



# Biofuel production from supercritical water gasification of sustainable biomass

F.J. Gutiérrez Ortiz<sup>\*</sup>

Departamento de Ingeniería Química y Ambiental, E.T.S. de Ingeniería, Universidad de Sevilla, Camino de los Descubrimientos, s/n., 41092 Sevilla, Spain

## ARTICLE INFO

### Keywords:

Supercritical water  
Gasification  
Biofuel  
Hydrogen  
Sustainability  
Process simulation

## ABSTRACT

A review of biofuel production from supercritical water gasification (SCWG) of sustainable biomass has been performed, mainly organic waste, following a critical thinking in this field of knowledge. Thus, sub- and supercritical water properties and hydrothermal processing are briefly commented on. Then, the feedstocks usable in SCWG are fully reviewed and a brief description of the studies on the kinetics and mechanisms of reactions is carried out. Next, thermodynamic and process simulation are discussed, aimed at producing liquid and gas biofuels. After that, a brief comment on the viability of SCWG processes to produce biofuels is provided based on techno-economic and lifecycle assessments. Finally, some remarks on where we are and where we should go are given in order to advance this technology towards its maturity. This review explains some misleading concepts applied to SCWG processes, provides a brief but comprehensive overview of the technology focused on producing biofuels in a sustainable way, allows a better understanding of the SCWG of biomass for biofuel production, and proposes a series of improvements to be made and examined in the future research.

## 1. Introduction

It has been more than four decades (1978) since Modell, Reid and Amin [1], all of them at the Massachusetts Institute of Technology (MIT), patented the conversion of solid or liquid organic materials into high energy gas with little or no undesirable char formation by reaction in supercritical water (SCW) through reactions conducted either in the presence or in the absence of a catalyst. Later, Modell [2] patented a method to oxidize in SCW, in such a way that toxic waste materials are converted into useful energy for power and heat and / or non-toxic materials. These hits can be considered to be the start-up of a research field focused on the use of supercritical water, which has been increasing since then. Thus, and focused on SCW Gasification (SCWG), a number of pilot and demonstration plants have been built to develop this research area, such as those at the University of Hawaii (USA), Pacific Northwest National Laboratory (USA), Forschungszentrum Karlsruhe (Germany), Hiroshima University (Japan), University of Twente (Netherlands), BTG Company (Netherlands), or State Key Laboratory of Multiphase Flow in Power Engineering (China). Currently, perhaps the most well-known facility is the VERENA plant in Germany. In addition, many other research groups have assembled facilities at lab- or bench- scale.

So far, a great deal of information has been obtained on this

emerging technology based on the gasification using supercritical water. However, this is still not enough to establish it as a mature technology in order to project a full-scale plant, with all the facets that it involves, and where different biofuels can be produced in a sustainable way.

Climate change, global warming, and greenhouse gases (GHG) have become common terms in everyday life. Despite the increase in prices and the apparent depletion of natural resources and raw materials, the increase in fossil fuel consumption has led to an increase in GHG emissions and the resulting global warming. This can be mitigated by using biofuels as they are carbon-neutral (CO<sub>2</sub> emissions by combustion are equal to CO<sub>2</sub> fixed by plants during photosynthesis). Therefore, the global drivers of a biology-based economy, the best use of natural resources, and the transition from linear to sustainable circular economies are essential. The conversion of waste into biofuels and energy is one of the keys to a circular economy, maintaining the value of resources in the market as long as possible, thus minimizing their net use, especially when the recovery of certain valuable compounds that may be present in waste is not feasible.

But what should we understand as a biofuel? It looks like that the origin of such a fuel must be biology-based, as aforementioned, and that it should have a minimum low heating value to be involved in a combustion process, such as those taking place in gas turbines, burners, or

<sup>\*</sup> Corresponding author.

E-mail address: [frajagutor@us.es](mailto:frajagutor@us.es).

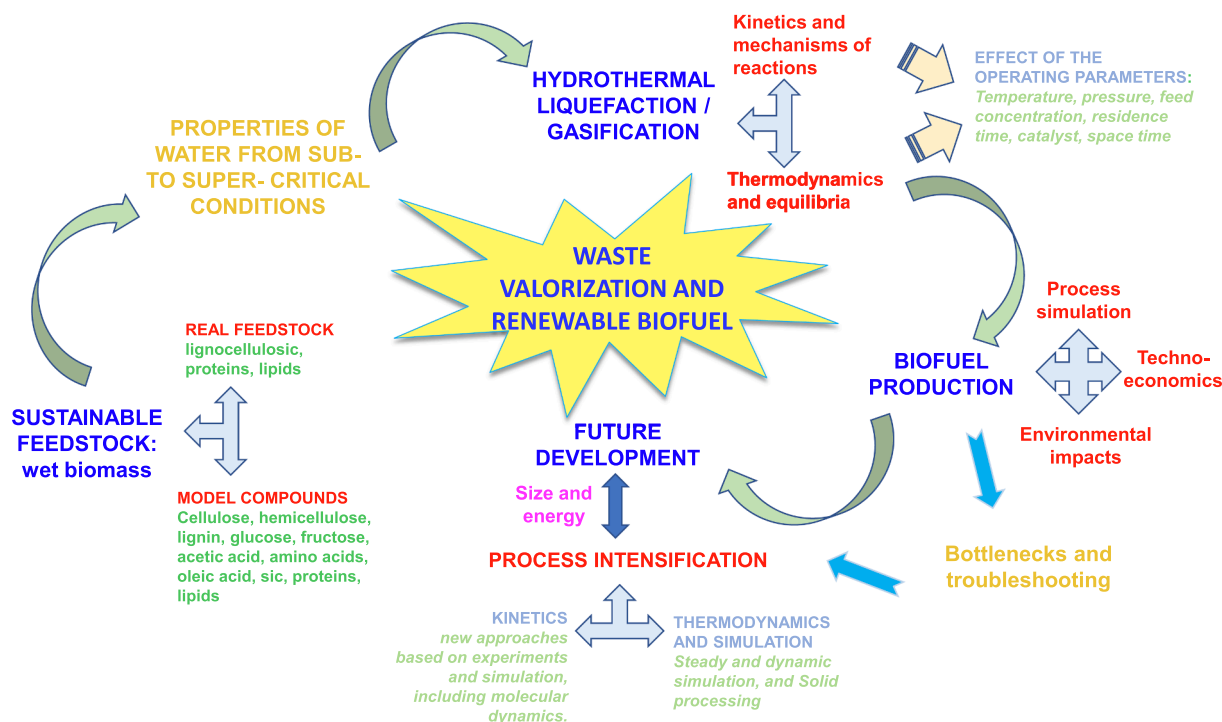


Fig. 1. Outline of the review paper.

internal combustion engines. Thus, many substances could be considered biofuels. As fuels coming from bio-based processes, liquid bio-oil produced in a liquefaction or pyrolysis, liquid biodiesel from transesterification, syngas obtained in a gasification process, and any other compounds derived from those, such as biomethane or SNG (synthetic natural gas), methanol or hydrogen, are biofuels.

Among all the potential biofuels, this review is focused on liquid biofuels with high volumetric energy density, such as green diesel, gasoline, or jet-fuel, but also on other fuel gases, such as hydrogen, methane or SNG, and even methanol. Likewise, biodiesel production under supercritical conditions is out of the scope of this review because these processes use supercritical alcohols (methanol or ethanol) and not supercritical water.

Currently, some review articles can be found dealing with different aspects of SCWG, such as model compounds, lignocellulosic or microalgae biomass, types of reactor, energy and exergy, thermodynamics, catalysts, techno-economics, hydrogen production, modeling and simulation [3-15]. In this review paper, a brief but comprehensive overview of the technology focused on producing biofuels in a sustainable way is provided, some misleading concepts applied to SCWG processes are explained, thus allowing a better understanding of the SCWG of biomass for biofuel production, and several improvements to be made and examined in the future research and development are also proposed.

In a somewhat more detailed way, in this review, a number of key aspects are cited and briefly discussed with a critical spirit, striving to engage most researchers to join this exciting technology but at the same time keeping our feet on the ground. After reading this review, the reader should realize that further research is still needed in different aspects of this field, such as catalytic and non-catalytic kinetic studies of potential feedstock to better understand the internal phenomena and to properly design the needed reactor, thermodynamic methods related to the SCW conditions in order to better simulate processes for biofuels production with energy integration, lifecycle assessment and techno-economic analysis to evaluate the viability of the proposed processes, as well as materials to make reactors capable of operating under such severe conditions, and new designs of auxiliary unit process such as efficient heat exchangers to pass through the critical point of water and

develop expanders capable to recover the huge energy available in the stream leaving the SCWG reactor. In this regard, some suggestions are given in the fifth section in order to advance our understanding of the phenomena and processes, thus boosting the use and real scale-up of this technology.

Fig. 1 shows a graphical outline of the contents dealt with in this review and how the different pieces are linked with each other to build a whole, from the sustainable feedstock to a SCWG process based on properties of water when changing from subcritical to supercritical conditions, the aspects related to SCWG and further action for scaling up by tackling new approaches and devices to overcome the shortcomings providing potential troubleshooting focused on moving the technology forward to its industrial development.

## 2. Subcritical and supercritical water

Most of the papers regarding sub-, near-, and super- critical water include the unique properties of water when pressure and temperature are increased more and more from atmospheric conditions to the critical point and beyond. Specifically, all review papers mention these properties, and generally almost nothing new is given from one to another. Furthermore, only a few review papers can be cited in this regard, and among them, three papers can be highlighted due to the extension and sharpness of their content [16-18]. In these references, the reader can learn more about the properties of water when it is below, near, and above the critical point (22.1 MPa, 374 °C). Next, the most relevant properties of water under the operating conditions in SCWG are mentioned and briefly discussed.

Near the critical temperature, the ionic product of water is two orders of magnitude higher than that at room temperature ( $10^{-12}$  at 350 °C and  $10^{-14}$  at 25 °C [19]), so it is a very effective medium for acid-base-catalyzed organic reactions, such as, for instance, biomass hydrolysis, under near critical conditions. However, it drastically decreases above the critical point; therefore, for electrolytes, this leads to a reduced solubility and allows the separation of inorganic salts present in water. Supercritical water (SCW) is above its critical point (374 °C and 22.1 MPa) and has lower densities than liquid water due to the distance

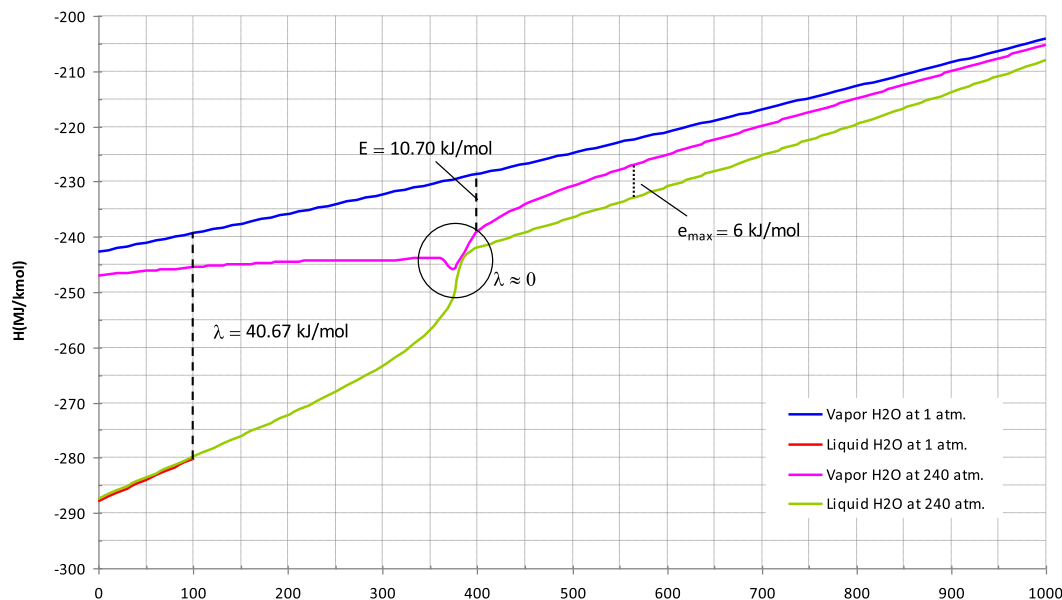


Fig. 2. Vaporization heat ( $\lambda$ ) and energy savings for water (supercritical pressure of 240 atm.) [7]

between the molecules is larger and there are less hydrogen bonds (the degree of hydrogen bonding between molecules is weaker), and transport properties similar to those of a gas, especially the viscosity that increases the diffusion coefficient and, hence, mass transfer is enhanced, and reaction rates are boosted when heterogeneous catalysts are used. Likewise, it has a high solvent capacity for organic compounds because of the very low value of the dielectric constant. These properties make SCW an excellent reaction medium and an ideal solvent for the conversion of organic matter present in waste into syngas ( $H_2$ , CO,  $CH_4$  and  $CO_2$ ).

In addition, some other features can be given [16-18]:

1. It allows the reactions taking place in a homogeneous way, i.e., in a single phase, where most organic compounds are miscible, as aforementioned. Under given operating conditions, when reactions are homogeneous, the reactants and products are in the same phase, and hence there is no mass transfer limitation as happens in heterogeneous reactions in which the reactants and / or products are in different phases.
2. It is very reactive and has catalytic activity that avoids or minimizes the use of catalysts, which is an economic and operational advantage.
3. It is a relatively dense medium at pressures higher than 22.1 MPa, thus allowing a reduction in reactor volume and more compact equipment, which reduces heat losses.
4. The increase in pressure is performed on a liquid by means of a pump, instead of on a gas by means of a compressor. Thus, the mechanical power is significantly lowered.
5.  $CO_2$  can be removed and stored, and the produced  $H_2$  is available under high pressure. Syngas leaving the SCWG reactor can be expanded to produce electricity, but after expansion, syngas can still be at enough pressure (15–30 bar) to be separated into different components, so pure  $CO_2$  can be sent for sequestration / storage, and  $H_2$  can also be obtained at 99.999% purity in a PSA system [20,21].
6. The high solvation of organic substances reduces the condensation likelihood of high molecular weight products, such as tars.
7. As the SCW solubility product is very low, the metals present in the aqueous waste stream can be separated under supercritical conditions, with a proper separator design.

In summary, SCW acts as a reaction medium, a solvent, a reactant, and even as a catalyst. This led to the study of SCW oxidation (SCWO) of waste because of the unique properties of SCW that aid in the destruction of hazardous waste. However, rather than converting toxic waste into inert material, the option of gasifying (SCWG) a waste allows producing a syngas with multiple applications focused on the waste valorization, which matches better with the sustainability concept, as further described in the next sections.

### 3. Hydrothermal processing

A process operating with water at high temperatures, but lower than  $374^\circ C$ , and high pressures, but lower than 22.1 MPa, is named hydrothermal liquefaction (HTL). Typical temperatures range from  $310$  to  $370^\circ C$ , and pressures range from 15 to 21 MPa. When the process is operating beyond the critical point, both in pressure and temperature, it is named SCW gasification (SCWG), also called hydrothermal gasification (HTG).

The advantage of HTL and HTG technologies over other thermochemical processes, such as pyrolysis, gasification, or torrefaction, is their ability to process (very) wet biomass, so that biomass feedstock drying is no longer needed as a previous stage, which is very important. In fact, HTL and HTG are specifically recommended for wet or very wet feedstock.

However, there is a misleading aspect when dealing with this kind of feedstock. It may be thought that this feature of HTL and SCWG implies that, because a large amount of thermal energy is needed for the drying process prior to the main thermochemical process (pyrolysis, etc.) due to the high latent heat of vaporization of water, these processes consumed less energy compared with many other biomass conversion processes, because latent heat is strongly reduced or avoided. Is this true?

To understand this, it should be remembered that enthalpy is a state function, and the change in enthalpy between two states is uniquely given, so any process from a determined liquid state to a given supercritical state requires the same amount of energy, regardless of the path taken. Thus, although the heat of vaporization decreases when pressure increases and disappears at the critical point, and therefore the energy for phase change ('latent heat') becomes null, this does not prevent the equivalent energy required in an SCW process from being equal to that of another process going from the same liquid state to the vapor / gas

state and achieves the given supercritical state. In the former, liquid water is first compressed to a pressure higher than its critical pressure and then heated to the final temperature without latent heat, but the total change in enthalpy is the same as if the process took place at a pressure below 22.1 MPa, then vaporized and finally heated to the same final temperature. Trying to deepen this a little more, if the pressure of both processes (below and above the critical point) is different, the pressure correction due to compression must be considered in the calculus of absolute enthalpy, normally based on using the elements at 1 bar and 298.15 K as the standard reference state. The pressure dependence of enthalpy is zero for ideal gases, and normally neglected, but it may be important for real gases, which can be obtained from an equation of state (EoS). In this regard, Banuti et al. [22] concluded that the supercritical fluid can be characterized as an ideal gas for temperatures greater than twice the critical temperature and pressures less than three times the critical pressure. Therefore, under these conditions, the states yield ideal gas properties, and the enthalpy is pressure-independent, so the change in enthalpy between two states is uniquely given even though the pressure of the states is different.

However, what happens around the critical point of the water? In this case, an EoS should be used, such as PRSK, as it was previously studied based on AspenPlus simulations and is shown in Fig. 2 [23].

