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A Practical Approach to Using Energy Integration in the Simulation of Biomass Thermochemical Processes: Application to Supercritical Water Gasification

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Featured Application: The specific application of this work is the effective energy integration of thermochemical processes dealing with nonconventional solids, such as solid biomass, in process simulation under chemical equilibrium so that all heat exchangers can be placed and designed, which allows for energy savings and complete energy and exergy analyses, thus providing a better feasibility assessment of any new thermochemical process under study and development. In this way, the method currently applied to the simulation of biomass is improved.

Abstract: Solid biomass is usually simulated by decomposing it into a solid phase (carbon, ash, and sulfur) and a gas phase (water and diatomic molecules of H_2, N_2, O_2, and Cl_2) from the proximate and ultimate analysis before entering a reactor operating under chemical equilibrium when using Aspen Plus. However, this method prevents the use of energy integration for the feed stream from the system inlet to the reactor. This paper proposes an approach to solving this issue, considering biomass with both known and unknown chemical compositions; the latter involves the decomposition of biomass into complex molecular compounds. Different process arrangements were assessed to achieve a realistic simulation, and a sensitivity analysis was carried out to examine the effect of the concentration and heating upstream of the reactor, focused on supercritical water gasification (SCWG) of orange peel. This process is very energy-intensive, so the approach is useful for a better calculation of the energy requirement and exergy losses in a plant; these are usually and mainly related to the train of heat exchangers. In addition to this application to SCWG, this approach can be used for any other thermochemical process, such as gasification, pyrolysis, or combustion, and for any real biomass. Upon a base case study using a wet biomass of 10,000 kg/h with 90 wt.% water where the SCWG reaction takes place at 240 bar and 800 °C, if the temperature at the SCWG reactor inlet increases from 350 °C to 400 °C, the heat exchange increases by 57% from 4 MW and by 34% if the water content decreases to 70 wt.%, although more heat relative to the solid is saved.

Keywords: supercritical water; gasification; simulation; biomass; heat integration; aspen plus

1. Introduction

Process simulation is an excellent tool for gaining insight into the performance of a chemical plant with many pieces of equipment using a number of different separation techniques and reactive systems. Simulation allows one to determine what might happen depending on operating conditions, including the temperature, pressure, type of feedstock, composition and concentration of components, reaction time, and other technical aspects such as energy and mass integration. In addition, on many occasions, experimentation may be too expensive or even impractical due to limitations in resources related to time, labor, and interferences or disturbances in a running plant. Experimentation cannot be substituted by process simulation, but this makes it possible to reach or complete some challenges where experimentation is too hard, thus promoting or dismissing a certain

research route. Additionally, process simulation can even complement experimentation by designing or assessing the more suitable operating arrangement for a process or by planning, in the most economical way, the laboratory and plant experiments required for the design, thus helping establish extreme boundary conditions or obtaining the behavior of a system within and outside the experimental boundaries.

Process study under chemical equilibrium is useful because, although many reactors are designed based on kinetics and rates of mass and heat transfer, the most suitable operating conditions can be inspected, determining whether the research of a new process is worthwhile (e.g., by carrying out a techno-economic assessment and a life cycle assessment). Hence, the simulation output can be used as a benchmark and even allows us to propose improvements in a process.

Another relevant aspect in chemical process simulation is energy integration, particularly if the process is energy-intensive, such as supercritical water gasification (SCWG), which is a developing technology that is very suitable for dealing with biomass or organic waste containing a large amount of water thanks to the special properties of supercritical water (SCW) [1–3]. The special properties of supercritical water lead to a high carbon-to-gas conversion and hydrogen yield, which is also predicted by thermodynamic calculations, and this has been achieved effectively with a suitable catalyst [4]. As an emerging technology, many researchers in SCWG strive to develop new concepts for process design or propose improvements by optimizing a previously developed one, which can only be performed by simulation. In this way, techno-economic and life cycle assessments make it possible to check the potential feasibility of the specific process implemented in a complete plant. Energy integration may cause a process to be energy self-sufficient or viable and allows for a more realistic exergy analysis, since the main exergy losses occur in units related to transfer heat, such as heat exchangers or furnaces. Furthermore, considering the high pressure at the reactor, the gaseous product stream leaving the reactor can be expanded, thus generating electrical power and still containing enough enthalpy and temperature to exchange heat with colder streams, such as the feed stream, before entering the reactor. In fact, heat integration aims to optimize energy and exergy efficiencies.

Aspen Plus [5] is a powerful chemical process simulation software with a database that includes a large list of components with their properties and suitable thermodynamic methods. However, simulation with fluids is more developed than simulation with solids, so there are feedstocks classified as nonconventional solids without a known chemical formula or structure, such as coal or biomass. This is because of their large number of components or the lack of properties related to this type of solid. Despite this, Aspen Plus is the best software for simulating chemical processes involving solids. Nonconventional solids are normally characterized empirically by a minimum set of attributes to be used in the simulation [6–8], but due to the lack of equilibrium and physical property data, they do not participate in phase equilibrium calculations and heat exchange. Currently, simulations using nonconventional solids are still performed in a very simplified way that hinders the process regarding complete and effective energy integration.

Therefore, there is a gap in the process simulation of thermochemical processes that use nonconventional solids as feedstock, which affects the heat integration of the feed stream with other process streams before entering the reactor. To our knowledge, nothing has been done to address this gap, so this paper proposes a new approach to simulating solid biomass in a different way, including the feed stream from the plant inlet to the reactor in the energy integration, which is omitted in the method currently used in process simulation. The new method is supported by the fundamental physicochemical principles discussed below, so it can be used with confidence in any thermochemical process dealing with a nonconventional solid.

