



# **Functional Materials for Waste-to-Energy Processes in Supercritical Water**

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**Abstract:** In response to increasing energy demand, various types of organic wastes, including industrial and municipal wastewaters, or biomass wastes, are considered reliable energy sources. Wastes are now treated in supercritical water (SCW) for non-fossil fuel production and energy recovery. Considering that SCW technologies are green and energetically effective, to implement them on a large scale is a worldwide interest. However, issues related to the stability and functionality of materials used in the harsh conditions of SCW reactors still need to be addressed. Here we present an overview on materials used in the SCW technologies for energy harvesting from wastes. There are catalysts based on metals or metal oxides, and we discuss on these materials' efficiency and selectivity in SCW conditions. We focus on processes relevant to the waste-to-energy field, such as supercritical water gasification (SCWG) and supercritical water oxidation (SCWO). We discuss the results reported, mainly in the last decades in connection to the current concept of supercritical pseudo-boiling (PB), a phenomenon occurring at the phase change from liquid-like (LL) to gas-like (GL) state of a fluid. This review aims to be a useful database that provides guidelines for the selection of the abovementioned functional materials (catalysts, catalysts supports, and sorbents) for the SCW process, starting from wastes and ending with energy-relevant products.

**Keywords:** supercritical water; waste treatment; supercritical water gasification; supercritical water oxidation; metal catalysts; metal oxides catalysts

# 1. Introduction

Waste is a material or a good that has reached the end of its life cycle, lost its economic value, and the function it had for the owner, and has become a source of pollution. It is obvious that for a sustainable waste management, all three aspects, economic, social, and environmental, should be addressed (see Introduction in [1]). For this, issues related to the generation, separation, collection, treatment, recycling and reuse, and final disposal of various types of wastes must be taken into account by stakeholders and decision makers [2]. In Europe, the waste management aims to be in line with the waste hierarchy, which prioritizes waste prevention, followed by preparing for reuse, recycling, other recovery and finally disposal as the least desirable option. Within the context of a circular economy [3], waste management focuses on promoting waste treatment options able to preserve the value and properties of waste materials by delivering high quality secondary raw materials to the economy [4].

The treatment in supercritical water of wastes is nowadays one of the most efficient options to obtain energy-relevant products and valuable compounds through recycling or recovery. For instance, chemical recycling of plastic wastes, with high conversion of



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**Copyright:** © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). polymers into their monomers, is done in supercritical water through a rapid, selective, clean and efficient process, useful for processing technically difficult wastes [5–10]. At the industrial scale, there are already companies exploring the chemical recycling of mixed waste plastic feedstock using supercritical water, as for example ReNewELP [9]. Their motto is: "We achieve in just 20 min what takes nature 200 million years: turning waste plastic into readily usable hydrocarbon feedstock" (https://renewelp.co.uk/technology/accessed on 22 September 2021). Electronic and electrical wastes (e-waste) can be treated in supercritical fluids for a high recovery rate of metals through environmentally friendly, highly efficient and effective oxidation and extraction processes [11]. For example, Cu and Pb were recovered from e-waste with an efficiency of 99.8% and 80%, respectively, while up to 90% of Sn, Zn, Cr, Cd, and Mn could be recovered if the e-waste was pre-treated in supercritical water [12].

Proposed initially at the Massachusetts Institute of Technology (MIT) in the 80s, for use on NASA's space facilities, the MODAR process was developed for the treatment of human wastes by oxidation in supercritical water [13], showing the capability of achieving high destruction efficiencies of hazardous organic constituents in a single step [14]. A similar project is supported by the European Space Agency, under the name MELiSSA (Micro-Ecological Life Support System Alternative). The MELiSSA project aims to fully recycle all the solid organic wastes generated in space, such as human waste, food waste, and non-edible parts of plants, using supercritical water as the reaction medium [15].

In the early 2000s, at the Karlsruhe Institute of Technology, the first dedicated pilot plant for the treatment of agricultural wastes started to demonstrate its capability for gasification of wet biomass under the conditions of supercritical water. Its name is VERENA (acronym for the German expression "experimental facility for the energetic exploitation of agricultural matter"), and it is based on allothermal, continuous flow process using supercritical water as a solvent for the conversion of organic matter into combustible gas [16].

At the Paul Scherrer Institute (PSI), around 2008, the SunCHem process for the production of bio-methane via continuous catalytic SCW gasification of microalgae was proposed [17,18]. Microalgae are a promising bio-resource since they do not compete with food crops and show higher photosynthetic efficiency and biomass production rates compared to terrestrial plants. The SunCHem process is a closed-loop system in which all the liquid (rich in nutrients) and gaseous effluents after the SCW gasification are recycled into the photo-bioreactor. Based on this process, the dedicated mobile gasification plant, KONTI-C, is now part of the Energy System Integration or ESI Platform at the PSI, a platform that offers suitable infrastructure to test energy production from biomass (biowaste) in all its various configurations (https://www.psi.ch/en/media/esi-platform accessed on 22 September 2021).

