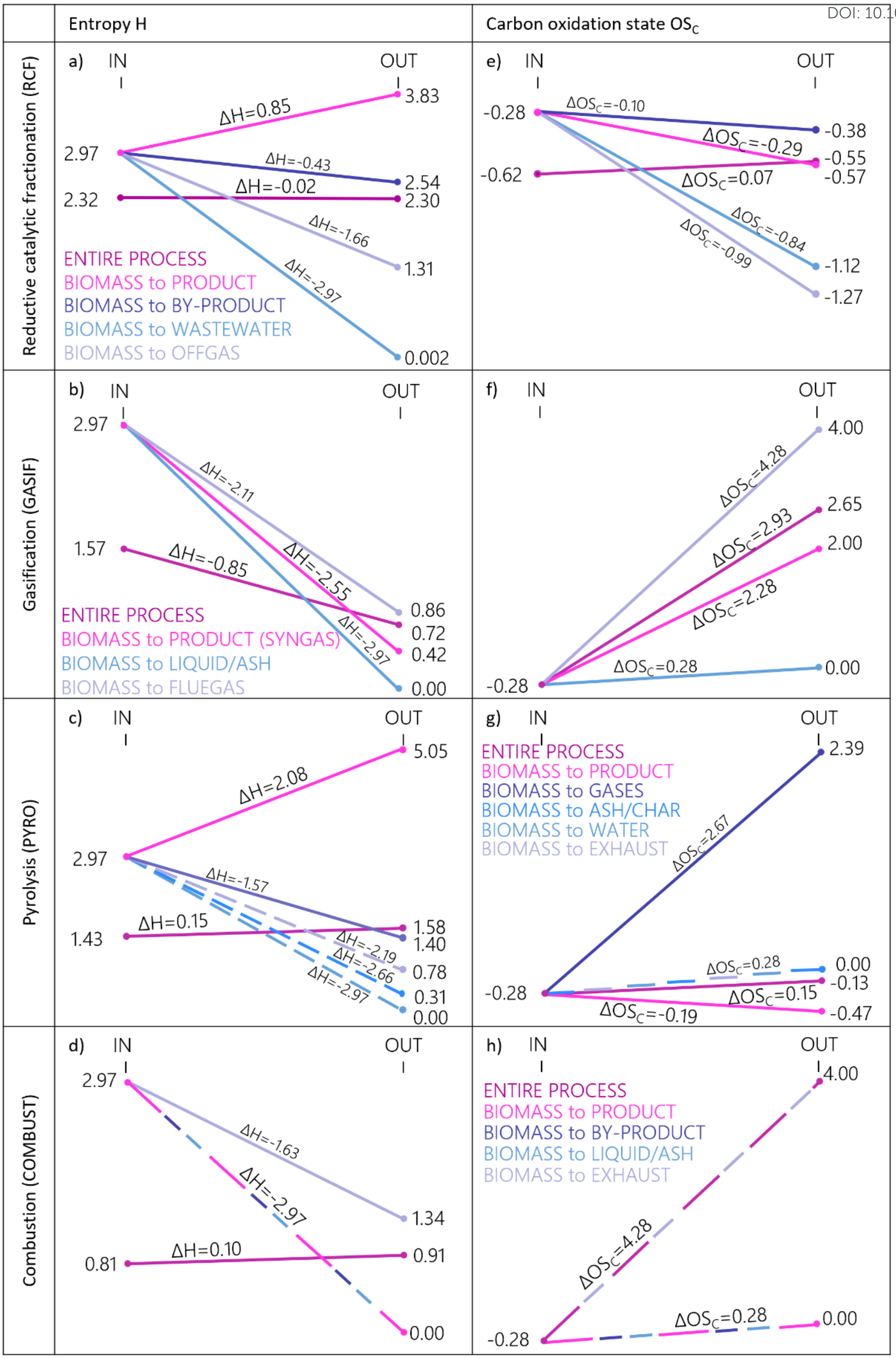

Fig. 2 – Results compositional entropy (ΔH) and carbon oxidation state (ΔOS_C) change for the investigated conversion processes: a) ΔH RCF, b) **Δ**H gasification, c) ΔH pyrolysis, d) ΔH combustion, e) ΔOS_C RCF, f) ΔOS_C gasification, g) ΔOS_C pyrolysis, and h) ΔOS_C combustion