Below the critical temperature, the enthalpy along the line of the dew point at high pressure (in magenta) differs significantly from the vapor enthalpy at low pressure (in blue), and this difference is greater when approaching the critical point, where the maximum deviation in enthalpy is found between the behavior at 1 atm and 240 atm. In addition, at 240 atm, the vaporization heat looks lower than that at 1 atm, so the change in the liquid enthalpy with pressure should not be neglected because it can play no lesser role in process simulation. Beyond the critical point, the gaseous state line, which better represents the supercritical state beyond the critical point in Aspen Plus (since gas is the stable phase of a compound at temperatures above its critical temperature), is very close to the line representing the process at atmospheric pressure and at very high temperatures (ideal gas conditions), so the trend seems to lead to the same curve when the temperature is twice higher than the critical temperature, as aforementioned, and a pressure above the critical pressure; then, the behavior is the same and no energy can be saved, i.e., latent heat is not avoided at all. However, this changes near the critical point and slightly above it, and, e.g., the specific enthalpy at 400 °C becomes 10.7 kJ/mol lower at 240 atm than at 1 atm, according to the PSRK EoS prediction. Therefore, the pressure effect is or may be quite significant around the critical point and latent heat can be decreased but not completely avoided; this is the case for the HTL process and the SCW process operating at not too high temperatures (<750 °C).

In any case, why is it so important to highlight that HTL and HTG are the most suitable processes for wet biomass? There are two reasons. First, and as aforementioned, when water moves toward near- and super-critical conditions, its properties make it a powerful reaction medium, solvent, reactant, or even catalyst; and second, the energy balance of these processes can and must be improved by applying energy integration through a heat exchanger network that allows recovering as much as possible not only the latent heat but also the sensitive heat or thermal energy in the stream leaving the reactor at high temperature and pressure. Thus, high thermal energy can be recovered and used, and even electrical power may be obtained by taking advantage of the pressure drop downstream from the SCWG reactor.

#### 4. Supercritical water gasification

In this section, mainly focused on biofuel production from SCWG of sustainable biomass, the feedstocks are treated first, then the kinetics and mechanism of reaction are discussed, followed by a description of thermodynamics and process simulation, and finally, the techno-economic assessment and lifecycle evaluation are debated.

##### 4.1. Feedstocks

There are many types of feedstocks dealt with in SCWG papers, but biogenic waste materials are the most interesting from a sustainability point of view because in this way waste is valorized, thus giving a valuable product such as syngas that can be converted into biofuels or chemicals. This route involves a conversion process from a wet organic waste, although the recovery and re-utilization of valuable compounds should be considered as a prior option to the use of a waste-to-energy process, including biofuel production. Once verified that the recovery of some of these compounds is not viable, the wet waste can enter an SCWG process.

A significant number of papers have been published on SCWG of real organic waste or model compounds of waste to gain insight into a specific SCWG process where feedstock concentration, pressure, temperature, residence time (especially in batch reactors), and type and specific amount of catalyst are usually the studied operating conditions. Most of these papers show the trend of some performance variables, such as feedstock conversion, gas yield, gas composition, liquid composition, and obtained char. Although there are already some review papers that have specifically dealt with this (e.g., [4,24]), some relevant studies are briefly commented on below.

Regarding real organic waste, different types of manure have been studied in SCW [25,26]. The first one by Bircan et al. [25] was performed in a batch reactor operating at 400 °C for 40 min, and it was concluded that the dioxins produced by hydrothermal gasification of chicken manure and cattle manure in both liquid and gas products were much lower than the concentration required by strict regulation levels in Japan, so no additional post-treatments are required. In the study by Cao et al. [26], chicken manure was almost completely gasified in a fluidized bed reactor at 25 MPa and 620 °C in the absence of catalyst and a carbon gasification efficiency (CGE) of up to 99.2% was achieved. Likewise, sewage sludge has been studied by different researchers; thus, Amrullah and Matsumura [27] used a continuous SS316 steel reactor (tube with ID: 2.17 mm, OD: 3.18 mm and length 12 m) at 25 MPa, reporting a CGE of 73% at 600 °C after 50 s. Furthermore, organic phosphorus was converted into inorganic phosphorus after 10 s, i.e., at the beginning of the process. Similarly, Chen et al. [28] tested the SCWG of sewage sludge in a 10 mL Hastelloy C276 batch reactor using a heating rate of 70 °C/min, at 750 °C and for 30 min, obtaining a gasification efficiency of 73.49% and a CGE of 61.16%. In addition, the use of a heterogeneous catalyst (RNi-Mo<sub>2</sub>) enhanced the hydrogen yield, which is a typical performance variable in most SCWG papers. On the other hand, food waste has been also studied by Chen et al. [29] in a quartz tube reactor using temperatures between 550 and 850 °C and a residence time between 1 and 15 min, concluding that CGE increased with the reaction temperature at the same residence time; it was 70% at 850 °C, 3 min and a concentration of 15 wt%. Fruit waste and agro-food residues were also tested by the Dalai and Kozinski research group [30] using an SS 316 tubular batch reactor (L: 10 in., OD: 0.5 in., ID: 0.37 in.) that has been used in many other studies performed by the same group. In this case, the operating conditions were 400–600 °C, a pressure roughly of 24 MPa, a reaction time of 15 to 45 min, and a biomass-to-water ratio equal to 1:5 and 1:10, using NaOH and K<sub>2</sub>CO<sub>3</sub> as catalysts. The CGE values were <46% for agro-food residues, and the highest H<sub>2</sub> yields were achieved at the longest reaction time of 45 min. Municipal waste leachate is another relevant waste studied by Molino et al. [31], with the aim of converting it into Synthetic Natural Gas (SNG) using a catalytic upgrade (with a Nickel-based catalyst) of the resulting gas phase as a second stage downstream from the SCWG reactor. H<sub>2</sub> and CH<sub>4</sub> concentrations varied in the range of 25 to 47 vol% and 11 to 18 vol% in the final syngas, respectively. Recently, as a last example of the variety of potential waste suitable for gasification in SCW, waste from the wine industry was tested in a batch reactor made of SS316 with a volume of 100 mL using different catalysts (Li<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub> and Cs<sub>2</sub>CO<sub>3</sub>) at 500 °C and 600 °C for a constant reaction time (60 min). Once again, as

**Table 1**  
SCWG studies of different real feedstocks.

Feedstock	Operating Conditions	Main Results	Ref.
Wastewater from polyethylene glycol	390 °C; 24 MPa; 6 L/h; 2 g/L residence time; 60–300 s; Ni/ZrO <sub>2</sub> catalyst (90, 180 g)	CGE: 87.1% (300 s; 180 g); H <sub>2</sub> yield of 74.3 mol/kg	[37]
Aqueous by-product	700 °C, 24 MPa, 0.12 L/h, < 10 g/L, RuNi/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> catalyst (1 g); WHSV 2.5 h <sup>-1</sup> .	polyethylene glycol CGE: 96.6%; H <sub>2</sub> yield of 41.0 mol/kg carbon	[38]
Sewage sludge	540 °C; 25 MPa; 9 g/h; 2 wt% sewage sludge; KOH catalyst (0.5 wt%)	CGE: 50%; H <sub>2</sub> yield of 15.49 mol/kg feedstock	[39]
Empty fruit bunches from oil palm	380 °C; 24 MPa; 13 mL batch reactor; 37.5 g/L; 32 min	15 mmol C / mL gas phase; CO <sub>2</sub> /CH <sub>4</sub> ratio: 11; 60 mmol H <sub>2</sub> / mL gas phase;	[40]
Wheat straw (WS), walnut shell (WW), and almond shell (AS)	440 °C; 25 MPa; 26 mL batch reactor; 1 wt%; 10–20 min	CGE: 44.92, 40.36, 38.68% for WS, AS and WW; H <sub>2</sub> yield: 7.25, 4.1 and 4.63 mol/kg WS, AS and WW for 10, 15 and 20 min, respectively	[41]
Acutodesmus obliquus microalgae	690 °C; 28 MPa; 150 g/h; 2–20 wt%; 140–150 s	CGE: 96 to 82% (2 to 20 wt%); H <sub>2</sub> yield of 13.6 mol/kg on average (17.6@2 wt%; 8.4@20 wt%)	[42]
Kraft black liquor	500 °C; 25 MPa; 0.4 L/h; 4.8 wt%; 11.2 min;	Gas yield of 18.31 mol gas/kg feed; H <sub>2</sub> yield: 7.87 mol/kg feedstock	[43]
Rice straw	440 °C; 26 MPa; 26 mL batch reactor; 2 wt%; 20 min	CGE: < 16%; H <sub>2</sub> yield: 5.56 mol/kg feedstock	[44]
Pinewood (PW) and wheat straw (WS)	500 °C; 23–25 MPa; 30 mL batch reactor; 9 wt%; biomass impregnated with Ni catalyst; 45 min	CGE: 34% for WS and 32 % for PW; H <sub>2</sub> yield of 5.3 mol/kg WS and 7.5 mol/kg PW	[45]
Beech sawdust (BS), municipal solid waste (MSW), hydrothermal char (HC), and malt spent grains (MG)	400 °C; 30 MPa; 23.6 mL batch reactor; 15 wt%; 16 h	CGE: 24.2, 27.6, 15.7, 23.1% for BS, MSW, HC, MG; H <sub>2</sub> yield of 1.1, 1.1, 1.3, 1.2 mol/kg for BS, MSW, HC, MG	[46]
Scenedesmus dimorphus microalgae	550 °C; 25 MPa; 6 L/h; 0.07–6.2 wt%;	CGE: 78 and 20 % at 0.07 and 6.2 wt%; Gas yield of 29 and 11 mol/kg at 0.07 and 6.2 wt%	[47]
Chlorella sp. Microalgae	380 °C; 22.5 MPa; 165 mL batch reactor; 4.9 wt%; 30 min	CGE: 5.7%; Gas yield of 1.5 mol/kg	[48]
Olive oil mill waste	700 °C; 23 MPa; 0.5 wt%; 180 g/h; 40.8 s;	H <sub>2</sub> yield of 112.5 mol/kg	[49]
Copper wastewater and biomass waste	650 °C; 22.5 MPa; 10 mL batch reactor; 0.1 g/mL + 2.5 mmol Cu <sup>2+</sup> ; 30 min	CGE: 99.2% (65.4% without Cu ions); H <sub>2</sub> yield of almost zero; Gas yield ≈ CO <sub>2</sub> yield of 35 mol/kg	[50]

Note for operating conditions: Temperature, pressure, flow rate or volume of batch reactor, concentration, residence time

expected, the experimental results indicated that a high temperature and the use of a catalyst increased both the CGE and the product gas yield, obtaining the highest H<sub>2</sub> and CH<sub>4</sub> yields with Cs<sub>2</sub>CO<sub>3</sub> at 600 °C.

Feedstock composition has a direct effect on SCWG performance and gas yields. As indicated by [7], based on previous research [32–36], and although some studies report other results, most of them establish that a high content of cellulose and hemicellulose leads to higher gas yields, especially cellulose if the hydrogen yield must be maximized; similarly,

**Table 2**  
SCWG studies of different model compounds.

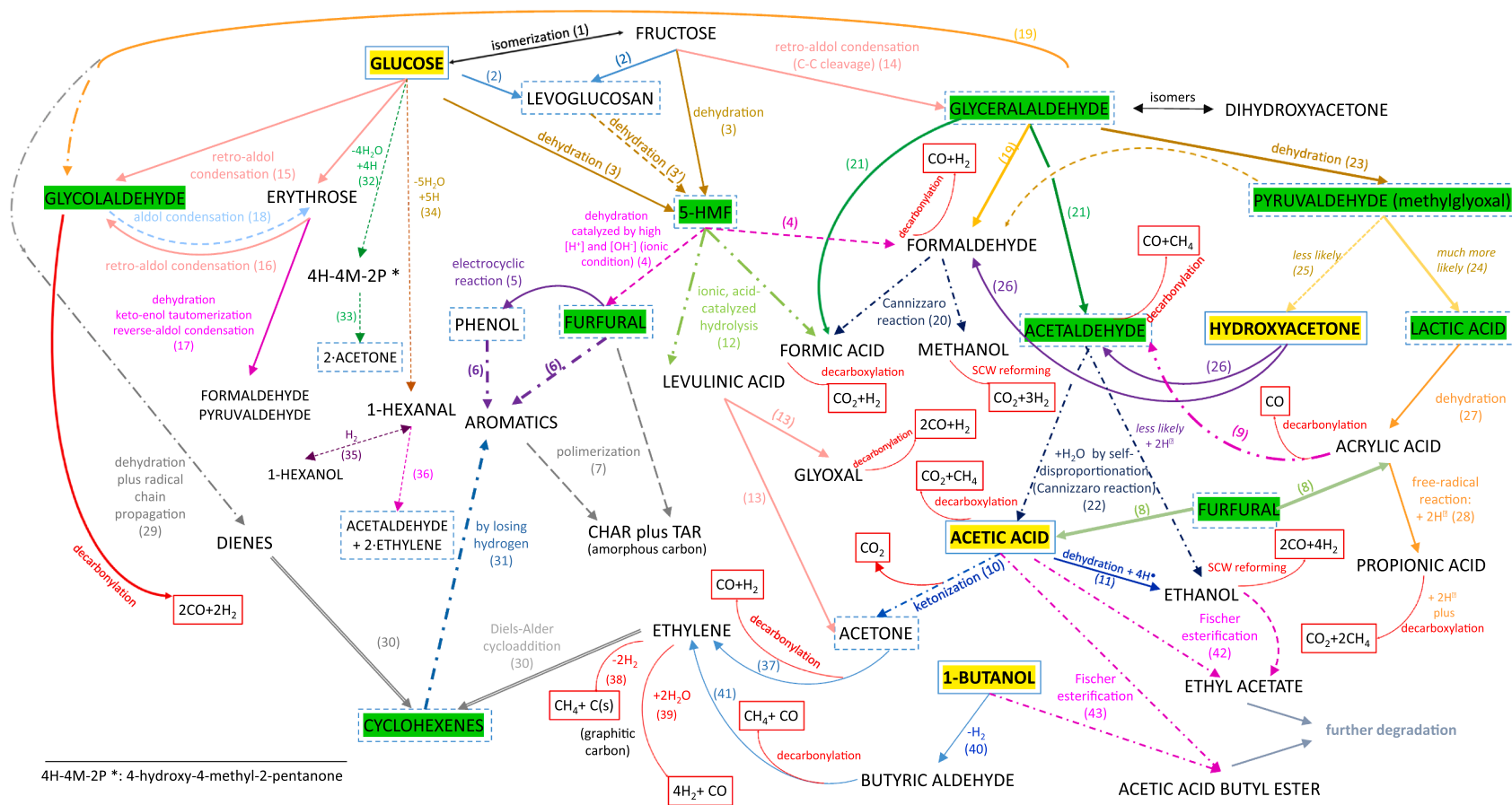
Model Compounds	Operating Conditions	Main Results	Ref.
Glycerol	850 °C; 24 MPa; 1 L/h; 5–30 wt% and 34–160 s;	H <sub>2</sub> yield of 3.54 to 1.92 mol/mol (5 to 30 wt%); Glycerol conversion: 99.8% and 91.7% (5 to 30 wt%)	[72]
Glucose	500 °C; 5 wt%; 10–1800 s; 5 wt% Ru/Al <sub>2</sub> O <sub>3</sub> catalyst	CGE: 5–35% at 20 and 1800 s; H <sub>2</sub> yield of 2.5–30 mmol/kg at 20 and 1800 s;	[58]
Fructose	700 °C; 25 MPa; 4 wt%; 60 s; 0.8 wt% KOH	CGE: 88% (98% with catalyst); H <sub>2</sub> yield of 3.37 mol/mol (10.67 mol/mol with catalyst)	[60]
Lactose	700 °C; 25 MPa; 4 wt%; 60 s; 0.8 wt% Na <sub>2</sub> CO <sub>3</sub>	CGE: 85% (96% with catalyst); H <sub>2</sub> yield of 16 mol/mol (22.4 mol/mol with catalyst)	[73]
Phenol	450 °C; 25 MPa; 3.95 mL batch reactor; 0.32 mol/L; 30 min; Ru content: 60%	CGE: 55%; H <sub>2</sub> yield of 1.82 mol/mol	[74]
Xylose	600 °C; 40 MPa; 100 mL batch reactor; 8 g/L water; 0.8 g KOH/L water	CGE: 85%; H <sub>2</sub> yield of 1.75 mol/mol	[55]
Guaiacol	600 °C, 25 MPa; 120 g/h; 0.05–1.0 wt%; 94 s	CGE: 23–18% (0.05–1.0 wt%); H <sub>2</sub> in gas phase: 66–28 vol% (0.05–1.0 wt%)	[67]
Alanine	650 °C; 25 MPa; 120 g/h; 1 wt%; 86 s	CGE: 85%; H <sub>2</sub> in gas phase: 25 vol%	[71]
Oleic acid	500 °C; 28 MPa; 600 mL batch reactor; 28 g/L; 0.5 wt% Ru/Al <sub>2</sub> O <sub>3</sub> pelletized catalyst; 30 min	CGE: 85%; H <sub>2</sub> yield of 1 mol/mol	[68]
Glucose / Glycine	663 °C; 24 MPa; 1 / 3 wt%; 128 s; Na <sub>2</sub> CO <sub>3</sub> catalyst (0.4 wt%)	CGE: 43.7%; H conversion to H <sub>2</sub> : 80.4%	[75]
Glucose / Phenol	400 °C; 25 MPa; 3.5 / 1.5 wt%; 240 s	Gas yield: 60 L gas/kg mixture; H <sub>2</sub> yield of 0.30 mol/kg	[35]
Phenol / Naphthalene / Acetic acid	550 °C; 25 MPa; 2 L/h; 1 / 1 / 1 wt%; 20 s;	H <sub>2</sub> yield of 35 mol/kg	[76]
Acetic acid / 1-Butanol / Hydroxyacetone / Glucose	800 °C; 24 MPa; 1 L/h; 15 / 2.5 / 2.5 / 2.5 wt%; 20 s	CGE: >90%; H <sub>2</sub> yield of 0.5 mol/mol mixture	[77]
Cellulose	650 °C; 26 MPa; 20 wt%; 50 min; K <sub>2</sub> CO <sub>3</sub> catalyst	Gas yield: 18 mol/kg; H <sub>2</sub> yield of 2.12 mol/kg	[51]
Lignin	650 °C; 26 MPa; 20 wt%; 50 min; K <sub>2</sub> CO <sub>3</sub> catalyst	Gas yield: 23.3 mol/kg; H <sub>2</sub> yield of 2.86 mol/kg	[51]

Note for operating conditions: Temperature, pressure, flow rate or volume of batch reactor, concentration, residence time

lignin can be well gasified above 600 °C in the presence of a catalyst although its gasification consumes hydrogen, thus reducing the gas yield and increasing the liquid yield and char, as well as inhibiting the decarbonylation reactions and favoring the pathway through dehydration reactions; in this regard, the presence of hemicellulose is positive, as it can hinder this negative effect of SCWG of lignin. The effect of composition is explained in more detail in Section 4.2.