The paper is structured as follows: Section 2 describes the current method and the new approach, Section 3 shows the results of the different arrangements or configurations regarding the flowsheet design for applying energy and material integration and discusses

the main results using the first principles, and, finally, Section 4 provides the conclusions achieved in this study.

2. Methodology

This section describes the current method used to simulate solid biomass, a nonconventional solid, as typically used in most simulation papers, and the new approach focused on achieving an effective integration of the feed stream both energetically and materially, thus improving the method usually applied.

2.1. The Current Simulation Method and the New Approach Applied to Solid Biomass

Typically, nonconventional solids are decomposed in a reactor block (RYield) from the proximate analysis (moisture, fixed carbon, volatile matter, and ash), the ultimate or elemental analysis (C, H, N, O, S, and Cl), and the sulfur analysis (pyritic, sulfate, or organic origin). The stream leaving the RYield block is calculated using an easy Fortran subroutine implemented as a yield calculator (Figure 1). This stream is composed of a solid phase (carbon, ash, and sulfur) and a gas phase (water vapor and diatomic molecules of H_2, N_2, O_2, and Cl_2). Additionally, the enthalpy is calculated using the enthalpy of formation and the heat capacities of these constituents, as well as the heat of combustion. Generally, the inert ash present in the stream leaving the RYield block is removed before entering an RGibbs block, where the minimization of the Gibbs free energy is performed using conventional components to model the chemical equilibrium. This way of simulating a process using a nonconventional solid as a feedstock and operating under chemical equilibrium has been used mostly in thermochemical processes, such as those concerning gasification, for more than a decade [9] and even more recently [10–12]. The same can be found in papers on supercritical water gasification (SCWG) [13–18]. A typical flowsheet is shown in Figure 2, where a dry biomass is mixed with a liquid water stream, pumped, and heated before entering the reactor, simulated as a combination of the RYield and RGibbs blocks.

Figure 1. Fortran subroutine used in the RYield block to decompose the feedstock.
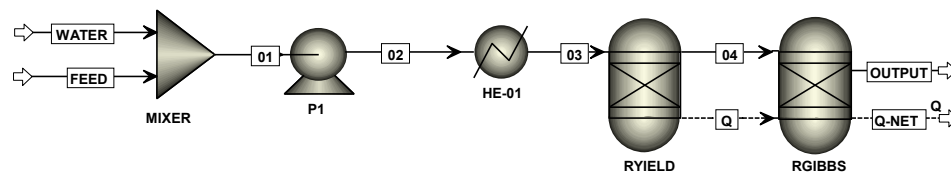
Figure 2. Typical flowsheet for the inlet section to the reactor of a thermochemical process.

However, the approach to a real reactor using RYield and RGibbs blocks, closely connected to each other and both operating under the same conditions, avoids the use of a train of heat exchangers from the feed stream to the reactor because dry nonconventional solids do not participate in heat exchange processes. This is a serious weakness, as it could reduce the energy requirement for the overall process. To our knowledge, this limitation has not been considered when a simulation is performed by a combination of RYield and RGibbs, thus preventing a complete energy integration from being applied to the process.

Figure 3 illustrates two arrangements involving a train of heat exchangers that progressively heat the feed stream containing solid biomass up to 800 °C, using an increase in temperature of 100 °C in all heat exchangers except the first, where the temperature increases from 25 °C to 100 °C. For any simulation performed, if the biomass does not have moisture at all, none of the heat exchangers work, so this train is useless (Figure 3a). Similarly, if the biomass has moisture, there is a certain heating of the biomass, and this is due to the water content; the final heating is the same as if the biomass is not fed. However, there is no change in the state from biomass to liquid or gas in the simulation output; even the moisture content is as high as 90%, which is unrealistic. However, if the biomass is fed without moisture and this is added as liquid water in another stream (Figure 3b), there is a change in state from liquid to supercritical (gas in Aspen Plus [19]). In addition, for any arrangement, a feed stream with only a nonconventional solid phase, with moisture but without the presence of a liquid phase, prevents the stream from being pumped. In this sense, Figure 2 works because the stream to be pumped is a slurry, i.e., a mixture of solids and liquids. However, although the flowsheet converges and provides a simulation output, the increase in pressure and its correspondent energy consumption is due only to the liquid water, so the flowsheet would be equivalent to another in which the water stream is pumped and then mixed with a feed stream (biomass) entering at the pumping pressure; in fact, the enthalpy flow is the same regardless of the pressure. In addition, the wet nonconventional solid, simulated by a mixture of a dry nonconventional solid and a stream of liquid water, participates in the heat exchange process to the extent that water does, i.e., the solid phase does not participate in the heat exchange. In this way, some researchers have used a flowsheet in which liquid water is pumped and heated but solid biomass directly enters the RYield block, and the stream leaving this unit is mixed with the water stream before it goes to the RGibbs block [20,21].
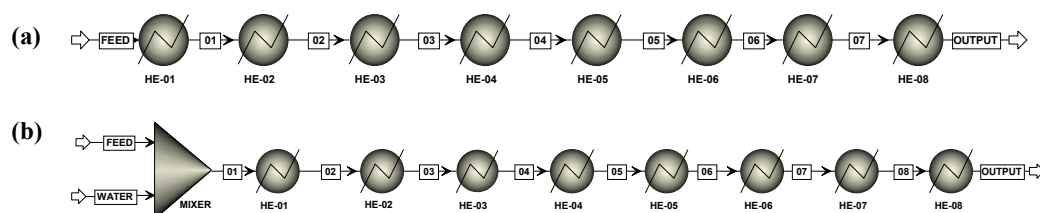
Figure 3. Train of heat exchangers to heat (**a**) wet/dry solid biomass and (**b**) dry biomass mixed with a liquid water stream.