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consisting of up to 200 different compounds[39]. An additional scenario was investigated based on the results of a GC-MS analysis in which 78 peaks were identified[54]. The quantifications of these peaks was based on relative peak area (%), as a rapid estimate for the mass fractions (since quantitative analysis is missing). The identified increase is driven by the bio-oil entropy increase of +2.08, and reveals that by implementing the new bio-oil composition, an increase is now identified with a $\Delta\mathrm{H}$ of +0.15. This demonstrates that the method is sensitive to real chemical information in a pyrolysis creates genuine molecular complexity at molecular level beyond depolymerisation, a complexity that is neglected by using representatives. While this may appear initially to reduce the robustness of the method, the level of composition at which the products are compared is easily adjustable, enabling different research questions to be answered depending on how the compositional distribution is defined. If a practitioner uses representatives, they will predict purification; if they use realistic bio-oil composition, they will predict a complexity change. The method therefore incentivises better compositional characterisation of bio-oil, which is a constructive and actionable outcome.
The carbon oxidation state (Fig. 2g) slightly increases (+0.15) over the entire process. The targeted product has a decrease of -0.19. Most of the other outputs have an OS_C of 0 (an increase compared to biomass) as they do not contain any carbon. However, the overall increase is caused by the generation of the gasses with an OS_C increase (CO and CO_2 , +2.00 and +4.00). Unlike gasification, pyrolysis largely preserves the carbon oxidation state of the feedstock in the liquid product, it mainly transforms complexity.

Combustion. A minor increase in entropy ($\Delta\mathbf{H}$ = +0.10,Fig. 2d) is observed for the complete combustion process; conversely, a decrease is observed from the biomass to the outgoing streams. The increase of the general process is caused by the excess air that is added as input, which dominates the input and thus decreases the ingoing entropy from +2.97 to +0.81. Furthermore, many of the outgoing streams are relatively pure, thus showing a decrease in entropy. As the product of this process is steam produced from water added to the process, this decrease does not directly originate from the biomass itself. The decrease in H for the exhaust, which is generated from the biomass itself, is less pronounced. This is due to the fact that the exhaust is now a mixture of excess air, water vapour, and the generated CO_2. In comparison to the biomass itself, the exhaust is less complex in composition.
The carbon oxidation state (Fig. 2h) increases throughout the process (+0.28), with each individual output stream also increasing (+0.28 to +4.28). Consequently, it can be deduced that, despite the lower complexity of the composition of the streams (lower $\mathbf{H}$), the streams that are formed possess a lower potential value. The exhaust displays a similar increase to that observed in the entire process, as all of the carbon present in the biomass is directed towards the exhaust. As the sole carbon present in the stream is CO_2, it has maximum attainable OS_C (+4.00). In reality, a fraction of the biomass is reduced to ashes and solid carbon, with an OS_C of 0.00. This results in a decrease in the size of the exhaust stream and consequently decreases the change of carbon oxidation state over the entire process as now a fraction of the carbon present in the system has an OS_C of 0.00.

Energy equivalence of state-variables

The energy equivalence calculations for each of the investigated case studies are reported in the ESI (ESI Novel state-based screening method H and OSC.xlsx and appendix G).