Although there are more studies using real waste as feedstock and the aforementioned references provided enough background on it, Table 1 shows additional references along with some details related to SCWG of sustainable biomass as feedstock.

In all of these studies, the biochemical composition of the adopted feedstock strongly affects the yield and characterization of the products.



4H-4M-2P\*: 4-hydroxy-4-methyl-2-pentanone

Fig. 3. Scheme of the potential reaction pathways of organics in SCW [77].

Because of that and also with the aim of getting insight into the behavior of specific compounds present in real waste, many other studies have been performed using model compounds. As most bio-based feedstocks are biomass and organic waste that are composed of cellulose, hemicellulose and lignin, these model compounds have been studied separately by several researchers [32,51-55]. All of them exhibit diverse behaviors in SCWG and have always been tested in batch reactors for a long residence time. Cellulose is a linear polysaccharide consisting of hundreds to thousands of glucose units linked by glycosidic bonds. Hemicelluloses are heteropolysaccharides consisting of sugar monomers, such as xylose, mannose, glucose, and galactose, and also some acids such as glucuronic acid and galacturonic acid. Lignin is an aromatic heteropolymer made by cross-linking phenolic precursors [56]. As expected, the conversion of such complex model compounds is not easy, and researchers have preferred to focus mainly on simpler representative compounds of cellulose, such as glucose [57-59] and fructose [60], hemicellulose, mainly xylose [61-63], since mannose and galactose have not yet been studied under SCW, and lignin, such as phenol [35,64,65] and guaiacol [66,67].

Similarly, oils, fats, and proteins are other renewable resources that can be gasified in supercritical water, in addition to carbohydrates. Under supercritical conditions, the first two have generally been processed using supercritical alcohols to produce biodiesel, and only very few studies can be found involving SCW, such as oleic acid in SCW [68] and ethyl oleate just below the critical point [69]. However, there are more studies on the gasification of some amino acids as model compounds of proteins, present in food waste or sewage sludge, and since amino acids are the main components of microalgae. In this sense, several amino acids have been tested, such as alanine, leucine, phenylalanine, serine, aspartic acid, glycine, valine, proline [70,71].

Table 2 shows the literature related to SCWG of model compounds with some details.

#### 4.2. Effect of the main operating parameters

Temperature, pressure, feedstock concentration and flowrate, and residence time are the most relevant operating variables that affect SCWG performance, which can be performed in a continuous reactor or in a batch reactor. In addition, if a catalyst is used, the type of catalyst, and the space time or the amount entered the reactor are also important.

Typical pressure and temperature ranges are between 23 and 30 MPa and between 450 and 800 °C, respectively. In most experimental studies conducted under SCW conditions, while pressure has a very slight effect [78,79], the higher the temperature, the higher the CGE and gas yields [30,33,72,80-82]. This matches well with the equilibrium computation [23,83], and can be understood since SCW gasification is globally endothermic, so equilibrium is favored by high temperatures, and these also favor reaction rates. Likewise, biomass concentration has been tested at very low values of 1–5 wt% and at very high values of up to 30–40 wt%. The former cases may be realistic and useful when starting a research, although these low values are not techno-economically feasible for an industrial process, especially if self-sufficiency energy is required, so at least 15 wt% should be used [20,84]. However, very high concentrations are far from being considered as biomass with high water content and could probably be better processed under other conditions, such as steam reforming. In any case, gas yields increase as the biomass concentration fed to the reactor decreases [85-87].

Residence time is a few seconds in a tubular reactor, which is quite significant [72,88,89], while the duration in a batch reactor is between minutes and hours. Consequently, the conversion will be higher in the latter type of reactor, but they are difficult to apply to an industrial plant, as effective heat integration is unlikely for batch reactors. Using a continuous tubular fixed-bed reactor with a certain amount of catalyst, a certain value of space time is obtained for application to other studies, even a larger scale. Kinetic studies with catalysts will be briefly reviewed in the next section.

#### 4.3. Kinetic studies and potential mechanisms of reactions

Most experimental papers have focused on examining the performance of batch reactors and, less frequently, continuous reactors using different feedstocks under SCW conditions. However, the number of kinetic studies is quite lower. Among all of them, we can highlight those that have contributed to predict the SCWG results [90-93]. Usually, reaction schemes assume first-order kinetics for most compounds and rarely second-order kinetics for some specific compounds when no catalyst is used. However, there may be parallel reactions involving different reaction orders for each considered compound and even non-linear interactions among different components of feedstock that would lead to non-first-order reactions, thus limiting the applicability of previous kinetics results.

In addition, some papers have greatly contributed to elucidate and propose reaction mechanisms [16,90,92-96] to understand and improve the conversion of feedstock into the final desired products, mainly CH<sub>4</sub> and H<sub>2</sub>.

So far, a potential route including the effect of feeding more than one model compound through different intermediates can be shown based on previous studies on the SCWG of the bio-oil aqueous phase by Gutiérrez Ortiz et al. [77,83] in addition to the aforementioned references, when no catalyst is added to the process (Fig. 3).

At first, a set of organic compounds experiences thermal decomposition through reaction intermediates where ionic and free radical reactions compete with each other, although above the critical point, free radical reactions are favored over ionic reactions; in fact, SCW stabilizes the free radicals. The reactions with free-radicals lead to bond cleavage (O-H, C-H, and C-O), so small formed compounds, such as acids, alcohols and aldehydes are progressively converted into gases.

Fig. 3 shows a scheme of potential reaction pathways involving 43 reactions that consider a feedstock of four model compounds (glucose, hydroxyacetone, acetic acid and 1-butanol, all highlighted in yellow); relevant intermediates are highlighted in green. Glucose can follow an isomerization reaction to produce fructose (both are the main components of cellulose), although it may be converted into 5-hydroxymethylfurfural (5-HMF) by acid catalyzed dehydration. This intermediate may be degraded to furfural and formaldehyde, which is not stable in SCW and decomposes to CO and H<sub>2</sub>. Furfural may form phenol via an electrocyclic reaction pathway, which can cause a decrease in the number of free radicals and, as a consequence, in the conversion of intermediates into gas. In addition, phenol and furfural can promote aromatic compounds or even polymerize, which leads to tars and carbon residues.

Glucose or fructose can also undergo *retro*-aldol condensation to produce glyceraldehyde, dihydroxyacetone, glycolaldehyde or erythrose. The first produces less H<sub>2</sub> and more CH<sub>4</sub>, and the third promotes the pathway to CO and H<sub>2</sub>; the second and fourth lead to pyruvaldehyde that gives CO<sub>2</sub> and CH<sub>4</sub>. These two gases are also obtained mainly if glyceraldehyde and pyruvaldehyde are transformed into acetaldehyde, which then reacts to produce acetic acid by incorporating H<sub>2</sub>O through self-disproportionation (Cannizzaro reaction). This can originate acetone or ethanol.

Among the latest intermediate products, formaldehyde produces H<sub>2</sub> by decarbonylation or can be converted to formic acid and methanol through a Cannizzaro reaction. In addition, dienes can be produced from glucose through dehydration and subsequent radical chain propagation, and then cyclic structures capable of aromatization may be generated by Diels-Alder cycloaddition of dienes along with ethylene, which comes from acetone produced by ketonization of acetic acid.

The CH<sub>4</sub> yield is initially higher than the H<sub>2</sub> yield, but CH<sub>4</sub> reforms with SCW producing H<sub>2</sub>, whose yield is further increased if the water-gas shift (WGS) reaction occurs. Note that methanation reactions (reverse reaction of CH<sub>4</sub> reforming) are very unlikely due to high temperatures and water amounts.

Additionally, xylose is converted into furfural by dehydration or glycolaldehyde, formaldehyde, and glyceraldehyde by *retro*-aldol

condensation [93]. Similarly, guaiacol and phenol can follow a pathway to syngas after progressively converting into cyclohexanol, which is then transformed into acetic acid and 1-propanol. However, phenol can also originate monocyclic aromatic hydrocarbons and polycyclic aromatic hydrocarbons; the latter result in char [96]. Tau Len-Kelly and Matsu-mura [97] determined that guaiacol hydrolysis leads to catechol and, finally, phenol and final gases (syngas), although benzene and char could also be formed.

Lactose is a disaccharide composed of glucose and galactose, so it is a larger model compound present in human milk and, hence, in dairy wastewater. It has also been gasified in SCW by Nanda et al. [73], who proposed a mechanism in which lactose was hydrolyzed below 550 °C to produce different organic acids and phenols, which above 600 °C were converted into small alcohols, some aldehydes, and even aromatics, all of them included in Fig. 3.

Sato et al. [70] tested five amino acids (alanine, leucine, phenylalanine, serine and aspartic acid) just below the critical point. These authors determined that there were two main paths: deamination to produce ammonia and organic acids, and decarboxylation to produce carbonic acid and amines. Likewise, Samanmulya et al. [71] also tested five amino acids (glycine, alanine, valine, leucine, and proline) in a tubular reactor under SCW conditions (500–600 °C, 25 MPa) without using a catalyst, and found that amino acids were converted to hydrogen, methyl, and isopropyl radicals from the corresponding amino acids. These authors conducted other studies with more amino acids, such as histidine and 4-methylimidazole [98] or aminobutyric acid and serine [99]. In all of these studies, the amino acid concentration was very low (1 wt%), so higher concentrations should be tested to make the process techno-economically feasible.

Furthermore, when there are carbohydrates and proteins, their intermediates (glucose, fructose, and amino acids) can react with each other through the Maillard reaction, thus leading to free radical scavengers that decrease the reaction rate of free radical chain reactions and, hence, the gas yield [4]. Therefore, the interaction between proteins and carbohydrates seems to be negative for gasification purposes in SCW.

In the case of gasification of larger molecules, such as cellulose, hemicellulose or lignin, some additional mechanisms have been suggested. Thus, Sasaki et al. [90] proposed a model in which microcrystalline cellulose was transformed into carbohydrates and a water-insoluble precipitate under subcritical conditions, obtaining additional intermediates from glucose monomers, such as fructose, erythrose, 5-HMF, glycolaldehyde, and glycerolaldehyde at longer reaction times. At supercritical temperatures, cellulose was rapidly converted, and the products of glucose degradation increased only slowly. Later, Tolonen et al. [100] found that crystalline cellulose is dissolved and depolymerized in supercritical water, leading to dissolved polymers and monosaccharides. The main intermediates of its SCWG of lignin seem to be guaiacol and catechol (this comes from hydrolysis of guaiacol) before obtaining phenol and final gases [101]. Similarly, proteins break down into amino acids, which decompose further by deamination and decarboxylation, even suffering recombination reactions that result in pyridines (C<sub>5</sub>H<sub>5</sub>N, aromatic with nitrogen), propionic acid (organic acids) and dimethylamine (amine) [102].

Regarding catalytic studies, Zhu et al. [58] found that the H<sub>2</sub> yield increases by a factor of 25 when Ru/Al<sub>2</sub>O<sub>3</sub> is used as a catalyst in the SCWG of glucose with respect to the non-catalytic performance, which gives an idea of the importance of using a suitable catalyst.

This is an example of how a suitable catalyst can significantly enhance CGE and the desired specific yields of H<sub>2</sub> and CH<sub>4</sub>. However, in this regard, sometimes an ambiguous justification for the use of catalysts in SCWG is read when a study on a given catalyst is aimed at reducing the reaction temperature, and hence the severity of the conditions. This may lead to confusion because an appropriate catalyst allows achieving higher gas yield in a specific SCWG reactor under certain operating conditions, but it is always limited by thermodynamics, which is favored at high temperatures in an SCWG process, because the overall set of

reactions is endothermic. Thus, at equilibrium, gas yields at 800 °C will be higher than at 600 °C, and the use of a catalyst cannot change this. Catalysts cannot affect the chemical equilibrium, but can reduce the activation energy, and hence, they allow the equilibrium to be achieved more quickly. Their mission is to boost the reaction rate and get a close approach to equilibrium, thus shortening the time as much as possible, i. e., using a reactor length as small as possible. In addition, as the reaction rate increases with temperature, the development of a catalyst at low temperatures is even more necessary because the reaction rate decreases as the temperature is reduced. Note that if a different temperature is set, another equilibrium condition is achieved. Therefore, there is a relationship between the use of catalysts and the operation at low temperature; in fact, at low temperatures, the use of catalysts becomes necessary to make the process effective, and at high temperatures, a catalyst might not be strictly necessary. In any case, at lower temperatures, lower gas yields and, especially, lower H<sub>2</sub> yields will be achieved.

In addition, since there may be a series of parallel and consecutive reactions in the SCWG of a given feedstock, new routes or reaction mechanisms may be followed, and different reaction rates may be established for each reaction when different catalysts are used, thus leading to different selectivities for each one, i. e., different amounts of desired product obtained per amount of all products present in all phases or even in one single phase (e.g., gas phase). If conversion is also considered, the product of conversion and selectivity leads to the yield of a certain product, so this can be defined as the amount of desired product obtained per amount of consumed reactant. This is the reason why the overall selectivity to gas biofuel may be increased when catalysts are used at low temperatures. In this way, some catalysts can promote hydrogen formation and other methane formation, i. e., higher H<sub>2</sub> or CH<sub>4</sub> yields, depending also on actual operating conditions.

Different heterogeneous and homogeneous catalysts have been tested in the HTL and SCWG processes. Among the former, studies using Nickel-based and Ruthenium-based catalysts with various supports [31,103-106] have been reported mainly. Regarding the latter, alkali catalysts -without support - such as NaOH, KOH or Na<sub>2</sub>CO<sub>3</sub> [30,60,107,108] have also been studied. However, these can be considered as homogeneous catalysts when they are added to water below the critical point, but not near or above it because salts are no longer soluble in SCW, and they become constitute a solid phase immersed in a gas or gas-like phase (at supercritical state). Nevertheless, there are not many studies reporting kinetic modelling of reactions, and most of them derive from Langmuir-Hinshelwood kinetics to explain the kinetics of the heterogeneous catalytic process, as it combines adsorption and desorption with a surface reaction. This kinetics becomes too simple for SCWG processes, as there may be reactions involving several steps or more than one catalytic site, and then the most common procedure consists of identifying a rate-limiting step; in this more general case, the Hougen-Watson formula can be used. Thus, it is typical that, when adsorption and desorption are distinct steps, heterogeneous catalysis occurs through multiple steps that can be approached in a simplified way by the Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics, so adsorption is considered a reversible single-step where the species react with vacant catalytic sites. Byrd et al. [109,110] developed similar kinetic models for SCWG of glucose and glycerol assuming that first glucose (or glycerol) is reversibly adsorbed on the catalyst, and once adsorbed, it reacts with water to produce a more complex molecule that decomposes to form intermediate products (the rate-limiting step) before these convert into CO<sub>2</sub> and H<sub>2</sub>. The model was validated using the experimental results, obtained in a continuous tubular fixed-bed reactor with Ru/Al<sub>2</sub>O<sub>3</sub> catalyst at 700–800 °C and 241 bar, which were very close to equilibrium. Tushar et al. [111] also developed a kinetic model based on the LHHW approach along with a mechanistic model applying the Eley-Rideal (ER) mechanism for glucose conversion in supercritical water. Likewise, the conversion data of SCWG of glycerol to hydrogen were experimentally studied in a tubular fixed-bed reactor using two commercial catalysts (Ni/Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> and Ru/Al<sub>2</sub>O<sub>3</sub>) and the turnover



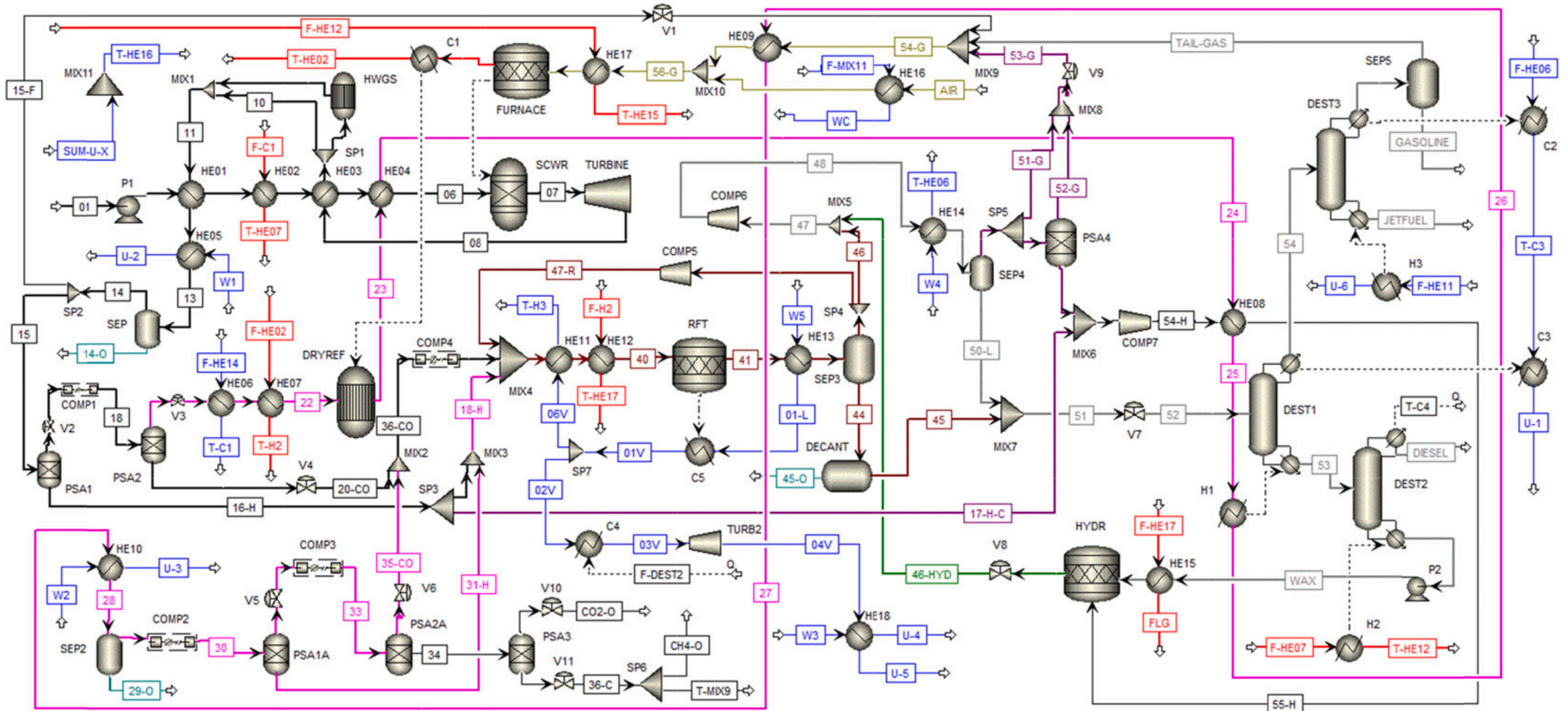


Fig. 4. Heat-integrated flowsheet of the process for Fischer-Tropsch biofuel production [123].

rates were stated, once normalized by the number of ostensible catalytic sites, and then the apparent activation energy and the values of the pre-exponential factor were obtained using the Arrhenius equation, thus providing a quantitative measure of catalytic activity for the tested catalysts [112]. More recently, Yang et al. [113] presented a kinetic model for phenol SCWG using a Ni-Ru bimetallic catalyst, where the external mass transfer and internal diffusion resistances could not be evaluated, thus limiting the real intrinsic kinetics. In fact, reaction rate equations followed a non-catalytic kinetic mechanism, which was expressed by the authors as macro-kinetics. In addition, they assumed first-order reactions in the concentration of each reactant, which nowadays seems to be a very simplified description.