In the proposed novel approach, the RYield block operates under the operating temperature of the feed at the process inlet, usually ambient temperature (here, set at 25 °C), instead of under the reaction temperature of the RGibbs block. In this way, the stream leaving the RYield can pass through a number of heat exchangers before entering an RGibbs block, thus making complete energy integration in the plant simulation possible.

Figure 4 shows the same train of heat exchangers as Figure 3 but adds an RYield block at the end of the system (Figure 4a) and at the beginning of the system (Figure 4b). The energy balance results are the same, as discussed later. By feeding a nonconventional solid (biomass) and placing the RYield at the end, the biomass conversion (decomposition prior to entering the RGibbs block) and the temperature rise take place in the RYield block because the heat exchangers do not work. However, if the RYield is located at the beginning, sensible heat could be used in a series of heat exchangers to raise the temperature from 25 to 800 °C (or whatever final temperature it was). The situation of this arrangement is the same as the use of dry solid biomass that is decomposed in an RYield block and a water stream that is mixed with the stream that leaves the RYield (Figure 4c). This is described and verified in the next section by building, solving, and comparing a series of different arrangements to illustrate the practical approach presented here.
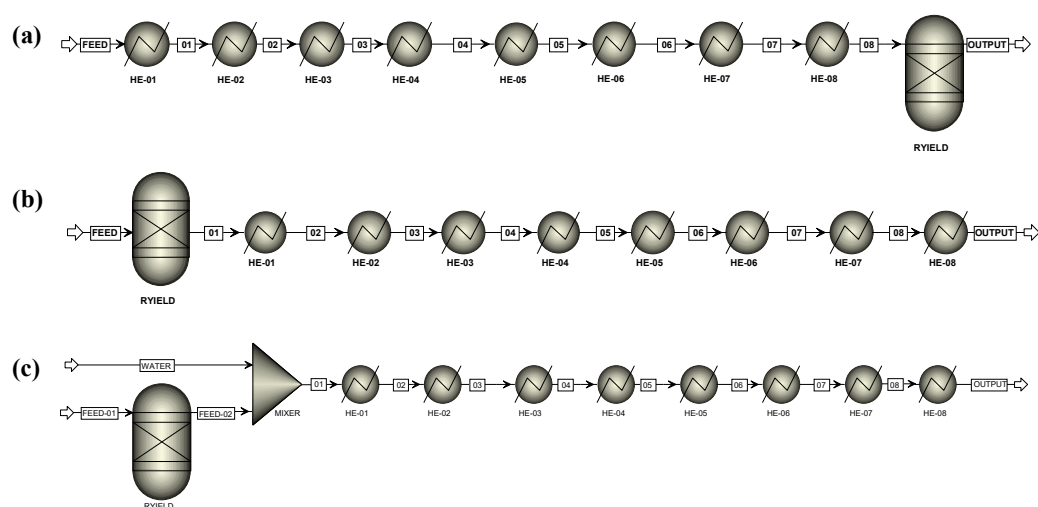

Figure 4. Arrangements where the RYield block is placed (**a**) at the end of the heat exchangers, (**b**) at the beginning, for a wet solid biomass, and (**c**) at the beginning, for a dry biomass mixed with a liquid water stream.

In the new method, the RYield block can provide the usual outlet stream composition (with C, S, H_2, N_2, O_2, and Cl_2) or a set of molecular compounds representative of the specific biomass if chemical analysis is available. The chemical composition of solid biomass is usually based on groups of chemicals such as cellulose, hemicellulose, lignin, proteins, fats, or sugars, and these or their representative model compounds can be assigned to the mass fraction according to previous experimental studies. Then, a flowsheet is designed where RYield operates under the operating conditions at the plant inlet, followed by a pump and a series of heat exchangers, before entering the RGibbs block. In this way, the result could be even more realistic in terms of energy.

2.2. Process Arrangements from the Feed Stream to the Reactor

To illustrate the methodology, orange peel was used. The industries related to orange juice, the jam industry, and fresh orange fruits produce millions of tons of citrus waste [22], and the number of papers on the valorization of orange peel is increasing [23]. As it has a large amount of water, a hydrothermal conversion process, such as supercritical water gasification (SCWG), could effectively convert this citrus waste into H_2 or biofuels.

Orange peel has been chemically characterized by a number of components [24,25] (wt.%): soluble sugar, 16.90; starch, 3.75; cellulose, 9.21; hemicellulose, 10.50; lignin, 0.84; pectin, 42.50; ash, 3.50; fats, 1.95; protein, 6.50; others, 4.35. This composition is given with tolerance ranges and could be approached by chemical compounds representative of those that are more complex without available data. Thus, cellulose and hemicellulose, polymeric in nature, have been widely studied, and glucose and xylose can be accepted as