Each of the produced products can be identified by two coordinates in the $\mathbf{H}$-OS_C plot. This plot as shown in Fig. 3 visually represents how each of the end products is situated compared to the biomass (2.97, -0.28) and the reference state pure CH_4 (0, -4.00). To transition from the biomass to the end products both a change in $\mathbf{H}$ on the horizontal axis and OS_C on the vertical axis occurs. These shifts require energy inputs which can theoretically be quantified. Equation (7) calculates thermodynamic minimum separation work W_{sep} as a result of changing the $\mathbf{H}$, while equation (8) calculates the thermodynamic minimum work W_{chem} for chemically transforming the biomass by changing the OS_C of the biomass Table 2 provides an overview of these energies together with the thermodynamic minimum work W_{min} required for the transition from biomass to end products. Based on these results, the chemical transformation W_{chem} clearly dominates over separation W_{sep}. The thermodynamic burden of biomass valorisation is not the purification, but rather the energy for

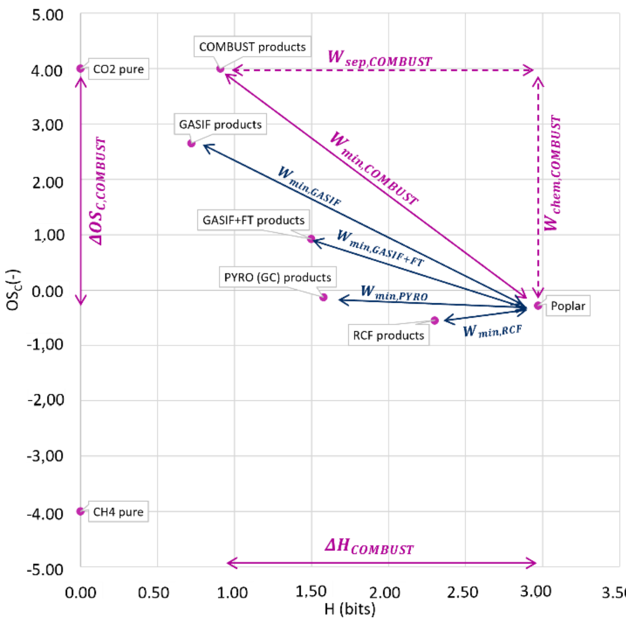

Fig. 3 H -OS_C plot poplar conversion processes representing states within the biomass processing flows for the investigated case studies: Reductive catalytic fractionation (RCF), gasification (GASIF) incl. Fischer-Tropsch (+FT), pyrolysis (PYRO), and combustion (COMBUST)

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Table 2 State-based screening metrics for poplar valorisation for the investigated case studies: Reductive catalytic fractionation (RCF), gasification (GASIF) incl. Fischer-Tropsch (+FT), pyrolysis (PYRO), and combustion (COMBUST) at 2000 dry metric tons of poplar per day

	W_{sep} (MW)	W_{chem} (MW)	W_{min} (MW)	W_{cap} (MW)	$D_{CH4, out}$ (MW)
RCF[a]	0.12/-0.15	18.0/10.2	18.1/ 10.0	-13.3/ 279	413/ 121
GASIF	11.5	-183	-172	-83.6	484
GASIF+FT	-0.36	23.7	23.3	118	282
PYRO	-2.29	15.2	12.9	109	291
COMBUST	21.7	-366	-345	-303	703

[a] Two values: considering lignin oil and carbohydrate-rich pulp as products, and only lignin oil as product

altering the oxidation state of the carbon. Though the relatively low value W_{sep}, it becomes increasingly important when processes with a similar ΔOS_C are investigated. This study deliberately investigated conversion pathways to represent a wide range of ΔOS_C value.

Combining Fig. 2 with the energy equivalences reveals three thermodynamically distinct scenarios. The main findings are summarised, while more detailed information can be found in Appendix G of the ESI.

First, structure preserving processes such as RCF show a near-zero ΔH (-0.02) with an internal stream-level complexity redistribution (+0.85 biomass-to-product). A fractionation occurs rather than a simplification. Lignin oil (the product) and the carbohydrate-rich pulp (by-product) become more oxidised, however, over the entire process a slight reduction (ΔOS_C = +0.07) occurs. This phenomenon can be observed with the W_{min} focussing on the products energy is required (+10.0 up to +18.1 MW), while considering the entire process energy gets released (-7.83 MW, Table 3).