In spite of all the effort carried out in studies of reaction kinetics and the incremental improvements achieved in the existing reaction mechanism schemes, the current state is not accurate enough to apply the corresponding dynamics of the reactant to reactor design with a minimum guarantee of reaching a reliable behavior, and hence a commercial viability. Therefore, more extensive studies on novel kinetic approaches, including catalysts, should be performed to boost the decomposition of some recalcitrant compounds, such as phenol or acetic acid, and to prevent the formation of char and even tar in SCWG, thus minimizing the deactivation of heterogeneous catalysts.

Currently, a relatively novel approach is the use of quantum chemistry composite methods for computational chemistry to predict the numerous reaction mechanisms at the molecular level. One of these methods of quantum chemistry calculations, based on the Complete Basis Set - specifically, *ab initio* CBS-QB3 (based only on theoretical principles, without using experimental data, which performs calculations using functional group additivity) - is the Reaction Mechanism Generator (RMG) software package developed by the Green's research group [114]. This tool can build a detailed kinetic model for a model compound (or a mixture of several compounds) plus a supercritical water system. It is a rate-based algorithm for model generation, where added species are predicted to be produced with higher rates, and species formed at rates below a user-defined tolerance are omitted. Kinetic models are constructed on the basis of a series of elementary chemical reaction steps using a general understanding of how molecules react. The mechanism generation and simulation conditions must match with the experimental conditions (for validation), and the simulation does not consider any chemistry taking place during the short heat-up and cooling-down times (i.e., transient stages). In this approach, the estimation of kinetic parameters is approximated, and the accuracy of RGM is very sensitive to the amount of data present in hierarchical trees used in the organization of functional group data to identify group contributions more quickly [115]; currently, uncertainty analysis, expansion of the database, new algorithms have been added to the software, and molecular representation is being addressed to improve the accuracy of RGM [116]. However, RGM has some limitations, and it does not cover molecular weight growth reactions, but only decomposition reactions, where the weight of molecules decreases. This is what takes place mainly in SCWG but not exclusively. Thus, RGM is not recommended for applications where cyclic transition compounds may be formed, and the use of other computational chemistry methods, such as Density Functional Theory (DFT), whose calculations can be performed using Gaussian 09, as proposed by Kang et al. [117], who have put RGM into question to be applied in SCW applications. In contrast to *ab initio* methods, DFT computes the energy on the basis of the electron density instead of a wave function. DFT limitations were shown by Burke ten years ago [118], mentioning, among others, the many approximations taken and the failures for strongly correlated systems. Recently, once stated that accuracies for many molecules are limited to 8.4–12.6 kJ/mol with functionals currently available, Burke et al. [119] have improved the quantum chemical accuracy (errors below 4.1 kJ/mol) in the test data by applying machine learning to calculate coupled cluster energies from DFT densities. The procedure for DFT calculations using

Gaussian 09 starts with setting an initial reaction model using the final reaction model in thermal decomposition. Water molecules are an input in each reaction pathway considered in the reaction model, and Gaussian 09 is applied to calculate the changes in the energy barrier. Then, they are compared with the reaction barriers in the absence of water molecules to clarify the reaction mechanism; in addition, and using experimental results, other reaction pathways are examined, in which water can participate [117]. All calculations are performed under (supercritical) operating conditions. There are several methods in DFT, and the B3LYP method provides fast speed and high accuracy. In any method of quantum chemistry calculations, consistency among different experimental data sets is crucial for identifying and quantifying product species using accurate methods of physicochemical analysis.

#### 4.4. Thermodynamics and process simulation for biofuel production

Thermodynamics limits the feasibility of a process, so the maximum values for some performance variables, such as product yields, energy and exergy efficiencies, and thermal energy and power, are stated by equilibrium under the operating conditions. Likewise, transport properties and chemical kinetic parameters influence the design of process units, not only in reactors but also in heat exchangers and separation units. Process design and assessment must use all these properties.

There are a number of thermodynamic studies related to SCWG and some review papers dealing with thermodynamics [12,119,120]. First, a suitable thermodynamic method is required, and, from two possible types, only the equations of state (EoS) can handle sub- and supercritical components of a mixture at the same time. Among all potential cubic EoS, predictive Soave-Redlich-Kwong (PSRK) has been reported to be a reliable thermodynamic method to be used in SCWG processes [23] after screening with other EoS such as Soave-Redlich-Kwong (SRK), Peng-Robinson (PR) and Peng-Robinson with the Boston- Mathias  $\alpha$ -function (PR-BM). This is a predictive EoS capable of foreseeing any interaction at any pressure by applying the UNIFAC method at low pressure (based on activity coefficients), and it is based on the SRK EoS but using the generalized Mathias-Copeman  $\alpha$ -function and the Holderbaum-Gemehling mixing rules [121]. A little later, another interesting thermodynamic paper was presented for a series of model compounds by Withag et al. [122], who also discussed the choice of SRK EoS with a modified Huron-Vidal mixing rule as a proper method. Likewise, Gutiérrez Ortiz et al. [83] performed a further discussion applied to some other model compounds, and the authors concluded that, even though all the studied methods presented a good fit to supercritical curves, the best EoS were PSRK and SR-Polar based on the modification of the SRK EoS proposed by Schwarzenhuber-Renon, as they exhibited minimal deviations in properties and thermodynamic functions between the liquid and vapor states.

On the other hand, two approaches to modelling the equilibrium may be followed: (1) the non-stoichiometric approach, where the Gibbs energy is minimized to calculate the equilibrium composition without providing the involved reactions but only the initial composition; and (2) the stoichiometric approach that needs to specify precise reaction mechanisms, but without considering instable chemical species and reaction intermediates [12]. Currently, commercial software is available to perform process simulation, such as Aspen Plus, Chemcad, or gPROM, among others, so the non-stoichiometric approach is mostly used because it is easy to use. Thus, for instance, Aspen Plus has a module named the 'RGibbs reactor' to compute the products composition at equilibrium as well as the heat needed / released to perform the overall reaction.

Apart from performing fundamental research on SCWG, such as kinetic studies and even on transport and thermodynamic properties, conceptual designs of processes based on SCWG are needed to move forward the technology providing other applications rather than the most extensively inspected one focused on hydrogen production, probably derived from the aim of most experimental studies. The so-designed

new processes can be implemented in software like Aspen Plus, where the performance of the overall process may be supported only by thermodynamics along with some specific transport properties or even by reliable kinetic models applied to the reaction units. While this aspect is not yet well developed, most of the simulated processes predict the results by assuming equilibrium, a certain approach to equilibrium, a given yield, or by performing a stoichiometric calculus depending on an established conversion for a determined set of reactions. Thus, it is possible to make the simulations more realistic in the absence of known kinetics, which would be the ideal option.

Once the main subsystem related to the SCWG process is developed, other subsystems are required to achieve a complete process focused on a target product, such as biofuels. In the development of a potential industrial process, suitable thermodynamic models must be specified for the different parts of the plant, and the process configuration along with the energy integration are of the utmost importance in order to make the process feasible. This must be assessed by performing TEA and LCA, as exposed in the next section.

Therefore, biofuels production from SCWG of different feedstocks is mainly reviewed in this section, as most experimental studies, if not all, are focused on obtaining a syngas with the highest H<sub>2</sub> and/or CH<sub>4</sub> yields. Thus, several options are possible from a syngas. Next, some processes based on SCWG are commented on because they have been very developed to produce liquid biofuels and gas biofuels, such as SNG and even methanol and hydrogen, whose production has been mostly studied.

The considered feedstock is usually that matching with sustainability in waste-to-energy (biofuels) processes, but other interesting feedstocks will also be briefly commented on, such as the use of microalgae, which is still under study.

#### 4.4.1. Production of liquid biofuel

There are only a few fully developed processes that produce liquid biofuels by Fischer-Tropsch synthesis from the syngas obtained by SCWG technology of different feedstocks.

Campanario and Gutiérrez Ortiz [123] designed a process including three additional subsystems to the SCWG section, consisting of a syngas upgrading, the Fischer-Tropsch synthesis loop and a final upgrading and refining of the Fischer-Tropsch products to make them similar to diesel, gasoline, and jet-fuel. Fig. 4 shows the complex flowsheet of the process implemented in Aspen Plus, involving several reaction units, separation units and other auxiliary equipment, especially a heat exchanger network. This plant was designed to obtain not only biofuels but also electrical power, as well as to avoid the use of external fuel (i.e., overall energy self-sufficiency). The feedstock was 60 t/h bio-oil aqueous phase, and with a total organic concentration of 35 wt% in the feed, 4.6 t/h biofuel was produced and 5.3 MWe was generated. In addition, 0.50 kg CO<sub>2</sub> / kg organic material was removed for sequestration.

Another fully developed new process for biofuel production (liquefied fuel gas, gasoline and diesel) based on SCWG was recently published [124], and Fig. 5 shows its conceptual design that was implemented in Aspen Plus. In this case, the municipal solid waste (MSW) reject fraction is fed into a fast pyrolysis reactor to produce bio-oil, which is separated into two phases by adding water. The oil-phase is upgraded by hydrodeoxygenation (HDO), and the aqueous-phase is fed into an SCWG reactor to produce hydrogen, which is further used in the HDO section. Once again, the overall process involves a large number of units and it was designed to be energy-self-sufficient and also to generate electrical power. Thus, for a feeding of 50 t/h MSW reject fraction, 10.6 MWe was generated and 5.2 t/h biofuel was produced.

The use of microalgae as feedstock implies an open discussion because its sustainability is debatable and a microalgae-based SCWG process might be too expensive, although probably in plants that were not fully developed and without a suitable process-energy configuration in relation to the significant thermal energy input. In this regard, Onigbajumo et al. [125] examined the integration of some options, such

as the use of solar energy, natural gas, or electricity. The feedstock was 17.53 t/h microalgae (75% water), and the syngas obtained was mixed with external H<sub>2</sub> to reach the ratios required in the Fischer-Tropsch synthesis, but it was not developed further. Fig. 6 shows a flowsheet of this process.

Similarly, Rahbari et al. [126] further developed the SCWG of microalgae (75% water) by assisting it with solar-thermal energy for process heating, and by adding the required H<sub>2</sub> by a photovoltaic powered electrolyzer. They also incorporated a syngas reformer and a Fischer-Tropsch synthesis unit for liquid fuel; the design of the latter is very similar to that previously reported by others [123]. For a plant of 16800 t/y microalgae, the authors obtained a production of 4200 t/h gasoline and 3800 t/y diesel, and electricity was produced but not enough to supply that required by the overall process.

#### 4.4.2. Production of gas biofuel

This section covers a number of more or less developed processes, mostly focused on hydrogen production, so they are simpler than the previous ones.

It has been a decade since the first papers including process simulation were published beyond the simple use to compute chemical equilibria compositions. A thermodynamic study published in 2011 involved a simple scheme of a lab plant for the SCW reforming of glycerol operating at equilibrium to examine the effect of different variables on gas yields, especially hydrogen yield [23], and where different EoS were fully discussed to obtain the most suitable. Likewise, using the same feedstock, Azadi [127] implemented another simple flowsheet where the SCW reactor was coupled with parabolic trough solar thermal collectors to heat co-currently fed molten salts mixture that provided the required energy for the SCW process. In another study carried out by Wongsakulphasatch et al. [128], a very simplified diagram for bioethanol SCW reforming was proposed to produce hydrogen to feed an SOFC, with a few process units. In a later article, Louw et al. [129] reported a simple scheme but incorporating a way to deal with solid biomass in Aspen, which is a weak point of this software. Thus, the SCWG reactor consisted of two reactors in the Aspen flowsheet: a RYield and a RGibbs (Fig. 7). The first one is required to allow the decomposition of solid feedstock (considered in Aspen as a non-conventional component) through a calculator block that results in a mixing of elements or molecules (C, H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and S) based on the ultimate analysis, proximate analysis, and sulfur analysis. Then, the syngas composition at chemical equilibrium under the operating conditions is obtained in the RGibbs.

Simple process simulation schemes have continued to be used in more recent thermodynamics studies [130,131].

One of the first overall processes that proposed the production of a determined product (distinct from hydrogen) from SCWG of biomass waste (glycerol coming from biodiesel production) was carried out by Serrera et al. [132] and focused on SNG production. Once the syngas is obtained in the SCWG reactor, it is conditioned through a PSA system in order to reach a stoichiometric number of 3, required for the subsequent methanation process. This was fully designed and consisted mainly of three adiabatic, fixed-bed reactors connected in series with intermediate gas cooling. The specific production ratio (per kg glycerol) was 0.17 kg CH<sub>4</sub> and 0.43 kWe, achieving an overall energy efficiency of up to 76.1% by accounting for the obtained cogeneration water. Previously, the same authors published another work aimed at producing methanol from SCW reforming of glycerol [21], where the conditioning of expanded and water-removed syngas by a pressure swing adsorber (PSA) system and the methanol loop was fully developed. The specific production ratio (per kg glycerol) was 0.270 kg MeOH and 0.27 kWe, achieving an overall energy efficiency of 38% and sequestering 0.38 kg CO<sub>2</sub> per kg glycerol.

Similarly, and looking for the use of solar energy for process heating at 250 °C, Salemmé et al. [133] considered three gasification processes to be installed downstream from the glucose SCWG reactor: first, adding

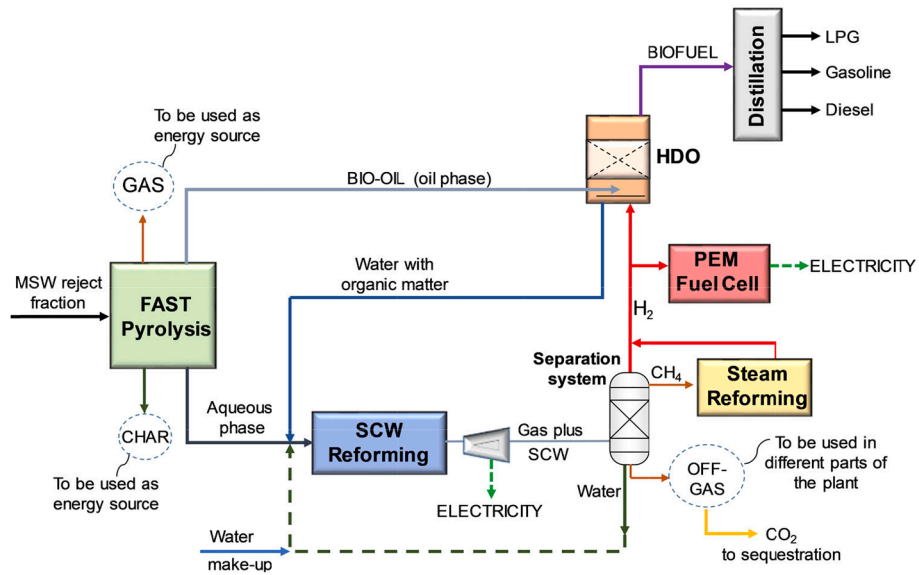


Fig. 5. Conceptual design of the process to valorize the MSW reject fraction [124].