model compounds [25,26] since they can be considered as repeated units. Similarly, natural lignin is a polymer mainly built from three monomers, and p-coumaryl alcohol is one of them (H-lignin) [27,28]. Under supercritical water conditions, at a temperature higher than 400 °C, the polymeric species can be completely converted into these representative model compounds and oligomers, as has already been reported regarding the conversion of cellulose to glucose [29]. The three most common soluble sugars are glucose, fructose, and sucrose [30]. Sucrose is composed of a glucose molecule and another fructose molecule, so the same amount is considered for each sugar (5.63 wt.%). Regarding proteins, proline is an amino acid present in orange peel [31]. Likewise, galacturonic acid is representative of pectin [30,32]. Starch generally has 20–25 wt.% amylose and 75–80 wt.% amylopectin [33], so 25 and 75 wt.% are adopted. Triolein, oleic acid, and glycerol are model compounds of fats [34,35], and the same proportion is used for each one. Finally, the remaining 4.35 wt.% can be modeled by ascorbic acid (3.5 wt.%) and other acids with a proportion of 0.25 wt.% (citric, malic, malonic, and oxalic acids) [32]. The elemental composition (wt.%) is C, 39.1; N, 0.8; H, 5.9; and O, 50.7 (dry basis but with 3.5 wt.% ash).

Different arrangements/flowsheets are designed to be evaluated (Figure 5)

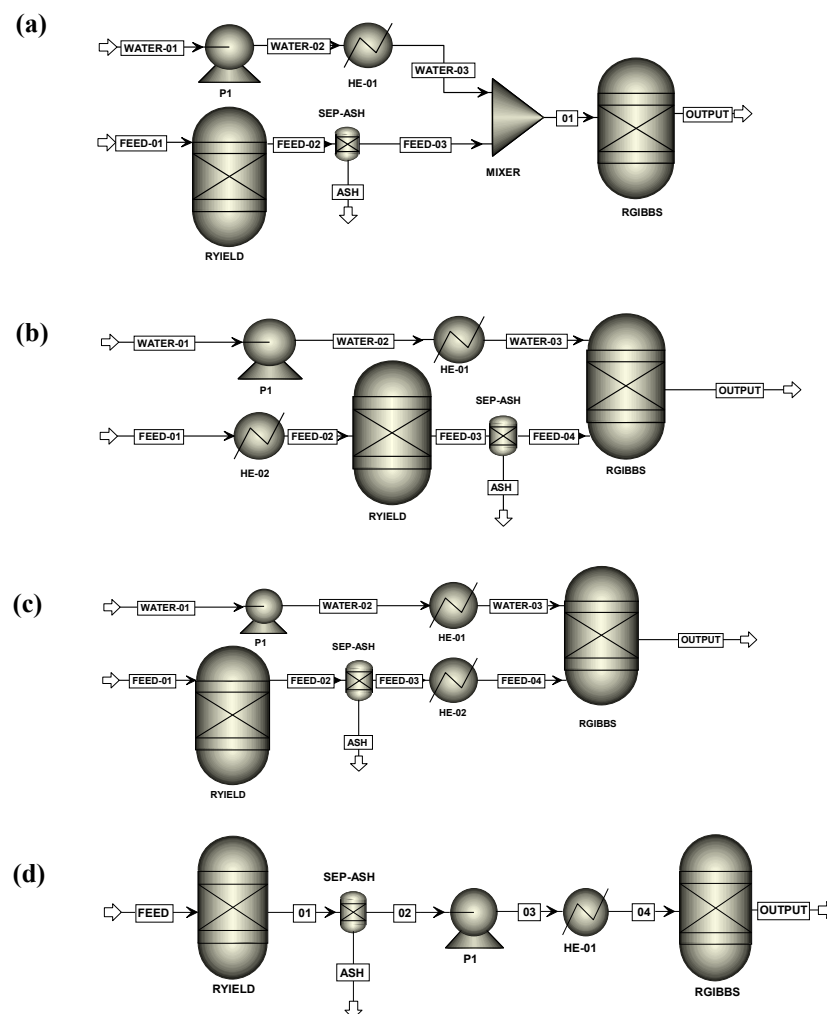**Figure 5.** Flowsheets or arrangements: ARR-1 (**a**), ARR-2 (**b**), ARR-3 and -4 (**c**), and ARR-5 (without pump) and -6 (**d**).

1. ARR-1: The RYield plus RGibbs blocks operate under reactor conditions. The RYield block decomposes the feedstock into C, H_2, and O_2 (Figure 5a).
2. ARR-2: The same as ARR-1, but RYield operates at the RGibbs inlet temperature using a preheater for the feed stream (Figure 5b).

3. ARR-3: The same as ARR-2, but RYield operates at ambient temperature, and the stream that leaves the block is heated (Figure 5c).
4. ARR-4: The same as ARR-3, but RYield decomposes solid biomass into its representative liquid model compounds (Figure 5c).
5. ARR-5: There is a unique feed stream for RYield since water is considered as moisture in the solid, thus simulating wet solid biomass. RYield operates at ambient temperature, and the stream leaving the block is heated. Solid biomass is decomposed into C, H_2, and O_2 (Figure 5d). A pump cannot be added because the stream is a mixture of solid and gas.
6. ARR-6: The same as ARR-5, but RYield decomposes the wet solid biomass into a series of representative liquid model compounds (Figure 5d). A pump is added to the system to increase the pressure to 240 bar, so the electrical input is calculated.

To perform the simulation, the thermodynamic method used in the RYield and RGibbs blocks must be the same. Three Equations of State (EoS) were applied: Peng–Robinson (PR), Soave–Redlich–Kwong (SRK), and predictive Soave–Redlich–Kwong (PSRK), which has been successfully applied to describe the supercritical state [19]. The SCWG reaction takes place at 240 bar and 800 °C, the mass flow of the feedstock is 10,000 kg/h with 90 wt.% water, and the temperature at the RGibbs block inlet is 350 °C (base case).