Second, processes that destroy and partially reconstruct molecular structure. Where gasification itself shows a great entropy decrease (-0.85 entire process, -2.55 to syngas), it comes with one of the greatest carbon value losses (ΔOS_C = +2.93 process, +2.28 product) identified with -83.6 MW of W_{cap}. However, the FT process partially reconstructs this value with a W_{cap} of 118 MW. Pyrolysis shows similar carbon value creation towards the products (W_{cap} = +109 MW).

Third, processes that destroy molecular structure such as gasification W_{cap} = -83.6 MW product) and combustion (W_{cap} = -303 MW). The theoretical maximum of OS_C +4.00 is generated with combustion resulting in the grave carbon losses. Though this process generates the most energy (W_{min} = -345 MW product), it comes at a clear carbon value loss.

Energy balances and TEA

A comprehensive overview of the TEA results, including a market study, process flowsheets, mass and energy balances, CAPEX and OPEX breakdown, and sensitivity tornado charts are included in the ESI for each of the conversion processes (Appendix C-F), while the most relevant findings are summarised in Table S47 (Appendix H).

Discussion and implications for decision support

Solely based on Fig. 2 and the energy equivalence, three distinct classes of biomass valorisation pathways can be identified. Pathways that preserve molecular structure show near-zero overall ΔH with internal complexity distribution, and a negative internal complexity redistribution to the end product, are thermodynamically modest. Pathways that destroy and partially reconstruct molecular structure (GASIF+FT, and PYRO) show large ΔH variations and moderate ΔOS_C changes are thermodynamically expensive or complex, with variable carbon value outcomes depending on reconstruction. Pathways that destroy the molecular structure entirely (COMBUST and GASIF) show a decreasing ΔH but catastrophic ΔOS_C increase, i.e., thermodynamically simple but carbon-value destroying. This classification emerges purely from the investigated state-variables and requires no TEA nor complete process modelling. Therefore they provide a screener with a genuine decision framework: choose your regime based on your target product requirements , then use the TEA to optimise within that regime.

We compared the results based on state-variables (ΔH and ΔOS_C) with current state-of-the-art decision-supporting assessments (TEA). An overview of the rankings obtained from the TEA (MSP and CED) and state variables (W_{min}, W_{cap}, and $D_{CH4,out}$) are provided in Table 3. As shown by the minimum thermodynamic work W_{min}. Across all investigated conversion processes, chemical transformation work (W_{chem}) exceeds separation work (W_{sep}) by orders of magnitude, indicating that biomass valorisation is fundamentally limited by redox transformations rather than purification. The results for MSP, CED and W_{min} are mostly consistent, only the CED of PYRO and GASIF switched rank. For $W_{min,ALL}$ and $W_{min,PROD}$ the same ranking is found though they tell two distinct stories. $W_{min,ALL}$ captures the minimum thermodynamic work considering all input and output streams so including how the process was conducted, thus depending on process-specific decisions. Conversely, $W_{min,PROD}$ captures the targeted transformation solely considering the biomass and its products independent of process decisions. Furthermore, looking at the step size in MSP and $W_{min,PROD}$ for COMBUST, GASIF and RCF they are of a similar quantity. Only RCF shows a large deviation which can be explained by the novelty of the process. RCF is not (yet) commercialised, so both the CED and MSP of the process have not been optimised. This highlight dependency of process-specific decisions of a TEA. In other words, though RCF might

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Table 3 Ranking conversion processes for process (MSP and CED)- and state-based variables (W_{min}, W_{cap}, $D_{CH4,out}$) with their accompanying values showing consistent results between MSP, CED, and W_{min}, while highlighting the expected inverse relationship with W_{cap} and $D_{CH4,out}$

	MSP[a] (€/kg)	CED[a] (MW)	$W_{min,ALL}$[a] (MW)	$W_{min,PROD}$[a] (MW)	$W_{cap,PROD}$[b]	$D_{CH4,out}$[a]
COMBUST	1 (0.11)	1 (2.81E-1)	1 (-458)	1 (-345)	4	4
GASIF	2 (0.24)	3 (6.64E1)	2 (-313)	2 (-172)	3	3
PYRO	3 (0.39)	2 (1.16E1)	3 (-16.1)	3 (13)	2/1	2/1
RCF	4 (1.90)	4 (2.97E3)	4 (-7.83)	4 (18)	1/2	1/2