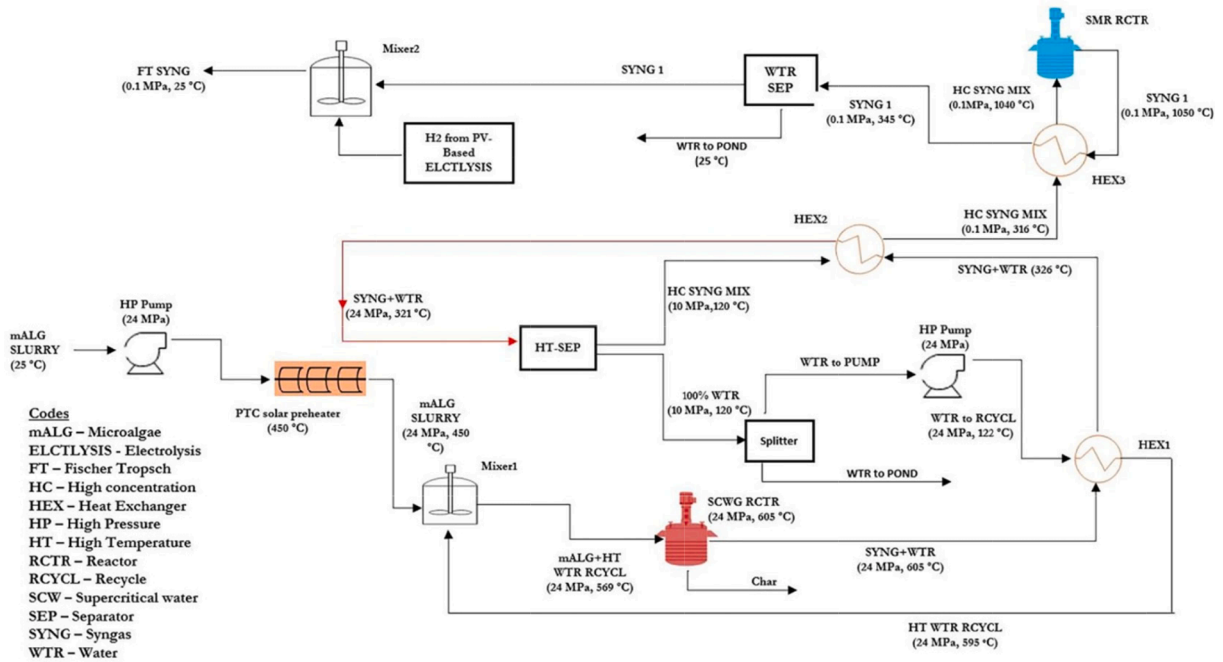


Fig. 6. Flow diagram of SCWG algae with solar-based preheating [125]

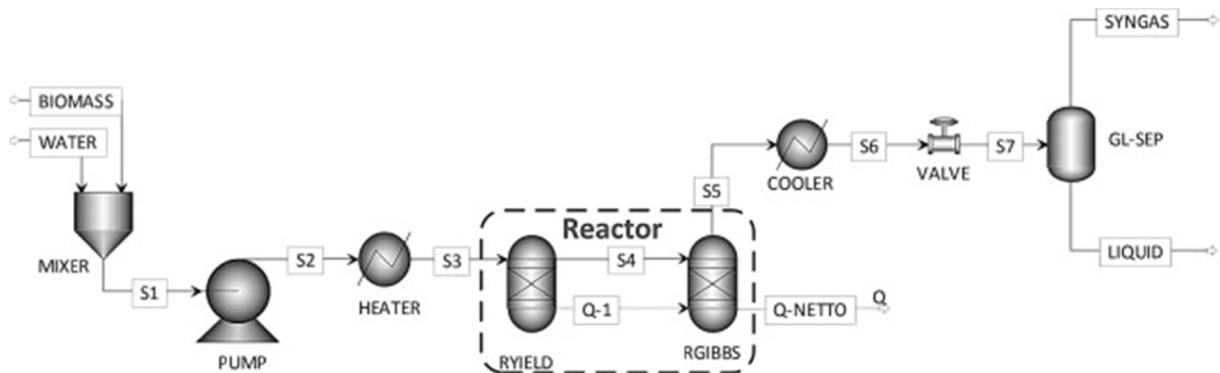


Fig. 7. Flow diagram of SCWG for H<sub>2</sub> production and power generation [129].

two water gas shift reactors and a PSA; second, an integrated membrane water gas shift reactor; and third, two flash separators and a PSA. These authors concluded that the optimal solar share of the second process was higher than that of the first one, and that solar integration in the third process was not feasible due to the high pressure and water content in the feedstock.

Likewise, two processes of SCWG of glycerol were proposed and simulated to achieve maximum electric power and hydrogen production while avoiding the use of external energy or fuel. One of the two options was an autothermal operation. Electric power was generated in the expansion of syngas leaving the SCWG reactor, and the hydrogen-rich stream was sent to a PEM fuel cell in order to increase the power, whose values were 1.59 MWe and 1.60 MWe per ton/h of glycerol for the non-autothermal and autothermal processes, respectively [20,134].

Also, some papers have been published on the H<sub>2</sub> production from SCWG of black liquor (BL) as waste from the pulp mill industry. Thus, Darmawan et al. [135] studied a process in which BL with a moisture content of 85 wt% is fed to an SCWG reactor and the produced syngas enters a chemical looping where H<sub>2</sub> is obtained, along with electric power and CO<sub>2</sub>; additionally, the second unit provides thermal energy to the first unit. The BL fed to the SCWG was 50 t/h and the obtained H<sub>2</sub> was 4.1 t/h. The authors obtained a total energy efficiency of 80%. Net electric power (in MWe) was not provided. In another study by Özdenkçi et al. [136], a stream of BL with 100 t/h was fed to the SCWG reactor and the plant configuration considered combined heat and power (CHP) production or H<sub>2</sub> production in SCWG reactors made of different materials. The maximum pure H<sub>2</sub> was 536 kg/h in the hydrogen production scenarios while up to 77.1 MW in the energy production scenarios. The authors mentioned that heat integration is needed to reduce the external energy need, but no attempt in this regard is observed in the published paper.

In addition, SCWG of soybean straw has been simulated by Okolie et al. [137], using a feeding of 1870 t/day (91.9% water) and pretreating it before entering a catalytic SCWG reactor (500 °C, 25 MPa). The product leaving the reactor consists of syngas, liquids, and char, so they need to be separated. Then, the gas is further purified, first by removing the H<sub>2</sub>-rich gas, and afterward to obtain a CO<sub>2</sub>-rich gas stream; the off-gas is sent to a combustor that provides thermal energy to the process. The H<sub>2</sub> production was 110 t/day and, although the process is well described, the flowsheet implemented in Aspen Plus is not fully developed with heat integration, so it could be optimized.

Equally, Hantoko et al. [138] also dealt with sewage sludge in SCW by process simulation, integrating SCWG with a combined cycle for power generation, so H<sub>2</sub> and electric power are obtained in this plant. Simulations were performed with a feeding of 100 kg/h. The authors obtained a maximum H<sub>2</sub> production of 9.7 kg/h and a maximum electric power of 15 kW. These results are positive, despite the fact that the Aspen flowsheet could be further developed because, although the authors included several heat exchangers to reduce the energy loss, more effort might be made in this regard.

Pig manure has been also studied in a process aimed at producing H<sub>2</sub> and recovering waste heat by Ren et al. [139]. The capacity is 650 t/day dry pig manure with a variable ratio of water to dry pig manure between 2 and 16. At a value of 7, the H<sub>2</sub> production was close to 500 kg/h and 37.5 % energy efficiency to H<sub>2</sub>, operating the SCWG reactor at 630 °C. Waste heat recovery was performed in a steam generator to produce heating steam and preheat slurry and oxygen (for the minimum heat required to attain auto-thermal operation), which increased the energy efficiency to almost 80%.

Ruya et al. [140] recently examined the SCWG of palm oil-derived waste under autothermal operation to produce hydrogen. These researchers also included waste heat recovery by generating low pressure steam to increase energy efficiency by 5–18%. Two steps were considered to increase the H<sub>2</sub> yield: first, H<sub>2</sub> was removed from the syngas leaving the SCWG reactor, and then this latter entered a steam reformer reactor where CH<sub>4</sub> was converted into H<sub>2</sub>. The resulting off-gas was sent

to a furnace to provide thermal heat to the process. In the Aspen flowsheet some heat exchangers are observed to better use the heat involved in the process. For 100 kg/h gasifier feed, a maximum H<sub>2</sub> yield of 1.5 kg/h was obtained.

#### 4.5. Techno-economic evaluation (TEA) and life cycle assessment (LCA)

Before a new process can become a reality, it must pass a techno-economic and environmental evaluation regarding the process feasibility.

Techno-economic assessment (TEA) is a very useful tool to stop or boost a technology to a potential commercial development once the economic viability is checked and technical improvements are identified for the process. Generally, in process engineering, some economic estimators, such as the minimum selling price, the net present value (NPV), the internal rate of return (IRR), or the payback period, as well as the cumulative discounted cash flow method of analysis, are frequently used.

Likewise, an environmental assessment is also important in an early stage of project development, and, like TEA, is also subject to limitations, mainly due to the lack of a full know-how of the process, frequently and directly related to technical specifications. Thus, TEA and LCA should be considered together, and the latter can affect the former in such a way that the target product or the way of production could even be changed. So far, TEA has normally been performed before LCA.

To carry out TEA and LCA, mass and energy balances are inputs required for computation, so those assessments are normally based on process simulation performed by commercial software, where the economy of scale can also be applied to the economy of a production process, among other sensitivity analyses.

In the previous section, it was stated that energy integration is crucial to make an SCWG process feasible because of the high required thermal energy. As this more efficient use of energy through the recovery of heat and even power allows reducing the needed external energy, the overall sustainability of the process increases, as van Doren et al. [141] pointed out.

Unfortunately, there are not many works on TEA and LCA of fully developed SCWG processes to be taken into account for scaling-up, so this requires further research.

An early work on the economic analysis of an SCWG process using sewage sludge as feedstock (5 t/h, with 80% water) is due to Gasafi et al. [142]. However, mass and energy balances were not provided by the authors, the flowsheet was too simple, with poor energy integration, and it was focused on the concept related to the unit built at the Research Center ('Forschungszentrum' in German) of Karlsruhe, in Germany, aimed at reducing the H<sub>2</sub> production costs.

Likewise, Langè and Pellegrini [143] performed an economic analysis of a combined production of hydrogen-energy using 35 t/h of empty fruit bunches (91.9% water) from the palm oil industry. Several sections are found in addition to the SCWG unit, such as a Selexol unit followed by a purification of H<sub>2</sub>, and the coupling turbogas power plant integrated (or not) in a combined cycle power plant, where H<sub>2</sub> can be burned, and the heat surplus of the clean flue gas is sent (or not) to a steam cycle to produce low-pressure steam. Among all scenarios studied by the authors, the best was when only H<sub>2</sub> is produced ( $\approx$  2 t/h), without excess of heat, thus presenting maximum values of IRR and NPV. Nevertheless, the flowsheet did not add energy integration, so other scenarios dealing with a surplus of power and/or heat might have been underestimated.

Galera and Gutiérrez Ortiz [144] carried out a TEA of the two processes previously developed relative to a supercritical water reforming (SCWR) and an auto-thermal supercritical water reforming (ASCWR), both fed with 1 t/h of glycerol [20,134], where the minimum hydrogen selling prices, at 10% IRR and 100% equity financing, were €4.61 per kg for SCWR and €4.95 per kg for ASCWR applying a discounted cash flow

analysis; these were considered as competitive prices by the authors. They also made a sensitivity analysis because the expected accuracy of the cost estimation method was about  $\pm 30\%$  total investment cost, thus concluding that the minimum  $H_2$  selling price varies  $\pm \text{€}1.15$  per kg  $H_2$  in SCWR and  $\pm \text{€}1.25$  per kg  $H_2$  in ASCWR. These authors also completed an LCA of  $H_2$  and power production in the non-autothermal SCW reforming of glycerol [145], where biogenic and fossil  $CO_2$  emissions were distinguished to quantify a more realistic GHG inventory of  $3.77 \text{ kg } CO_2\text{-eq}$  per kg produced  $H_2$ .

In the aforementioned reference by Özdenkçi et al. [136], the authors also performed a TEA and obtained a hydrogen production cost ranging from  $\text{€}1.46$  to  $\text{€}3.19$  per kg, depending on the material used in the SCWG reactor.

In a very recent paper by Barros et al. [146], a TEA was reported from the SCWG of black liquor (BL) based on a very simple Aspen flowsheet, where the authors concluded that the overall cost of the process was roughly  $\text{€}0.05$  per kg BL. However, the process is not fully developed and, as the researchers realized upon simulations, the main energy requirements for scaling up this process depend on the needed heat exchangers and the required pressurizing of the black liquor solution (that should have been optimized).

Do et al. [147] performed a TEA in a bio-heavy-oil production process based on SCWG of sewage sludge, using a feed basis of  $100 \text{ t/d}$  (80% water) in a very complete flowsheet that includes several separation and purification units. The minimum fuel selling price was  $\text{€}0.78$  per L, but this process can only produce  $8 \text{ t/d}$  bio heavy-oil along with  $7 \text{ t/h}$  inorganic matter and tar, as well as  $4.2 \text{ t/d}$  water-soluble organics to be discharged into the wastewater, which can imply a high environmental load, thus putting its sustainability into question.

In the study on the SCWG of soybean straw by Okolie et al. [137], a discounted cash flow analysis allowed computing the minimum  $H_2$  selling price of  $\text{€}1.64$  per kg soybean straw, with a 10% IRR.

As a continuation of the work on a novel process to produce liquid biofuels from SCWG of the bio-oil aqueous phase by Fischer-Tropsch (FT) synthesis [123], the same authors performed a TEA [84] and a further LCA [148]. In the first, feeding  $60 \text{ t/h}$  in a stream with 25 wt% organics,  $2.74 \text{ t/h}$  biofuels were produced and a power of  $5.72 \text{ MWe}$  was generated. Using a 10% IRR and 100% equity financing, the minimum

selling prices for refined FT-gasoline, FT-diesel and FT-jet fuel were  $\text{€}1.20$ ,  $\text{€}0.93$  and  $\text{€}0.26$  per kg feedstock, respectively. In the second, three case studies on  $H_2$  needed for hydrotreatment of the oil-phase of bio-oil were evaluated: (1) the proposed process involves the production of  $H_2$  by steam reforming of natural gas, (2) the required  $H_2$  comes from the SCWG process, thus significantly reducing the FT biofuels, and (3) the aqueous phase is fully reformed to  $H_2$  with surplus. The minimum global warming potential (GWP) at 25 wt% organics was  $11 \text{ g } CO_2\text{-eq}$  per MJ-biofuel for the case (2) with  $CO_2$  storage. Fig. 8 shows the system boundary of the sections involved in the LCA performed following the guidelines of ISO 14040/44:2006 [149] and using SimaPro software.

Likewise, in the aforementioned study on the production of biofuels and power from the MSW reject fraction, a very low gate fee of  $\text{€}16.7$  per ton was obtained considering the industrial selling prices of fossil fuels and electricity in a full plant [124]. The gate fee is revenue obtained from the authorities for taking on of the waste and its treatment, so it was calculated instead of the minimum selling prices of biofuels.

In the aforementioned reference on the SCWG of microalgae by Onigbajumo et al. [125], the authors performed a comparative study from an economic point of view among the three considered alternatives focused on energy requirements, concluding that the best options were the use of natural gas alone or along with solar parabolic troughs. The minimum fuel selling prices ranged from  $\text{€}32$  to  $\text{€}45$  per GJ.

In the same way, the authors who studied the SCWG of microalgae for FT biofuel production [126] also performed an economic analysis considering three configurations in the plant: steam methane reforming along with solar energy where  $CH_4$  is converted into syngas; partial oxidation / dry reforming with hydrogen supplied from an electrolyzer; and autothermal reforming where both  $H_2$  and heat are combined [150]. They concluded that the best configuration was the first, thus obtaining a leveled fuel cost of  $\text{€}2.3$  per L gasoline equivalent.

Regarding the greenhouse gas footprint of SCWG of algae, an estimate value of GHG emissions of  $11.1 \text{ kg}$  per kg  $H_2$  was given by Gemechu and Kumar [151], mentioning that 70% of the GHG emissions in SCWG are due to the algae feedstock production as a consequence of electricity consumption.

Finally, in the paper by Ren et al. [139] on autothermal SCWG of pig manure, the authors performed an LCA using  $1 \text{ kg } H_2$  as functional unit,

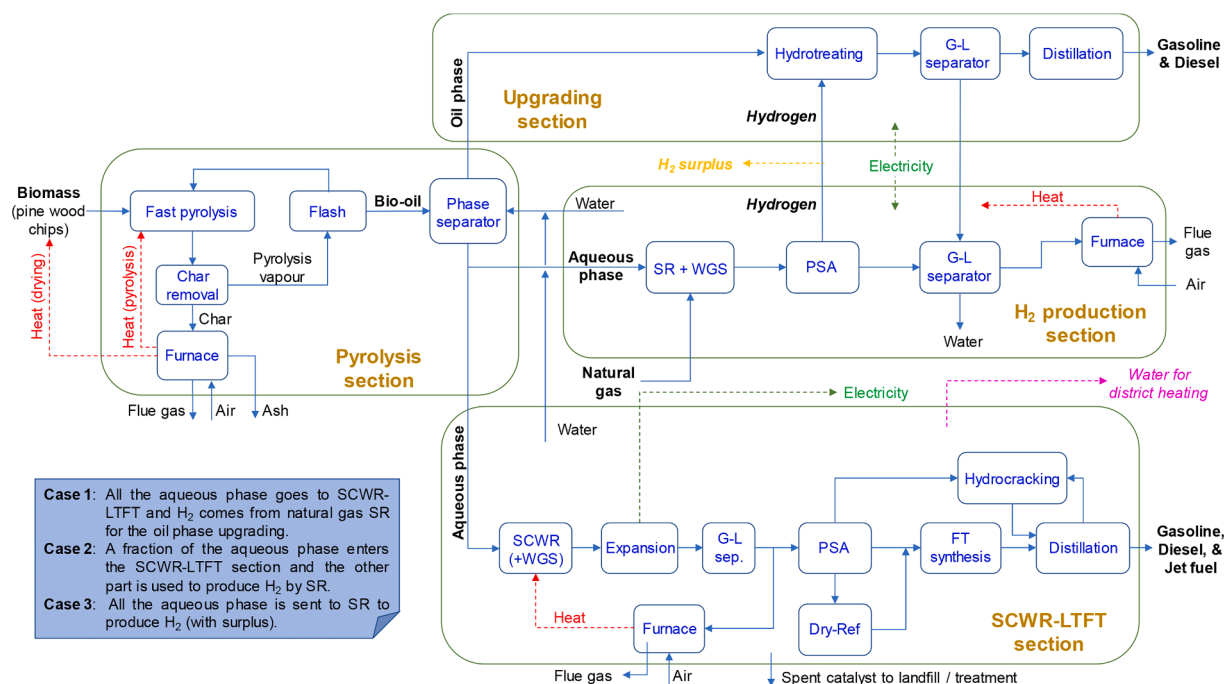


Fig. 8. System boundary with the four sections involved in the LCA study [148].