Figure 6 shows the Fortran subroutine implemented to decompose the wet biomass into model compounds related to the more complex chemical composition.
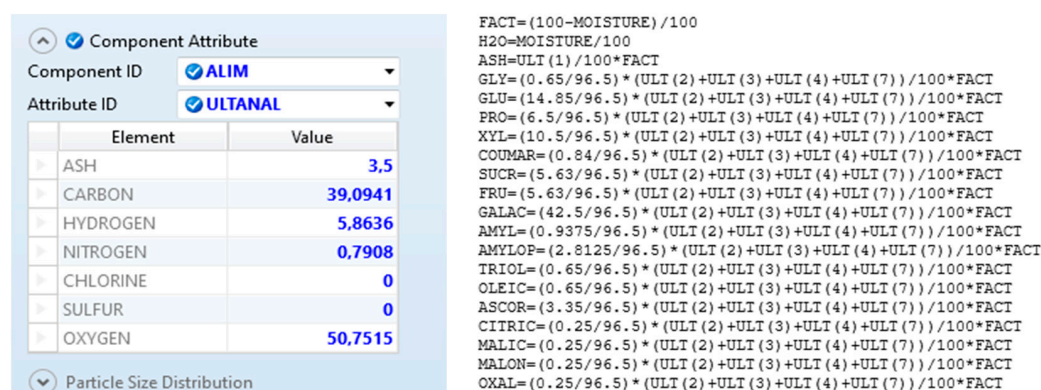

Figure 6. Fortran subroutine for decomposing orange peel into its molecular components (RYield block). Note: Commas have been used as decimal separator instead of points in the left part of this Figure.

2.3. Validation of the New Approach

There are very few experimental studies on the SCWG of orange peel [36], but the use of simulated chemical equilibrium in an RGibbs block has been reported to produce a reasonably good match with the experimental results for glycerol and alkanes [37]. Likewise, acceptable correlations were reported between the simulation output under chemical equilibrium and the experimental data obtained for glycerol, corn starch, and saw dust [13] and for the black liquor of wheat straw in supercritical water at 750 °C [38]. In this paper, the suitability of the chemical equilibrium in predicting the performance of the SCWG reactor is compared with the experimental data of two previous studies, using glycerol at a reaction temperature of 800 °C with an Ni-based catalyst [39] and a simulated bio-oil aqueous phase fraction consisting of a mixture of acetic acid, acetol, 1-butanol, and glucose over an Ni-based catalyst [40] at 800 °C. In addition, the experimental data of the SCWG of cornstarch [41] and the simulation output in an SCWG process [42] have also been used for validation.

Nevertheless, the simulation output of this study is not focused on biomass conversion, carbon-to-gas conversion, the hydrogen yield, the syngas yield, or the catalyst performance, which could require a comparison with experimental results beyond the good match

between the simulation output under chemical equilibrium and the experimental results of several biomasses using a catalyst and high temperatures, equal to the one used in this study (800 °C). The focus of the study is on how the feed stream can be dealt with to effectively heat it up before entering the reactor, using, e.g., a process stream coming from downstream of the reactor (energy and material integration) to save energy. This is a design aspect rather than an operation result to achieve a better evaluation of a process in a chemical plant to be examined by simulation. This approach allows one to save energy in a real process that does not affect the final conversion or yields with respect to the current method used because the mass balance in a reactor operating under equilibrium is always the same for both the current method and the new method proposed here. In fact, the approach presented here can be applied to process units in a chemical plant with confidence because the results, discussion, and conclusions are based on fundamental physicochemical principles, as shown in the next section.

3. Results and Discussion

The use of SRK, PR, or PSRK EoS gave slightly different, but qualitatively the same, numerical results, so the relevant results are provided using PSRK EoS only.

As the first main result, the stream leaving the system from the RGibbs block has the same composition, enthalpy, and any other property in all arrangements and regardless of the decomposition carried out in the RYield. Therefore, it is not necessary to exactly specify all the chemical species present in the feed stream to perform the method based on the minimization of the total Gibbs free energy of the system, and only the mass composition of the elements constitutive of the biomass (mainly, C, H, O, N, Cl, and S) is required. This result can be explained by the way the method works. The key lies in how the stream leaving the RGibbs block is calculated: An expression of the total Gibbs free energy of the system is implemented, accounting for the number of moles of reactants, products, and inert compounds (i.e., all species present) in all phases, so the number of moles of each species in each phase subject to the stoichiometric constraints is varied until a solution is found that minimizes the total Gibbs energy of the system to achieve chemical equilibrium between reactants and products. This is typically accomplished using the Lagrange multipliers method.

It might seem that because the formation free energy and fugacity coefficients of all the compounds, present in both the feed and the product of the reactor, are required to compute their chemical potentials in the minimization of the Gibbs free energy method, the feed entering the RGibbs block would change the composition of the stream leaving the reactor. However, this is not the case, and by using the elemental analysis as the input, the result is the same if the mass of chemical elements in the feed is conserved. The composition of the stream leaving the RGibbs block is always the following for all arrangements (kg/h): H_2, 99.0; CO, 221.3; CO_2, 1025.4; CH_4, 21.7; N_2, 7.5; NH_3, 0.5; H_2O, 8589.6. In the ash separator, 35 kg/h of ash is removed from the biomass entering the reactor. This method is a nonstoichiometric approach in which no reactions are provided and no equilibrium constants are used.