[a] the lowest value gets the best ranking
[b] the highest value gets the best ranking

seem energetically infeasible now, it has the potential to move much closer to the MSP of PYRO. Therefore, the state-based screening can help future researchers estimate what the MSP should be to become competitive. The ranking agreement between MSP and W_{min} is high, with only minor deviations (e.g., PYRO vs GASIF), confirming that thermodynamic minimum work captures the dominant cost trends.

Where W_{min} estimated how difficult the transformation from biomass to product is, the two other state-based parameters (W_{cap} and $D_{CH4,out}$) focus on how useful the transformation is and where the value of the product is positioned in the bioeconomy compared to the reference state of CH_4. Ideally, W_{cap} should be as high as possible indicating a transition towards the desired state, whereas $D_{CH4,out}$ should be as low as possible in which the product is situated closer to the reference state. These rankings again show a similar result to the MSP, only now in reverse order. This is a crucial insight in the transition to a steady-state bioeconomy RCF and PYRO switch positions depending if only focussing on the target product lignin oil or if the carbohydrate-rich pulp is considered as product as well. The TEA parameter to compare these values to would be the revenues under market equilibrium, however, due to the process dependency, compositional variability, and immature markets, this becomes difficult. COMBUST and GASIF, two more commercialised processes, follow the same trend as the revenues based on market value and product stream size. We thus demonstrate that state-variables could serve as a proxy to situate the potential revenues from novel biomass valorisation processes. The bioeconomy is complex to capture, making it difficult to estimate future scenarios. By focussing the fundamental properties, the core drivers of the bioeconomy can be identified.

Two additional scenarios were investigated. First, an additional process, upgrading the gasification outputs with FT (GASIF+FT), was investigated, however, the results are excluded from Table 3. This process is more difficult to compare to the other processes as the upgrading can only occur following the gasification process. Second, the influence of implementing a heat integration network (HEN) was investigated. Where the process-based parameters drastically change after implementation, the state-variables remain unchanged. These findings substantiate the hypothesis that the selected state-based parameters represent the thermodynamic minimum independent of engineering optimisation (e.g., heat integration). Process -level optimisation determine proximity to this thermodynamic minimum. We elaborate these scenarios in Appendix I of the ESI.

Lastly, the state-based screening (ΔH and ΔOS_C) were calculated over each process step individually in order to identify how it evolves through the process. A detailed analysis was conducted, and the results are reported in Appendix J of the ESI. This demonstrates that the state-based method is not intended to replace process-based assessments, since it does not provide insight into what occurs between the beginning and end states. By operating at the molecular-state level and deliberately excluding process-specific decisions and assumptions, it offers an initial screening to address the gaps where process-based assessments lack applicability, with the objective of guiding decisions when considering different end products from available biomass feedstocks. In other words, the goal of the state-based screening is not to make decisions about a specific process that one wants to optimise, but rather to provide a fundamental basis for decisions relating to biomass and end products and provide corresponding thermodynamic insights. While processes, economic conditions, and heat integration potential may change depending on future scenarios, fundamentals remain the same.

For biomass valorisation, besides the composition of the final product, the sourcing of the feedstock is an important parameter as well, considering its geospatial spread. The analogy of compositional entropy can be applied to the geospatial distribution of lignocellulosic biomass. Once more, the concentration, now at the geospatial level, can be translated into entropies. These entropies are hereafter referred to as geospatial entropy. A plethora of definitions of geospatial entropy have already been developed[55], however, the most appropriate definition for biomass valorisation needs to be selected. In this study, only one type of biomass feedstock, poplar, was analysed. As a result, variations in feedstock sourcing were not considered, and the effects of geospatial distribution and geospatial entropy were not incorporated.