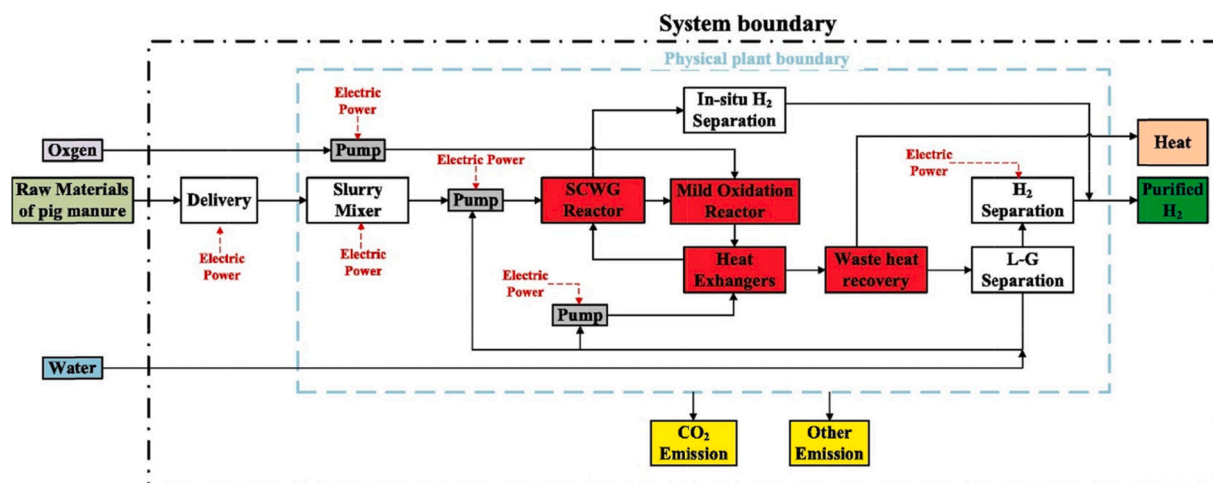


Fig. 9. System boundary for LCA of the autothermal SCWG of pig manure [139].

taking the system boundary shown in Fig. 9. The minimum GWP was 1.73 kg CO<sub>2</sub>-eq per kg H<sub>2</sub> under optimal conditions with carbon capture and storage, which was stated as a low value, below others found in the literature.

## 5. Challenges and future prospects: *Quo eamus?*

Now, we have a global idea of where we are, but where should we go?

In this section, some own suggestions and recommendations are given in order to advance SCWG technology for a sustainable biofuel production, and some of the aspects discussed above may serve as a reference.

First, process intensification could reduce the time required for the first commercial applications of SCWG. This was already noted by Cocero [152], although this study focused only on a few units. In fact, process intensification allows not only a reduction in the size of the plant or process units, but also a decrease in the required specific energy and in waste formation. As a consequence, the processing capability is notably increased. The first feature is the clearest, and for processes at high pressure (>22.1 MPa) this is not hard to get. In addition, compact heat exchangers allow better heat transfer, so they need to be developed for the operating conditions of SCWG processes. Accordingly, the process can become less expensive. In doing so, the time to market will probably be shorter, the process will be safer, and the environmental impacts will be lower, thus improving the process sustainability. Among the guiding principles of process intensification, molecules and clusters of molecules are the bricks to build novel approaches. In this way, molecular dynamics simulation may contribute to a better understanding of the static and transport properties of supercritical fluids, as previously noted [12]. In addition, suitable catalysts may permit the molecules of reactants to selectively overcome the activation energy barrier, thus decreasing the energy required by the reactions that will occur in a faster way. Likewise, the driving forces may be optimized at all scales (micro- and macroscale) and the corresponding specific surface areas may be maximized (thinking about heat exchangers as both isolated units and joined the reactors). Here, techniques such as microfluidic devices or even the theory of chaos can help enhance the mass and heat transfer in reactors, separation units and heat exchangers, so they should be further examined in order to develop the process intensification applied to SCWG processes.

As can be observed, within process intensification, some other aspects have been expressly cited, such as the development of heat exchangers and catalysts. In fact, the author considers these to be two of the main bottlenecks in the current state of SCWG technology along with

new and integrated ways for process heating. In addition, novel approaches to clarifying the kinetics may be boosted using modern tools, such as quantum chemistry calculations, and reaction mechanisms must be refined and unified.

Another challenge is the material used to make the process units operating not only at high pressure and temperature, but also with potentially corrosive compounds. Process intensification can cushion this need, since a smaller size for tubular reactors makes it possible to reduce the wall thickness, but corrosiveness must be considered on any scale. In this way, the development of expanders to recover the huge (thermal and pressure) energy is of the utmost importance.

With respect to thermodynamics and process simulation, some improvements are still required. On the one hand, more data regarding interaction parameters in the EoS are required and more data should be available in databases such as NIST or DECHEMA, to make the use of EoS more consistent and robust. On the other hand, regarding the process simulation two aspects are relevant: (1) the solid processing should be further developed so that wet solid biomass can be directly dealt with in a reaction system, based not only on the proximate and ultimate analysis (and sulfur analysis) but also on its composition, including handling of polymers, and (2) modeling and simulation are normally performed at steady state, but once the process is further developed and even studied following TEA and LCA methods, a dynamic simulation would provide the transient behavior of the plant and also give an idea of how the system may be controlled. In fact, instrumentation and process control should be thought and specified during the design stage of the project, as they may involve some local configurations for specific equipment (e.g., heat exchange control) and affect the controllability of the overall process. Rahbari et al. [150] included a partial dynamic simulation focused on the solar resource, as it is intermittent.

Further studies on TEA and LCA are required with novel processes that necessarily must incorporate mass and energy integration among process streams and utilities and by a suitable heat exchanger network. Regarding the TEA of SCWG processes, this is performed based on the class estimate 3 (project definition level between 1% and 15%) and class estimate 4 (project definition level between 10% and 40%), generally an intermediate, of the five accepted classifications of capital cost estimates found in the process industries, as Turton et al. [153] described. Thus, the estimates are between a concept study purpose and another one involving budget, authorization, or control, so the methodology is mixed but primarily stochastic. In any case, the class estimate depends on the process development, so not only new TEA studies are required, but also existing TEA should be revisited in order to scale up the class estimate and make the industrial plant more realistic with a more accurate techno-economic assessment, and hence a more correct LCA.

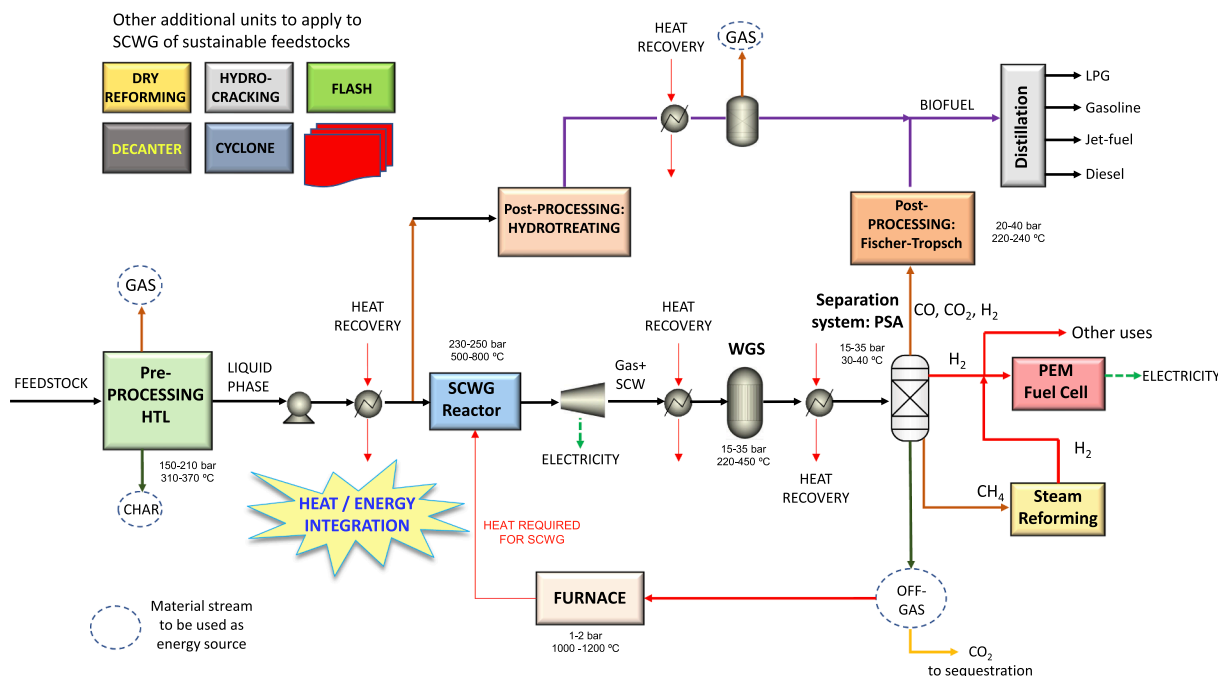


Fig. 10. An overall block diagram to build a new SCWG process from sustainable biomass.

Moreover, when designing a new process where SCWG is present, different technologies should be simultaneously implied and applied to a novel industrial process, even technologies that, a priori, could compete with each other. Thus, for example, the combined hydrothermal liquefaction and catalytic hydrothermal gasification system patented by Elliot et al. [154]. In this regard, HTL could convert wet solid biomass into a liquid bio-crude that is further processed in an SCWG section to syngas.

Fig. 10 shows a conceptual design to develop an overall SCWG process aimed at producing biofuels from sustainable feedstock, including a number of potential equipment to use.

Lastly, two final remarks can be added: (1) all the required development should be performed keeping in mind the needed sustainability for all of us and future generations, not only from an environmental point of view but also considering ethics and safety for people, and (2) the many research groups working on SCWG, and frequently striving to achieve similar targets, could work together, at least as many as possible, with a good organization, so the time to make this technology feasible for society would be shorter.

## 6. Conclusions

In this paper, the main and fundamental aspects of the SCW technology applied to sustainable biomass have been commented on and critically discussed. After that, biofuel production based on SCW gasification within a wider system is reviewed by considering process simulation, as well as techno-economic evaluation and life cycle assessment. In the last section, several suggestions are given relative to how to contribute to move forward this technology.

### CRedit authorship contribution statement

F.J. Gutiérrez Ortiz: Conceptualization, Methodology, Formal analysis, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgements

The author thanks the Consejería de Economía y Conocimiento (Junta de Andalucía) for the financial support of his PAIDI 2020 Research Project coded as P18-RT-2521.

## References

- [1] Modell M. Gasification process. United States Patent 4,113,446 1978.
- [2] Modell M. Processing methods for the oxidation of organics in supercritical water. United States Patent 4,338,199 1982.
- [3] Azadi P, Farnood R. Review of heterogeneous catalysts for sub- and supercritical water gasification of biomass and wastes. *Int J Hydrogen Energy* 2011;36(16): 9529–41. <https://doi.org/10.1016/j.ijhydene.2011.05.081>.
- [4] Rodríguez Correa C, Kruse A. Supercritical water gasification of biomass for hydrogen production – Review. *J Supercrit Fluids* 2018;133:573–90. <https://doi.org/10.1016/j.supflu.2017.09.019>.
- [5] Okolie JA, Epelle EI, Nanda S, Castello D, Dalai AK, Kozinski JA. Modeling and process optimization of hydrothermal gasification for hydrogen production: A comprehensive review. *J Supercrit Fluids* 2021;173:105199. <https://doi.org/10.1016/j.supflu.2021.105199>.
- [6] Farobie O, Matsumura Y, Syaftika N, Amrullah A, Hartulistiyo E, Bayu A, et al. Recent advancement on hydrogen production from macroalgae via supercritical water gasification. *Bioresour Technol Reports* 2021;16:100844. <https://doi.org/10.1016/j.biteb.2021.100844>.
- [7] Lee CS, Conradie AV, Lester E. Review of supercritical water gasification with lignocellulosic real biomass as the feedstocks: Process parameters, biomass composition, catalyst development, reactor design and its challenges. *Chem Eng J* 2021;415:128837. <https://doi.org/10.1016/j.cej.2021.128837>.
- [8] Pinkard BR, Gorman DJ, Tiwari K, Kramlich JC, Reinhall PG, Novoselov IV. Review of Gasification of Organic Compounds in Continuous-Flow, Supercritical Water Reactors. *Ind Eng Chem Res* 2018;57(10):3471–81. <https://doi.org/10.1021/acs.iecr.8b00068>.
- [9] Zhang Y, Li L, Xu P, Liu B, Shuai Y, Li B. Hydrogen production through biomass gasification in supercritical water: A review from exergy aspect. *Int J Hydrogen Energy* 2019;44(30):15727–36. <https://doi.org/10.1016/j.ijhydene.2019.01.151>.
- [10] Ibrahim ABA, Akilli H. Supercritical water gasification of wastewater sludge for hydrogen production. *Int J Hydrogen Energy* 2019;44(21):10328–49. <https://doi.org/10.1016/j.ijhydene.2019.02.184>.