Because only equality constraints (conservation of the atoms of the elements present in the feed) are involved in the minimization problem, the solution can be obtained by adding as many Lagrange multipliers as there are elements present in the feed. They represent the element potentials [43–45] in such a way that the chemical potential of a component is just the sum of the products of the element potentials multiplied by the number of element moles present in its chemical formula. Thus, each atom of a given element adds the same amount to the Gibbs free energy of the system, regardless of the molecule or phase in which it is present.

Therefore, the only unknown variables of the problem are these multipliers, along with the total number of moles in each phase at the given temperature (T) and pressure (P), irrespective of the number of chemical species present.

Chemical reactions make the system components not independent, and, by the Gibbs phase rule, a minimum number of components leads to a minimum number of independent reactions. The former corresponds to the number of elements present in the feed along with the dominant species in equilibrium. More components involve more reactions, but the number of degrees of freedom is the same, thus explaining the result obtained in the simulation.

Table 1 illustrates the validation of the model used in the simulation, as described in the previous section, when the biomass is glycerol with the same concentration used in this paper and using an Ni-based catalyst with a space velocity of 5 h^{-1} at 800 °C. Note that the experimental data match the equilibrium very well. Similarly, this Table also shows a good fit between the experimental data of an aqueous fraction of bio-oil simulated by three organic compounds (15 wt.% acetic acid, 2.5 wt.% acetol, and 2.5 wt.% glucose) at 800 °C and a space velocity of 10 h^{-1} of the same Ni-based catalyst used for glycerol. Both experimental studies were carried out at 240 bar. Likewise, it also shows the excellent match between the experiment and the simulation output using cornstarch as the biomass with a feed concentration of 10.4 wt.% at 715 °C and 280 bar.

Table 1. Comparison of the composition of the product gas in experimental and simulation studies.

Compound	Experimental Yield (mol/mol)	Equilibrium Yield (mol/mol)	Deviation	Reference
H_2	5.27	5.320	−0.050	[39]
CO_2	2.11	1.990	0.120	[39]
CO	0.27	0.790	−0.520	[39]
CH_4	0.32	0.220	0.100	[39]
H_2	2.41	2.400	0.010	[40]
CO_2	1.48	1.290	0.190	[40]
CO	0.29	0.580	−0.290	[40]
CH_4	0.45	0.430	0.020	[40]
H_2	0.55	0.552	−0.002	[42]
CO_2	0.35	0.345	0.005	[42]
CO	0.03	0.027	0.003	[42]
CH_4	0.06	0.076	−0.016	[42]

As a second result, the overall energy balance does not change from one arrangement to another, since the enthalpy is a thermodynamic state function, and the system outlet is always the same for all arrangements and regardless of the decomposition in the RYield. For a conventional component, the absolute enthalpy is calculated using elements at 1 atm and 25 °C (standard reference state), involving only two inputs for a condensed state, such as the feedstock used in SCWG: the chemical energy of formation from the elements and the thermal energy or sensible heat required to heat the components from 25 °C to the final temperature at constant pressure. Other inputs, such as the energy required for the phase change, heat of mixing, or pressure correction, barely affect the absolute enthalpy of solids and liquids. For a nonconventional component that leads to the use of an RYield block, the model used by Aspen to compute the enthalpy is based on correlations for the heat of combustion, the standard formation enthalpy, and the heat capacity.

Table 2 shows the heat loads of each process unit for all arrangements, where the ash enthalpy is not considered in the analysis due to its small value. The RYield + RGibbs can be arranged to use the sensible heat term of the feed stream for heat integration in such a way that the RYield contribution is just the difference between the standard formation enthalpies of streams leaving and entering this block.

Table 2. Heat loads (kW) of the process units for different arrangements (base case).

	ARR-1, 2	**ARR-3**	**ARR-4**	**ARR-5**	**ARR-6**
RYIELD	2279.75	1816.67	40.49	1867.31	18.99
SEP-ASH	balance	balance	balance	balance	balance
PUMP [*]	177.40	177.40	177.40	-	186.65
HE01	3855.61	3855.61	3855.61	5950.79	4089.70
HE02	-	165.44	211.37	-	-
RGIBBS	4560.36	4850.45	6580.75	3036.75	6559.52
RYIELD + RGIBBS	6840.11	6667.12	6621.24	4904.05	6578.51
SYSTEM	10,873.45	10,873.45	10,873.45	10,873.45	10,873.45

(*) For the pump, the numbers are electrical power rather than head loads (kWe).

ARR-1 and ARR-2, typically found in the literature, give the same RYield contribution to the energy balance, regardless of the temperature profile in the system, including the temperature in the RYield block and the temperature at the HE01 outlet. The heater placed at the inlet of the RYield block in ARR-2 to simulate the heating of the feed stream does not work with nonconventional solids, and thus the exchanged heat is null. Therefore, ARR-1 and ARR-2 are the same arrangement, close to that shown in Figure 2, and none allow for heat integration with respect to the organic stream fed to the process (clearly, HE01 can be considered for it due to liquid water). The operation of RYield and RGibbs blocks at the same temperature and pressure as the real reactor (ARR-1) hinders the use of a heat exchanger for heat integration with a process stream, such as that leaving the SCW reactor. In this configuration, the independent water stream can be used for energy integration.