Conclusions

This study proposes a state-based screening method using statistical entropy H and carbon oxidation states OS_C to facilitate expedited decision-making processes in lignocellulosic biomass valorisation. Based on the thermodynamic origin of the state-viables, the minimum thermodynamic work W_{min} needed

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for the biomass transformation were determined. These results show that, across the full OS_C range considered in this case study, OS_C has a stronger influence on W_{min} than H. The key parameters are: (i) W_{min}, which indicates the difficulty of converting biomass into products and follows the same ranking as the MSP; (ii) W_{cap}, which indicates the usefulness of the transformation; and (iii) $D_{CH4,out}$, which shows how close the product is to the desired reference state and follows the same ranking as the revenues of the most commercial processes.

The framework distinguished which pathways are fundamentally favourable, not how to optimise them. By focussing solely on state variables, an initial screening can be performed independently of specific process conditions. Consequently, these state variables can be calculated without the need for a detailed process flowsheet or TEA. Comparative analysis of conversion processes and their TEA results show overall results that are in line with the state-based screening. However, they also highlight the considerable reliance of process-based assessments on the decisions taken, such as including a heat integration network (HEN), whereas H and OS_C were found to be independent of these decisions. This underscores the role of state-based screening in guiding early decisions when detailed data for process-based assessments is lacking. The approach is not intended to replace process-based assessment, but rather to address the information gaps where they cannot be used, or as an analytical complement.

List of symbols and abbreviations

H: Statistical entropy
OS_C: Carbon oxidation state
RCF: Reductive catalytic fractionation
GASIF (+FT): Gasification (+ Fischer-Tropsch synthesis)
PYRO: Pyrolysis
COMBUST: Combustion
S: Boltzmann entropy
H_j:Compositional entropy of material flow j
j: Material flow
i: Chemical compound in material flow j
C_{ij}: Concentration of i in j
m_j/m_{tot} : mass of material flow j/the entire process X
H_X: Compositional entropy of process X
OS_C: Carbon oxidation state of carbon
$OS_{x\neq C}$: Oxidation state of non-carbon atoms
$N_C/N_{x\neq C}$: Amount of carbon and non-carbon atoms
N_{ij}: molar concentration of compound i in flow j
$OS_{C,X}$: Average carbon oxidation state for process X
W_{min}: Minimum thermodynamic work for transforming the biomass to the end product
W_{sep}: Thermodynamic separation work
W_{chem}: Thermodynamic chemical transformation work
D_{CH4}: Distance-to-methane metric
D_{sep}/D_{chem}: Distance-to-methane at separation and chemical transformation level
$D_{CH4,out}/D_{CH4,feed}$: Distance-to-methane of the outgoing and feed streams
W_{cap}: Thermodynamic work captured by the process
$W_{min,PROD}$: Minimum thermodynamic work for transforming biomass to the desired end product
$W_{min,ALL}$: Minimum thermodynamic work for transforming all inputs to outputs of the biomass conversion process
HEN: Heat integration network

Author contributions

Britt Segers: Writing – original draft, Writing – review & editing, Conceptualization, Methodology, Data Curation, Formal Analysis, Validation, Visualization, **Philippe Nimmegeers:** Writing – original draft, Writing – review & editing, Conceptualization, Methodology, Resources, Supervision. **Pieter Billen:** Writing – original draft, Writing – review & editing, Conceptualization, Methodology, Resources, Supervision. All have read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

Data for this article, including a thorough description of the process flowsheet simulations, techno-economic assessments, and entropy and carbon oxidation state calculations have been included as part of the Supplementary Information (ESI Novel state-based screening method.pdf and ESI Novel state-based screening method H and OSC.xlsx).

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Data availability statement: Screening for carbon value in a future bioeconomy through carbon oxidation states and statistical entropy

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DATA AVAILABILITY STATEMENT

Data for this article, including a thorough description of the process flowsheet simulations, techno-economic assessments, and entropy and carbon oxidation state calculations have been included as part of the Supplementary Information (ESI Novel state-based screening method.pdf and ESI Novel state-based screening method H and OSC.xlsx).