- [11] Ferreira-Pinto L, Silva Parizi MP, Carvalho de Araújo PC, Zanette AF, Cardozo-Filho L. Experimental basic factors in the production of H<sub>2</sub> via supercritical water gasification. *Int J Hydrogen Energy* 2019;44(47):25365–83. <https://doi.org/10.1016/j.ijhydene.2019.08.023>.
- [12] Gutiérrez Ortiz FJ, Kruse A. The use of process simulation in supercritical fluids applications. *React Chem Eng* 2020;5(3):424–51. <https://doi.org/10.1039/C9RE00465C>.
- [13] Gutiérrez Ortiz FJ. Techno-economic assessment of supercritical processes for biofuel production. *J Supercrit Fluids* 2020;160:104788. <https://doi.org/10.1016/j.supflu.2020.104788>.
- [14] Hu Y, Gong M, Xing X, Wang H, Zeng Y, Xu CC. Supercritical water gasification of biomass model compounds: A review. *Renew Sustain Energy Rev* 2020;118:12–4. <https://doi.org/10.1016/j.rser.2019.109529>.
- [15] Abdpour S, Santos RM. Recent advances in heterogeneous catalysis for supercritical water oxidation/gasification processes: Insight into catalyst development. *Process Saf Environ Prot* 2021;149:169–84. <https://doi.org/10.1016/j.psep.2020.10.047>.
- [16] Savage PE. Organic Chemical Reactions in Supercritical Water. *Chem Rev* 1999;99(2):603–22. <https://doi.org/10.1021/cr9700989>.
- [17] Matsumura Y, Minowa T, Potic B, Kersten S, Prins W, Vanswaaij W, et al. Biomass gasification in near- and super-critical water: Status and prospects. *Biomass Bioenergy* 2005;29(4):269–92. <https://doi.org/10.1016/j.biombioe.2005.04.006>.
- [18] Kruse A. Supercritical water gasification. *Biofuel. Bioprod Biorefin.* 2008:415–37. <https://doi.org/10.1002/bbb.93>.
- [19] Toor SS, Rosendahl L, Rudolf A. Hydrothermal liquefaction of biomass: A review of subcritical water technologies. *Energy* 2011;36(5):2328–42. <https://doi.org/10.1016/j.energy.2011.03.013>.
- [20] Gutiérrez Ortiz FJ, Ollero P, Serrera A, Galera S. Optimization of power and hydrogen production from glycerol by supercritical water reforming. *Chem Eng J* 2013;218:309–18. <https://doi.org/10.1016/j.cej.2012.12.035>.
- [21] Gutiérrez Ortiz FJ, Serrera A, Galera S, Ollero P. Methanol synthesis from syngas obtained by supercritical water reforming of glycerol. *Fuel* 2013;105:739–51. <https://doi.org/10.1016/j.fuel.2012.09.073>.
- [22] Banuti DT, Raju M, Ma PC, Ihme M, Hickey JP. Seven questions about supercritical fluids – towards a new fluid state diagram. *AIAA SciTech Forum - 55th AIAA Aerosp Sci Meet* 2017:1–15. <https://doi.org/10.2514/6.2017-1106>.
- [23] Gutiérrez Ortiz FJ, Ollero P, Serrera A, Sanz A. Thermodynamic study of the supercritical water reforming of glycerol. *Int J Hydrogen Energy* 2011;36(15):8994–9013. <https://doi.org/10.1016/j.ijhydene.2011.04.095>.
- [24] Okolie JA, Rana R, Nanda S, Dalai AK, Kozinski JA. Supercritical water gasification of biomass: A state-of-the-art review of process parameters, reaction mechanisms and catalysis. *Sustain Energy Fuels* 2019;3(3):578–98. <https://doi.org/10.1039/C8SE00565F>.
- [25] Yildiz Bircan S, Kanamori R, Hasegawa Y, Ohba K, Matsumoto K, Kitagawa K. GC-MS ultra trace analysis of dioxins produced through hydrothermal gasification of biowastes. *Microchem J* 2011;99(2):556–60. <https://doi.org/10.1016/j.microc.2011.07.009>.
- [26] Cao W, Cao C, Guo L, Jin H, Dargusch M, Bernhardt D, et al. Hydrogen production from supercritical water gasification of chicken manure. *Int J Hydrogen Energy* 2016;41(48):22722–31. <https://doi.org/10.1016/j.ijhydene.2016.09.031>.
- [27] Amrullah A, Matsumura Y. Supercritical water gasification of sewage sludge in continuous reactor. *Bioresour Technol* 2018;249:276–83. <https://doi.org/10.1016/j.biortech.2017.10.002>.
- [28] Chen Y, Yi L, Wei W, Jin H, Guo L. Hydrogen production by sewage sludge gasification in supercritical water with high heating rate batch reactor. *Energy* 2022;238:121740. <https://doi.org/10.1016/j.energy.2021.121740>.
- [29] Chen J, Fan Yi, E J, Cao W, Zhang F, Gong J, et al. Effects analysis on the gasification kinetic characteristics of food waste in supercritical water. *Fuel* 2019;241:94–104. <https://doi.org/10.1016/j.fuel.2018.12.012>.
- [30] Nanda S, Isen J, Dalai AK, Kozinski JA. Gasification of fruit wastes and agro-food residues in supercritical water. *Energy Convers Manag* 2016;110:296–306. <https://doi.org/10.1016/j.enconman.2015.11.060>.
- [31] Molino A, Migliori M, Blasi A, Davoli M, Marino T, Chianese S, et al. Municipal waste leachate conversion via catalytic supercritical water gasification process. *Fuel* 2017;206:155–61. <https://doi.org/10.1016/j.fuel.2017.05.091>.
- [32] Yoshida T, Matsumura Y. Gasification of cellulose, xylan, and lignin mixtures in supercritical water. *Ind Eng Chem Res* 2001;40(23):5469–74. <https://doi.org/10.1021/ie0101590>.
- [33] Yoshida T, Oshima Y, Matsumura Y. Gasification of biomass model compounds and real biomass in supercritical water. *Biomass Bioenergy* 2004;26(1):71–8. [https://doi.org/10.1016/S0961-9534\(03\)00063-1](https://doi.org/10.1016/S0961-9534(03)00063-1).
- [34] Goodwin AK, Rorrer GL. Conversion of Xylose and Xylose-Phenol Mixtures to Hydrogen-Rich Gas by Supercritical Water in an Isothermal Microtube Flow Reactor. *Energy Fuels* 2009;23(7):3818–25. <https://doi.org/10.1021/ef900227u>.
- [35] Castello D, Kruse A, Fiori L. Low temperature supercritical water gasification of biomass constituents: Glucose/phenol mixtures. *Biomass Bioenergy* 2015;73:84–94. <https://doi.org/10.1016/j.biombioe.2014.12.010>.
- [36] Güngören Madenoğlu T, Sağlam M, Yüksel M, Ballice L. Hydrothermal gasification of biomass model compounds (cellulose and lignin alkali) and model mixtures. *J Supercrit Fluids* 2016;115:79–85. <https://doi.org/10.1016/j.supflu.2016.04.017>.
- [37] Yan Bo, Wu J, Xie C, He F, Wei C. Supercritical water gasification with Ni/ZrO<sub>2</sub> catalyst for hydrogen production from model wastewater of polyethylene glycol. *J Supercrit Fluids* 2009;50(2):155–61. <https://doi.org/10.1016/j.supflu.2009.04.015>.
- [38] Zhang L, Champagne P, (Charles) Xu C. Supercritical water gasification of an aqueous by-product from biomass hydrothermal liquefaction with novel Ru modified Ni catalysts. *Bioresour Technol* 2011;102(17):8279–87. <https://doi.org/10.1016/j.biortech.2011.06.051>.
- [39] Chen Y, Guo L, Cao W, Jin H, Guo S, Zhang X. Hydrogen production by sewage sludge gasification in supercritical water with a fluidized bed reactor. *Int J Hydrogen Energy* 2013;38(29):12991–9. <https://doi.org/10.1016/j.ijhydene.2013.03.165>.
- [40] Sivasangar S, Zainal Z, Salmiaton A, Taufiq-Yap YH. Supercritical water gasification of empty fruit bunches from oil palm for hydrogen production. *Fuel* 2015;143:563–9. <https://doi.org/10.1016/j.fuel.2014.11.073>.
- [41] Safari F, Salimi M, Tavasoli A, Ateai A. Non-catalytic conversion of wheat straw, walnut shell and almond shell into hydrogen rich gas in supercritical water media. *Chinese J Chem Eng* 2016;24(8):1097–103. <https://doi.org/10.1016/j.cjche.2016.03.002>.
- [42] Elsayed S, Boukis N, Patzelt D, Hindersin S, Kerner M, Sauer J. Gasification of Microalgae Using Supercritical Water and the Potential of Effluent Recycling. *Chem Eng Technol* 2016;39(2):335–42. <https://doi.org/10.1002/ceat.201500146>.
- [43] De Blasio C, De Gisi S, Molino A, Simonetti M, Santarelli M, Björklund-Sänkiahö M. Concerning operational aspects in supercritical water gasification of kraft black liquor. *Renew Energy* 2019;130:891–901. <https://doi.org/10.1016/j.renene.2018.07.004>.
- [44] Salimi M, Nejadi B, Karimi A, Tavasoli A. Hydrothermal gasification performance of Iranian rice straw in supercritical water media for hydrogen-rich gas production. *Bioresour* 2016;11:6362–77. <https://doi.org/10.15376/biores.11.3.6362-6377>.
- [45] Nanda S, Reddy SN, Dalai AK, Kozinski JA. Subcritical and supercritical water gasification of lignocellulosic biomass impregnated with nickel nanocatalyst for hydrogen production. *Int J Hydrogen Energy* 2016;41(9):4907–21. <https://doi.org/10.1016/j.ijhydene.2015.10.060>.
- [46] Castello D, Rolli B, Kruse A, Fiori L. Supercritical water gasification of biomass in a ceramic reactor: Long-time batch experiments. *Energies* 2017;10:1–17. <https://doi.org/10.3390/en1011734>.
- [47] Molino A, Marino T, Larocca V, Casella P, Rimauro J, Cerbone A, et al. Supercritical water gasification of scenedesmus dimorphus  $\mu$ -algae. *Int J Chem React Eng* 2017;15. <https://doi.org/10.1515/ijcre-2016-0218>.
- [48] Samiee-Zafarghandi R, Karimi-Sabet J, Abdoli MA, Karbassi A. Increasing microalgal carbohydrate content for hydrothermal gasification purposes. *Renew Energy* 2018;116:710–9. <https://doi.org/10.1016/j.renene.2017.10.020>.
- [49] Casademont P, Cardozo-Filho L, Meurer E, Sánchez-Oneto J, Portela JR. Gasification of olive oil mill waste by supercritical water in a continuous reactor. *J Supercrit Fluids* 2018;142:10–21. <https://doi.org/10.1016/j.supflu.2018.06.001>.
- [50] Chen Q, Yang J, Jin H, Wang Y. Simultaneous treatment of copper wastewater and biomass waste in supercritical water. *J Supercrit Fluids* 2018;138:143–6. <https://doi.org/10.1016/j.supflu.2018.04.014>.
- [51] Kang K, Azargohar R, Dalai AK, Wang H. Hydrogen production from lignin, cellulose and waste biomass via supercritical water gasification: Catalyst activity and process optimization study. *Energy Convers Manag* 2016;117:528–37. <https://doi.org/10.1016/j.enconman.2016.03.008>.
- [52] Osada M, Sato T, Watanabe M, Adschiri T, Arai K. Low-temperature catalytic gasification of lignin and cellulose with a ruthenium catalyst in supercritical water. *Energy Fuels* 2004;18(2):327–33. <https://doi.org/10.1021/ef034026y>.
- [53] Azadi P, Khan S, Strobel F, Azadi F, Farnood R. Hydrogen production from cellulose, lignin, bark and model carbohydrates in supercritical water using nickel and ruthenium catalysts. *Appl Catal B Environ* 2012;117–118:330–8. <https://doi.org/10.1016/j.apcatb.2012.01.035>.
- [54] Resende FLP, Savage PE. Kinetic model for noncatalytic supercritical water gasification of cellulose and lignin. *AIChE J* 2010;56:2412–20. <https://doi.org/10.1002/aic.12165>.
- [55] Gökçaya DS, Sağlam M, Yüksel M, Madenoğlu TG, Ballice L. Characterization of products evolved from supercritical water gasification of xylose (principal sugar in hemicellulose). *Energy Sources, Part A Recover Util Environ Eff* 2016;38(11):1503–11. <https://doi.org/10.1080/15667036.2014.914109>.
- [56] Lebo, Stuart E. Jr.; Gargulak, Jerry D.; McNally TJ. Lignin 1. Kirk-Othmer Encyclopedia of Chemical Technology. Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc. 2001.
- [57] Rorrer GL, Goodwin A, Paul B. Conversion of glucose to hydrogen gas by supercritical water within a microchannel reactor. *AIChE Annu Meet Conf Proc* 2006:4106–14.
- [58] Zhu C, Guo L, Jin H, Huang J, Li S, Lian X. Effects of reaction time and catalyst on gasification of glucose in supercritical water: Detailed reaction pathway and mechanisms. *Int J Hydrogen Energy* 2016;41(16):6630–9. <https://doi.org/10.1016/j.ijhydene.2016.03.035>.
- [59] Yu-Wu QM, Weiss-Hortala E, Barna R. Hydrothermal conversion of glucose in multiscale batch processes. Analysis of the gas, liquid and solid residues. *J Supercrit Fluids* 2013;79:76–83. <https://doi.org/10.1016/j.supflu.2013.03.003>.
- [60] Nanda S, Reddy SN, Hunter HN, Dalai AK, Kozinski JA. Supercritical water gasification of fructose as a model compound for waste fruits and vegetables. *J Supercrit Fluids* 2015;104:112–21. <https://doi.org/10.1016/j.supflu.2015.05.009>.
- [61] Goodwin AK, Rorrer GL. Reaction rates for supercritical water gasification of xylose in a micro-tubular reactor. *Chem Eng J* 2010;163(1–2):10–21. <https://doi.org/10.1016/j.cej.2010.07.013>.

- [62] Gökkaya DS, Sağlam M, Yuksel M, Ballice L. Hydrothermal gasification of xylose: Effects of reaction temperature, pressure, and K<sub>2</sub>CO<sub>3</sub> as a catalyst on product distribution. *Biomass Bioenergy* 2016;91:26–36. <https://doi.org/10.1016/j.biombioe.2016.04.013>.
- [63] Chalermaktrakul T, Matsumura Y. Effect of Acetic Acid Addition on Decomposition of Xylose in Supercritical Water. *Energy Fuels* 2018;32(2):1754–60. <https://doi.org/10.1021/acs.energyfuels.7b02720>.
- [64] Selvi Gökkaya D, Sağlam M, Yuksel M, Ballice L. Supercritical water gasification of phenol as a model for plant biomass. *Int J Hydrogen Energy* 2015;40(34):11133–9. <https://doi.org/10.1016/j.ijhydene.2015.04.078>.
- [65] Saisu M, Sato T, Watanabe M, Adschiri T, Arai K. Conversion of lignin with supercritical water-phenol mixtures. *Energy Fuels* 2003;17(4):922–8. <https://doi.org/10.1021/ef0202844>.
- [66] DiLeo GJ, Neff ME, Savage PE. Gasification of guaiacol and phenol in supercritical water. *Energy Fuels* 2007;21(4):2340–5. <https://doi.org/10.1021/ef070056f>.
- [67] Changsuwan P, Paksung N, Inoue S, Inoue T, Kawai Y, Noguchi T, et al. Conversion of guaiacol in supercritical water gasification: Detailed effect of feedstock concentration. *J Supercrit Fluids* 2018;142:32–7. <https://doi.org/10.1016/j.supflu.2018.05.024>.
- [68] Youssef EA, Nakhla G, Charpentier PA. Oleic acid gasification over supported metal catalysts in supercritical water: Hydrogen production and product distribution. *Int J Hydrogen Energy* 2011;36:4830–42. <https://doi.org/10.1016/j.ijhydene.2011.01.116>.
- [69] Changi S, Pinnarat T, Savage PE, Taufiq-Yap YH. Modeling hydrolysis and esterification kinetics for biofuel processes. *Ind Eng Chem Res*. 2011;50:3206–11. <https://doi.org/10.1021/ie1023047>.
- [70] Sato N, Quitain AT, Kang K, Daimon H, Fujie K. Reaction Kinetics of Amino Acid Decomposition in High-Temperature and High-Pressure. *Water* 2004;43(13):3217–22. <https://doi.org/10.1021/ie020733n>.
- [71] Samanmulya T, Inoue S, Inoue T, Kawai Y, Kubota H, Munetsuna H, et al. Gasification Characteristics of Amino Acids in Supercritical Water. *J Japan Inst Energy* 2014;93(9):936–43. <https://doi.org/10.3775/jie.93.936>.
- [72] Gutiérrez Ortiz FJ, Serrera A, Galera S, Ollero P. Experimental study of the supercritical water reforming of glycerol without the addition of a catalyst. *Energy* 2013;56:193–206. <https://doi.org/10.1016/j.energy.2013.04.046>.
- [73] Nanda S, Reddy SN, Hunter HN, Butler IS, Kozinski JA. Supercritical Water Gasification of Lactose as a Model Compound for Valorization of Dairy Industry Effluents. *Ind Eng Chem Res* 2015;54(38):9296–306. <https://doi.org/10.1021/acs.iecr.5b02603>.
- [74] Zhang J, Dasgupta A, Chen Z, Xu D, Savage PE, Guo Y. Supercritical water gasification of phenol over Ni-Ru bimetallic catalysts. *Water Res* 2019;152:12–20. <https://doi.org/10.1016/j.watres.2018.12.030>.
- [75] Caputo G, Dispenza M, Rubio P, Scargiali F, Marotta G, Brucato A. Supercritical water gasification of microalgae and their constituents in a continuous reactor. *J Supercrit Fluids* 2016;118:163–70. <https://doi.org/10.1016/j.supflu.2016.08.007>.
- [76] Wang Y, Gao F, Yang J, Zhao G, Fang C, Guo Y, et al. Interactive effects of phenol, naphthalene and acetic acid during the supercritical water gasification process. *Environ Prog Sustain Energy* 2018;37(3):1140–8. <https://doi.org/10.1002/ep.12752>.
- [77] Gutiérrez Ortiz FJ, Campanario FJ, Ollero P. Effect of mixing bio-oil aqueous phase model compounds on hydrogen production in non-catalytic supercritical reforming. *React Chem Eng* 2017;2(5):679–87. <https://doi.org/10.1039/C7RE00090A>.
- [78] Susanti RF, Veriansyah B, Kim J-D, Kim J, Lee Y-W. Continuous supercritical water gasification of isooctane: A promising reactor design. *Int J Hydrogen Energy* 2010;35(5):1957–70. <https://doi.org/10.1016/j.ijhydene.2009.12.157>.
- [79] Therdtianwong S, Srisiriwat N, Therdtianwong A, Croiset E. Hydrogen production from bioethanol reforming in supercritical water. *J Supercrit Fluids* 2011;57(1):58–65. <https://doi.org/10.1016/j.supflu.2011.02.005>.
- [80] Lu Y, Guo L, Ji C, Zhang X, Hao X, Yan Q. Hydrogen production by biomass gasification in supercritical water: A parametric study. *Int J Hydrogen Energy* 2006;31(7):822–31. <https://doi.org/10.1016/j.ijhydene.2005.08.011>.
- [81] Pairojpiriyakul T, Kiatkittipong W, Assabumrungrat S, Croiset E. Hydrogen production from supercritical water reforming of glycerol in an empty Inconel 625 reactor. *Int J Hydrogen Energy* 2014;39(1):159–70. <https://doi.org/10.1016/j.ijhydene.2013.09.148>.
- [82] Su H, Kanchanapit E, Wang D, Zheng R, Huang Z, Chen Y, et al. Production of H<sub>2</sub>-rich syngas from gasification of unsorted food waste in supercritical water. *Waste Manag* 2020;102:520–7. <https://doi.org/10.1016/j.wasman.2019.11.018>.
- [83] Gutiérrez Ortiz FJ, Campanario FJ, Ollero P. Supercritical water reforming of model compounds of bio-oil aqueous phase: Acetic acid, acetol, butanol and glucose. *Chem Eng J* 2016;298:243–58. <https://doi.org/10.1016/j.cej.2016.04.002>.
- [84] Campanario FJ, Gutiérrez Ortiz FJ. Techno-economic assessment of bio-oil aqueous phase-to-liquids via Fischer-Tropsch synthesis and based on supercritical water reforming. *Energy Convers Manag* 2017;154:591–602. <https://doi.org/10.1016/j.enconman.2017.10.096>.
- [85] Gadhe J, Gupta R. Hydrogen production by methanol reforming in supercritical water: Catalysis by in-situ-generated copper nanoparticles. *Int J Hydrogen Energy* 2007;32(13):2374–81. <https://doi.org/10.1016/j.ijhydene.2006.10.050>.
- [86] Elif D, Nezihe A. Hydrogen production by supercritical water gasification of fruit pulp in the presence of Ru/C. *Int J Hydrogen Energy* 2016;41(19):8073–83. <https://doi.org/10.1016/j.ijhydene.2015.12.005>.
- [87] Kumar A, Reddy SN. In Situ Sub- and Supercritical Water Gasification of Nano-Nickel (Ni<sub>2</sub><sup>+</sup>) Impregnated Biomass for H<sub>2</sub> Production. *Ind Eng Chem Res* 2019;58(12):4780–93. <https://doi.org/10.1021/acs.iecr.9b00425>.
- [88] Byrd AJ, Pant KK, Gupta RB. Hydrogen production from ethanol by reforming in supercritical water using Ru/Al<sub>2</sub>O<sub>3</sub> catalyst. *Energy Fuels* 2007;21(6):3541–7. <https://doi.org/10.1021/ef700269z>.
- [89] Hendry D, Venkatasamy C, Wilkinson N, Jacoby W. Exploration of the effect of process variables on the production of high-value fuel gas from glucose via supercritical water gasification. *Bioresour Technol* 2011;102(3):3480–7. <https://doi.org/10.1016/j.biortech.2010.11.003>.
- [90] Sasaki M, Adschiri T, Arai K. Kinetics of Cellulose Conversion at 25 MPa in Sub- and Supercritical Water. *AIChE J* 2004;50(1):192–202. <https://doi.org/10.1002/aic.10018>.
- [91] Yong TLK, Matsumura Y. Kinetics analysis of phenol and benzene decomposition in supercritical water. *J Supercrit Fluids* 2014;87:73–82. <https://doi.org/10.1016/j.supflu.2013.12.018>.
- [92] Huelsman CM, Savage PE. Intermediates and kinetics for phenol gasification in supercritical water. *Phys Chem Chem Phys* 2012;14:2900–10. <https://doi.org/10.1039/c2cp23910h>.
- [93] Aida TM, Shiraishi N, Kubo M, Watanabe M, Smith RL. Reaction kinetics of d-xylose in sub- and supercritical water. *J Supercrit Fluids* 2010;55(1):208–16. <https://doi.org/10.1016/j.supflu.2010.08.013>.
- [94] Bühler W, Dinjus E, Ederer HJ, Kruse A, Mas C. Ionic reactions and pyrolysis of glycerol as competing reaction pathways in near- and supercritical water. *J Supercrit Fluids* 2002;22(1):37–53. [https://doi.org/10.1016/S0896-8446\(01\)00105-X](https://doi.org/10.1016/S0896-8446(01)00105-X).
- [95] Kruse A, Dinjus E. Hot compressed water as reaction medium and reactant. Properties and synthesis reactions. *J Supercrit Fluids* 2007;39(3):362–80. <https://doi.org/10.1016/j.supflu.2006.03.016>.
- [96] Zhu C, Guo L, Jin H, Ou Z, Wei W, Huang J. Gasification of guaiacol in supercritical water: Detailed reaction pathway and mechanisms. *Int J Hydrogen Energy* 2018;43(31):14078–86. <https://doi.org/10.1016/j.ijhydene.2018.05.136>.
- [97] Tau Len-Kelly Y, Matsumura Y. Kinetic analysis of guaiacol conversion in sub- and supercritical water. *Ind Eng Chem Res* 2013;52(26):9048–59. <https://doi.org/10.1021/ie4009748>.
- [98] Samanmulya T, Farobie O, Matsumura Y. Gasification characteristics of histidine and 4-methylimidazole under supercritical water conditions. *Biomass Convers Biorefinery* 2017;7(4):487–94. <https://doi.org/10.1007/s13399-017-0242-1>.
- [99] Samanmulya T, Farobie O, Matsumura Y. Gasification characteristics of aminobutyric acid and serine as model compounds of proteins under supercritical water conditions. *J Japan Pet Inst* 2017;60:34–40. <https://doi.org/10.1627/jpi.60.34>.
- [100] Tolonen LK, Juvonen M, Niemelä K, Mikkelsen A, Tenkanen M, Sixta H. Supercritical water treatment for cello-oligosaccharide production from microcrystalline cellulose. *Carbohydr Res* 2015;401:16–23. <https://doi.org/10.1016/j.carres.2014.10.012>.
- [101] Forchheim D, Hornung U, Kempe P, Kruse A, Steinbach D. Influence of RANEY Nickel on the formation of intermediates in the degradation of lignin. *Int J Chem Eng* 2012;2012:1–8. <https://doi.org/10.1155/2012/589749>.
- [102] Khorasani R, Khodaparasti MS, Tavakoli O. Hydrogen production from dairy wastewater using catalytic supercritical water gasification: Mechanism and reaction pathway. *Int J Hydrogen Energy* 2021;46(43):22368–84. <https://doi.org/10.1016/j.ijhydene.2021.04.089>.
- [103] Behnia I, Yuan Z, Charpentier P, Xu C. Production of methane and hydrogen via supercritical water gasification of renewable glucose at a relatively low temperature: Effects of metal catalysts and supports. *Fuel Process Technol* 2016;143:27–34. <https://doi.org/10.1016/j.fuproc.2015.11.006>.
- [104] Gutiérrez Ortiz FJ, Campanario FJ, Aguilera PG, Ollero P. Supercritical water reforming of glycerol: Performance of Ru and Ni catalysts on Al<sub>2</sub>O<sub>3</sub> support. *Energy* 2016;96:561–8. <https://doi.org/10.1016/j.energy.2015.12.090>.
- [105] Remón J, Arcelus-Arriaga P, García L, Arauzo J. Simultaneous production of gaseous and liquid biofuels from the synergetic co-valorisation of bio-oil and crude glycerol in supercritical water. *Appl Energy* 2018;228:2275–87. <https://doi.org/10.1016/j.apenergy.2018.07.093>.
- [106] Shan Y-Q, Yin L-X, Djandja OS, Wang Z-C, Duan P-G. Supercritical water gasification of waste water produced from hydrothermal liquefaction of microalgae over Ru catalyst for production of H<sub>2</sub> rich gas fuel. *Fuel* 2021;292:120288. <https://doi.org/10.1016/j.fuel.2021.120288>.
- [107] Gökkaya DS, Akgül G, Sağlam M, Yuksel M, Ballice L. Supercritical conversion of wastes from wine industry: Effects of concentration, temperature and group 1A carbonates. *J Supercrit Fluids* 2021;176:105319. <https://doi.org/10.1016/j.supflu.2021.105319>.
- [108] Nanda S, Dalai AK, Gökalp I, Kozinski JA. Valorization of horse manure through catalytic supercritical water gasification. *Waste Manag* 2016;52:147–58. <https://doi.org/10.1016/j.wasman.2016.03.049>.
- [109] Byrd AJ, Pant KK, Gupta RB. Hydrogen production from glucose using Ru/Al<sub>2</sub>O<sub>3</sub> catalyst in supercritical water. *AIChE Annu Meet* 2007;46(11):3574–9.
- [110] Byrd A, Pant K, Gupta R. Hydrogen production from glycerol by reforming in supercritical water over Ru/Al<sub>2</sub>O<sub>3</sub> catalyst. *Fuel* 2008;87(13-14):2956–60. <https://doi.org/10.1016/j.fuel.2008.04.024>.
- [111] Tushar MSHK, Dutta A, Xu C. Simulation and kinetic modeling of supercritical water gasification of biomass. *Int J Hydrogen Energy* 2015;40(13):4481–93. <https://doi.org/10.1016/j.ijhydene.2015.02.033>.
- [112] Gutiérrez Ortiz FJ, Campanario FJ, Ollero P. Turnover rates for the supercritical water reforming of glycerol on supported Ni and Ru catalysts. *Fuel* 2016;180:417–23. <https://doi.org/10.1016/j.fuel.2016.04.065>.