In ARR-3, the contribution of RYield, operating at 240 bar but at 25 °C, is reduced due to heat exchanged in HE02, which allows a certain heat integration to increase the temperature from 25 to 350 °C, and also to the greater impact in the RGibbs block, since all inputs are now at 350 °C (in ARR-1,2 the temperature of the stream coming from the RYield block is 800 °C). In ARR-4, solid biomass is converted into a series of liquid model compounds representative of that specific biomass, instead of solid C and gaseous H_2 and O_2, leading to a very small contribution of RYield. Somewhat more heat is exchanged in HE02 as a result of the state and composition of the stream that passes through.

The behavior of ARR-5 is similar to that of ARR-3, and the pressure in RYield must be the same as that of RGibbs, because if it were ambient pressure, the heat exchanged in HE01 would increase significantly due to the gaseous state of part of the stream leaving the RYield block. Finally, the arrangement ARR-6 is similar to ARR-4, with a lower contribution of RYield, which is almost irrelevant, and a slightly higher electrical consumption in the pump. Heat exchange takes place in one heater (HE01). The energy required in the SCWG reactor (RYield + RGibbs) is the lowest of all arrangements after ARR-5.

It is shown that, if the RYield block operates at ambient temperature, the sensible heat can be used for energy integration, which is possible for ARR-3 to ARR-6 where the organic feed stream is definitively included in heat integration. At this point, we wonder what process arrangement is the best for applying energy integration to the SCWG of solid biomass. As we want to use as much sensible heat as possible in the heat exchangers placed between the stream entering the process and the reactor inlet using other process streams downstream of it, we should select the arrangement that requires the lowest thermal power for the reaction (RYield + RGibbs). However, the heat load in HE01 must be realistic, i.e., somewhat higher than, but also close to, that of the case in which only water is heated, as there is 90 wt.% water in the biomass. Therefore, ARR-5 is unrealistic, as the heat load in HE01 is 54% higher than for ARR-1,2. This is because the vapor fraction of the stream leaving HE01 in ARR-5 is 21% (the liquid and solid fractions are 75% and 4%, respectively). The high vapor fraction significantly reduces the absolute mass enthalpy, leading to a larger amount of heat exchanged in HE01. Furthermore, ARR-5 does not include a pump, so its

electrical power cannot be calculated. If the pressure in HE01 were 1 atm, the results would be even more unrealistic because the heat exchanged would increase to 7840 kW, since the vapor fraction would be 96%. Therefore, the most realistic arrangements are ARR-3, -4, and -6. The former involves heating a stream with a vapor fraction of 60% (a solid fraction of 40%) in HE02, while the other two arrangements (-4 and -6) handle always-liquid streams if the temperature is below the critical temperature of the water. The three arrangements are approaches to the feed consisting of 10 wt.% solid biomass and 90 wt.% water. ARR-6 is the most compact process arrangement that leads to the minimum energy required for the reaction and, hence, the maximum sensitive heat that can be exchanged using energy and material integration. Thus, it should be the first option for designing the process in order to apply energy integration to the thermochemical process, although ARR-4 and -3 could also be used, any of them being preferred to the typical arrangements found in the literature that follow ARR-1, 2, which does not allow for the energy integration of the biomass stream, or ARR-5, which does not lead to faithful results. Although the energy saving is not too high in the selected application (SCWG) due to the huge amount of water, if this were significantly decreased, the energy saving would increase considerably.

The main operating parameters include the temperature, pressure, type of feedstock, composition and concentration of components, reaction time, and type of catalyst and its load if it is used. When an operation is considered under chemical equilibrium, the temperature, pressure, type of feedstock, composition, and concentration of components are the most relevant parameters, as the reaction time and catalyst do not have an effect. As the critical pressure of SCW is very high (>221 bar), this parameter has been kept constant at a slightly higher value (240 bar) to consider pressure losses, but it would not be realistic to use higher pressures. Therefore, once the feedstock is decided, the most significant parameters are the temperature and the feed concentration.

To examine the effect of the feed concentration and the temperature at the RGibbs inlet on the energy balance, and hence on the heat integration, a sensitivity analysis was performed. Three biomass concentrations (10, 20, and 30 wt.%) and three temperatures at the RGibbs inlet (350, 400, and 800 °C) were used based on the schemes drawn in Figures 2 and 3. To illustrate it, Figure 7 shows the results using the ARR-6 arrangement.

The thermal power obtained was similar in all case studies, i.e., for every combination of organic concentration (wt.%) and temperature (°C). The RYield contribution increases with the organic concentration, while the contributions of RGibbs and HE01 decrease with this variable due to the lower amount of water. However, the contribution of RYield is very small in all cases and barely affects the energy balance, so this depends only on the contributions of RGibbs and HE01. The former decreases with temperature, while the latter increases, practically by the same amount.

For the RYield and RGibbs blocks, the thermal level needed to provide this energy must be the same as in the SCW reactor, i.e., a temperature higher than 800 °C for heat transfer, which is the thermal level used for the reactor in this study. This implies that a suitable heat source, such as a furnace, is needed. Although the most significant fraction of energy must come from an energy source with a high thermal level (>800 °C) for the combination of RYield and RGibbs, there is also significant heat exchanged in HE01 that makes it possible to save energy by integrating the feed stream with another process stream (such as that leaving the SCW reactor) so that the use of utilities is reduced.