- [113] Yang M, Zhang J, Guo Y. Supercritical water gasification of phenol over Ni-Ru bimetallic catalyst: Intermediates and kinetics. *J Supercrit Fluids* 2020;160:104810. <https://doi.org/10.1016/j.supflu.2020.104810>.
- [114] The William H. Green research group at M. Reaction Mechanism Generator -RMG 2013;26. <https://rmg.mit.edu/>.
- [115] Gao CW, Allen JW, Green WH, West RH. Reaction Mechanism Generator : Automatic construction of chemical. *Comput Phys Commun* 2016;203:212–25. <https://doi.org/10.1016/j.cpc.2016.02.013>.
- [116] Liu M, Grinberg Dana A, Johnson MS, Goldman MJ, Jocher A, Payne AM, et al. Reaction Mechanism Generator v3.0. *Advances in Automatic Mechanism Generation* 2021;61(6):2686–96. <https://doi.org/10.1021/acs.jcim.0c01480>.
- [117] Kang J, Sim S, Jung H, Han B, Lee Y-W. Desulfurization of hexyl sulfide and hexanethiol using supercritical water. *J Supercrit Fluids* 2020;158:104734. <https://doi.org/10.1016/j.supflu.2019.104734>.
- [118] Burke K. Perspective on density functional theory. *J. Chem. Phys.* 2012;136(15):150901. <https://doi.org/10.1063/1.4704546>.
- [119] Chen J, Liang J, Xu Z, E J. Assessment of supercritical water gasification process for combustible gas production from thermodynamic, environmental and techno-economic perspectives: A review. *Energy Convers Manag* 2020;226:113497. <https://doi.org/10.1016/j.enconman.2020.113497>.
- [120] Okolie JA, Epelle EI, Nanda S, Castello D, Dalai AK, Kozinski JA. Modeling and process optimization of hydrothermal gasification for hydrogen production: A comprehensive review. *J Supercrit Fluids* 2021;173:105199. <https://doi.org/10.1016/j.supflu.2021.105199>.
- [121] Holderbaum T, Gmehling J. PSRK: A Group Contribution Equation of State Based on UNIFAC. *Fluid Phase Equilib* 1991;70(2-3):251–65. [https://doi.org/10.1016/0378-3812\(91\)85038-V](https://doi.org/10.1016/0378-3812(91)85038-V).
- [122] Withag JAM, Smeets JR, Bramer EA, Brem G. System model for gasification of biomass model compounds in supercritical water – A thermodynamic analysis. *J Supercrit Fluids* 2012;61:157–66. <https://doi.org/10.1016/j.supflu.2011.10.012>.
- [123] Campanario FJ, Gutiérrez Ortiz FJ. Fischer-Tropsch biofuels production from syngas obtained by supercritical water reforming of the bio-oil aqueous phase. *Energy Convers Manag* 2017;150:599–613. <https://doi.org/10.1016/j.enconman.2017.08.053>.
- [124] Gutiérrez Ortiz FJ, Kruse A, Ramos F, Ollero P. Integral energy valorization of municipal solid waste reject fraction to biofuels. *Energy Convers Manag* 2019;180:1167–84. <https://doi.org/10.1016/j.enconman.2018.10.085>.
- [125] Onigbajumo A, Taghipour A, Ramirez J, Will G, Ong T-C, Couperthwaite S, et al. Techno-economic assessment of solar thermal and alternative energy integration in supercritical water gasification of microalgae. *Energy Convers Manag* 2021;230:113807. <https://doi.org/10.1016/j.enconman.2020.113807>.
- [126] Rahbari A, Shirazi A, Venkataraman MB, Pye J. A solar fuel plant via supercritical water gasification integrated with Fischer-Tropsch synthesis: Steady-state modelling and techno-economic assessment. *Energy Convers Manag* 2019;184:636–48. <https://doi.org/10.1016/j.enconman.2019.01.033>.
- [127] Azadi P. An integrated approach for the production of hydrogen and methane by catalytic hydrothermal glycerol reforming coupled with parabolic trough solar thermal collectors 2012;7.
- [128] Wongsakulphasatch S, Kiatkittipong W, Assabumrungrat S. Comparative study of fuel gas production for SOFC from steam and supercritical-water reforming of bioethanol. *Int J Hydrogen Energy* 2013;38(14):5555–62. <https://doi.org/10.1016/j.ijhydene.2013.02.125>.
- [129] Louw J, Schwarz CE, Knoetze JH, Burger AJ. Thermodynamic modelling of supercritical water gasification: Investigating the effect of biomass composition to aid in the selection of appropriate feedstock material. *Bioresour Technol* 2014;174:11–23. <https://doi.org/10.1016/j.biortech.2014.09.129>.
- [130] Hantoko D, Su H, Yan Mi, Kanchanapit E, Susanto H, Wang G, et al. Thermodynamic study on the integrated supercritical water gasification with reforming process for hydrogen production: Effects of operating parameters. *Int J Hydrogen Energy* 2018;43(37):17620–32. <https://doi.org/10.1016/j.ijhydene.2018.07.198>.
- [131] Kumar M, Oyedun AO, Kumar A. A comparative analysis of hydrogen production from the thermochemical conversion of algal biomass. *Int J Hydrogen Energy* 2019;44(21):10384–97. <https://doi.org/10.1016/j.ijhydene.2019.02.220>.
- [132] Serrera A, Gutiérrez Ortiz FJ, Ollero P. Syngas methanation from the supercritical water reforming of glycerol. *Energy* 2014;76:584–92. <https://doi.org/10.1016/j.energy.2014.08.056>.
- [133] Salemm L, Simeone M, Chiron R, Salatino P. Analysis of the energy efficiency of solar aided biomass gasification for pure hydrogen production. *Int J Hydrogen Energy* 2014;39(27):14622–32. <https://doi.org/10.1016/j.ijhydene.2014.07.041>.
- [134] Gutiérrez Ortiz FJ, Ollero P, Serrera A, Galera S. Autothermal reforming of glycerol with supercritical water for maximum power through a turbine plus a fuel cell. *Energy Fuels* 2013;27(1):576–87. <https://doi.org/10.1021/ef301509n>.
- [135] Darmawan A, Ajiwibowo MW, Biddinika MK, Tokimatsu K, Aziz M. Black liquor-based hydrogen and power co-production: Combination of supercritical water gasification and syngas chemical looping. *Appl Energy* 2019;252:4–6. <https://doi.org/10.1016/j.apenergy.2019.113446>.
- [136] Özdenççi K, De Blasio C, Sarwar G, Melin K, Koskinen J, Alopaeus V. Techno-economic feasibility of supercritical water gasification of black liquor. *Energy* 2019;189:116284. <https://doi.org/10.1016/j.energy.2019.116284>.
- [137] Okolie JA, Nanda S, Dalai AK, Kozinski JA. Techno-economic evaluation and sensitivity analysis of a conceptual design for supercritical water gasification of soybean straw to produce hydrogen. *Bioresour Technol* 2021;331:125005. <https://doi.org/10.1016/j.biortech.2021.125005>.
- [138] Hantoko D, Yan Mi, Kanchanapit E, Adnan MA, Antoni, Mubeen I, et al. Supercritical water gasification of sewage sludge and combined cycle for H2 and power production – A thermodynamic study. *Int J Hydrogen Energy* 2019;44(45):24459–70. <https://doi.org/10.1016/j.ijhydene.2019.07.210>.
- [139] Ren C, Guo S, Wang Yu, Liu S, Du M, Chen Y, et al. Thermodynamic analysis and optimization of auto-thermal supercritical water gasification polygeneration system of pig manure. *Chem Eng J* 2022;427:131938. <https://doi.org/10.1016/j.cej.2021.131938>.
- [140] Ruya PM, Lim SS, Purwadi R, Zunita M. Sustainable hydrogen production from oil palm derived wastes through autothermal operation of supercritical water gasification system. *Energy* 2020;208:118280. <https://doi.org/10.1016/j.energy.2020.118280>.
- [141] Gerber Van Doren L, Posmanik R, Bicalho FA, Tester JW, Sills DL. Prospects for energy recovery during hydrothermal and biological processing of waste biomass. *Bioresour Technol* 2017;225:67–74. <https://doi.org/10.1016/j.biortech.2016.11.030>.
- [142] Gasafi E, Reinecke M-Y, Kruse A, Schebek L. Economic analysis of sewage sludge gasification in supercritical water for hydrogen production. *Biomass Bioenergy* 2008;32(12):1085–96. <https://doi.org/10.1016/j.biombioe.2008.02.021>.
- [143] Pellegrini LA, Lange S, Chimica D, Chimica I, Natta G, Milano P. Economic analysis of a combined production of hydrogen-energy from empty fruit bunches 2013;9. <https://doi.org/10.1016/j.biombioe.2013.08.039>.
- [144] Galera S, Gutiérrez Ortiz FJ. Techno-economic assessment of hydrogen and power production from supercritical water reforming of glycerol. *Fuel* 2015;96:637–45. <https://doi.org/10.1016/j.fuel.2014.12.033>.
- [145] Galera S, Gutiérrez Ortiz FJ. Life cycle assessment of hydrogen and power production by supercritical water reforming of glycerol. *Energy Convers Manag* 2015;96:637–45. <https://doi.org/10.1016/j.enconman.2015.03.031>.
- [146] Barros TV, Carregosa JdC, Wisniewski Jr A, Freitas ACD, Guirardello R, Ferreira-Pinto L, et al. Assessment of black liquor hydrothermal treatment under sub- and supercritical conditions: Products distribution and economic perspectives. *Chemosphere* 2022;286:131774. <https://doi.org/10.1016/j.chemosphere.2021.131774>.
- [147] Do TX, Mujahid R, Lim HS, Kim JK, Il LY, Kim J. Techno-economic analysis of bio heavy-oil production from sewage sludge using supercritical and subcritical water. *Renew. Energy* 2020;151:30–42. <https://doi.org/10.1016/j.renene.2019.10.138>.
- [148] Gutiérrez Ortiz FJ, Alonso-Fariñas B, Campanario FJ, Kruse A. Life cycle assessment of the Fischer-Tropsch biofuels production by supercritical water reforming of the bio-oil aqueous phase. *Energy* 2020;210:118648. <https://doi.org/10.1016/j.energy.2020.118648>.
- [149] ISO 14044. Environmental management – life cycle assessment – requirements and guidelines. *Int Organ Stand Geneva* 2006. <https://www.iso.org/standard/> (accessed July 14, 2020).
- [150] Rahbari A, Shirazi A, Venkataraman MB, Pye J. Solar fuels from supercritical water gasification of algae: Impacts of low-cost hydrogen on reformer configurations. *Appl Energy* 2021;288:116620. <https://doi.org/10.1016/j.apenergy.2021.116620>.
- [151] Gemechu ED, Kumar A. The environmental performance of hydrogen production pathways based on renewable sources. *INC* 2021. <https://doi.org/10.1016/b978-0-12-820539-6.00012-1>.
- [152] Cocero MJ. Supercritical water processes : Future prospects 2018;134:124–32. <https://doi.org/10.1016/j.supflu.2017.11.018>.
- [153] Turton R, Shaiwitz JA, Bhattacharyya D. *Analysis, Synthesis, and Design of Chemical Processes. Fifth Edition.* Prentice-Hall; 2018.
- [154] Elliott DC, Neuenschwander GG, Hart TR. Combined hydrothermal liquefaction and catalytic hydrothermal gasification system and process for conversion of biomass feedstocks. *US Patent* 9758728, 2013.