In fact, and as a final note, although the temperature at the SCWG reactor inlet should be as close to the reaction temperature (800 °C in this study) as possible to save more energy, in practice, the temperature achieved in the train of heat exchangers, represented by HE01 in this study, is usually lower, approximately 350–400 °C, rather than 800 °C, especially if the product leaving the SCW reactor passes through an expander to produce electrical energy, as proposed in previous studies published by the authors and other researchers [3].
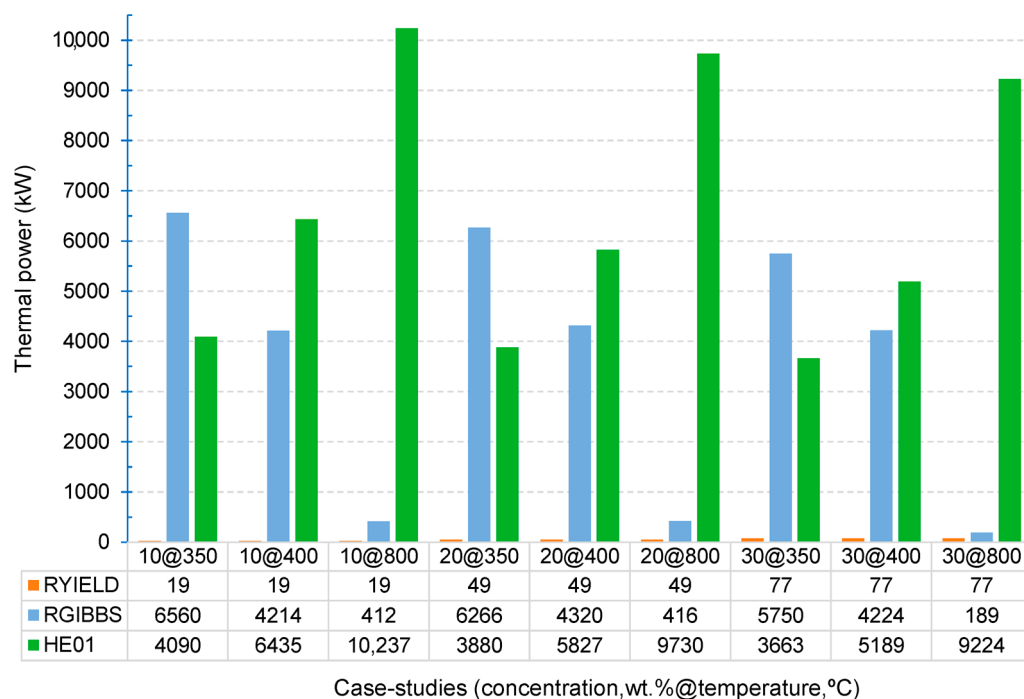
Figure 7. Sensitivity analysis for the thermal power (heat load) of the SCWG of orange peel for ARR-6 at different concentrations (wt.%) and temperatures (°C); (concentration@temperature). Note: These numbers in the bottom table correspond to the thermal power represented on the ordinate axis. Therefore, the unit is kW for all of them.

4. Conclusions

In this paper, we have shown that dry nonconventional solids do not participate in heat exchange processes, so energy integration cannot be carried out with the feed stream. Likewise, wet nonconventional solids participate in the heat exchange processes, but this simulation is not realistic because, having a high moisture (90 wt.%), the phase is always solid even though the temperature is higher than the critical temperature of water, which is not true. However, if the wet nonconventional solid is simulated by a mixture of a dry nonconventional solid and a stream of liquid water, the feed stream partially participates in the heat exchange processes to the extent that water does; however, the solid fraction is not really heated. The overall energy balance does not vary if the decomposition of biomass is placed at the beginning or at the end of the system. However, if the solid is nonconventional and the decomposition is performed at the end, both the conversion and the temperature rise take place in the RYield, because the heat exchangers do nothing. If the biomass decomposition is carried out at the beginning (and the conversion took place at ambient temperature), sensible heat can be used (and saved) by a series of heat exchangers to raise the temperature from 25 to 800 °C (or whatever final temperature it was).

Upon a base case study using a wet biomass of 10,000 kg/h with 90 wt.% water, where the SCWG reaction takes place at 240 bar and 800 °C, if the temperature at the SCWG reactor inlet increases from 350 °C to 400 °C, the heat exchange increases by 57% from 4 MW and by 34% if the water content decreases to 70 wt.%, although more heat relative to the solid is saved.

Thus, a practical approach is proposed for applying heat integration for the supercritical water gasification (SCWG) of solid biomass under chemical equilibrium as an alternative to the current method found in the literature. In the new approach, the biomass is decomposed into conventional compounds at ambient temperature, so only enthalpy formation is considered in its energy balance, and the stream leaving can be really pumped and heated to the temperature at the reactor inlet. In this way, sensible heat can be exchanged by a train of heat exchangers, thus saving energy in the process by energy and material

integration. This approach may be applied considering the stream entering the SCWG reactor operating under chemical equilibrium. Two possibilities or routes are proposed depending on how the decomposition is made: (1) following the typical decomposition into a solid phase (carbon, ash, and sulfur) and a gas phase (water and diatomic molecules of H_2, N_2, O_2, and Cl_2), or (2) into a set of molecular compounds representative of biomass if the chemical composition is available. This novel method is helpful for evaluating processes under research and development using simulation and can be used for any thermochemical process other than the SCWG of biomass, where the amount of sensitive heat to be exchanged is likely much higher because of the lower amount of water.

The results can be explained using the fundamental physicochemical principles, i.e., thermodynamics, mass and energy balances, and chemical equilibrium, so energy and exergy efficiencies can be assessed with confidence. The application of this approach would affect the use and design of heat exchangers to be placed for feed preheating before entering the SCWG reactor or any other reactor in a thermochemical process of biomass.

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