The aforementioned processes are possible due to the unique thermodynamic, transport and solvent properties of water above its critical point ( $T > T_{cr} = 647$  K,  $p > p_{cr} = 221$  bar). With the knowledge delivered through the fundamental research in the field of supercritical fluids, it is now possible to finely tune the properties of water for the optimization of the operating parameters of SCW reactors. As an example, at 230 bar and in a temperature interval of about 6 K, the water density drops by a factor of three, the specific enthalpy increases ~500 J kg<sup>-1</sup> [19], the self-diffusion coefficient doubles, and the dielectric constant drops to a half [20].

Two processes that occur in SCW are the most relevant for energy harvesting and/or recovery from the waste sources: gasification and oxidation. The main benefit of the gasification in SCW is that the energy-consuming drying pre-treatment of the organic feedstock is omitted when using water as solvent [21]. Oxidation under SCW conditions has the main advantage over classical wet oxidation of decreasing reaction time, as complete destruction of the organic compounds can be achieved in seconds [22]. Although considered a clean and efficient processes, the main obstacle to implementing SCW technologies at large industrial scale is the high operating cost coming from the necessity to work under high

temperature and high pressure conditions, and from the technical challenges related to corrosion and salt deposition causing the plugging of pipes in SCW plants. Decreasing the temperature of the SCW process, shortening the reaction time to avoid corrosion and developing reliable methods for salt separation and removal from the SCW streams are the solutions to overcome this obstacle.

Materials employed in the SCW processes as catalysts allow cost-efficient operation of SCW reactors at lower temperatures, shorten the reaction time by increasing the process rates, and suppress the formation of by-products while enhancing the selectivity to the specific reactions and products with desirable properties, as for example the elemental composition and the heating value of the combustible gases/fuels. For example, the SCW reforming of glycerol to produce H<sub>2</sub>-rich combustible gas can be performed at 923 K when using Ni-based catalyst [23] comparing to a reaction temperature of 1073 K for the non-catalytic process [24]. Moreover, the CO<sub>2</sub> molar yields reached 100% when the SCWO of phenol, a toxic compound found in the wastewaters, was performed in the presence of a commercial catalyst named CARULITE (MnO<sub>2</sub> + CuO on Al<sub>2</sub>O<sub>3</sub>) compared to CO<sub>2</sub> yields of no more than 10% when the reaction is non-catalytic [25].

Heterogeneous as well as homogenous catalysis in SCW are presented as strategies to reduce the high operation cost as main problem in the development of SCW technologies. The main advantage of heterogeneous catalysis in SCW is related to the ability to recover and reuse the catalyst, as the recyclability of homogeneous catalysts is still an issue to be investigated. However, the heterogeneous catalysts' deactivation by sintering and poisoning due to the presence of sulfur, nitrogen, or coke is still a big challenge [26]. For instance, only a few ppm of sulfur could deactivate the Ru-based catalyst used to obtain CH<sub>4</sub>-rich combustible gas by SCWG of lignin [27] and microalgae [17]. Commercial ZnO sorbent material has been used for sulfur removal with good performance under SCW conditions [28].

Screening the literature, we found many studies reporting results on catalysis under SCW conditions. Over the years, the major findings of these studies have been summarized and presented as reviews. Catalytic hydrothermal gasification was overviewed in [26,29–33], while the catalytic oxidation in SCW was reviewed in [34,35].

In the present review, we focus on the role of functional materials (catalysts, sorbents, and supports) in the SCW processes starting from wastes and ending with energy-relevant products. First, we start by summarizing the main findings of fundamental research on the structure and thermodynamics of water above the critical point and the water properties' effects on the performance of SCW processes. In the second part, we give a few details about gasification and oxidation in SCW. The final part is dedicated to overview the main studies reporting results on metal and metal oxides used as active materials for catalysis or adsorption in SCWG and SCWO.

#### 2. Supercritical Water as Reaction Medium

First, it is important to note that, when issues related to the fundamental research on supercritical water are discussed, the acronym used is  $scH_2O$  [19,36], instead of the abbreviation SCW, which is mostly used when referring to the applications of water in supercritical conditions. For being consistent, the abbreviation SCW is used in this review.

Water above the critical point has been described in textbooks as a single phase of a fluid with properties highly sensitive to pressure. During isobaric heating, while the density of SCW decreases, the features of the solution change from those of an aqueous solution to those of a non-aqueous solution and eventually to a gaseous solution. In consequence, it is expected that the reaction mechanisms change from those involving ions to those involving radicals [36] (p. 120).

The supercritical region in the phase diagram of a fluid is divided into two different regimes, the liquid-like (LL) and the gas-like (GL), by the transitional lines most frequently named Frenkel and Widom [37–40]. The transition at the Frenkel line is dynamic, and across this line the LL and GL phases are different in terms of diffusion mechanisms [38,41]. Across

the Widom line (or Nishikawa's ridge [42,43]) the transition is purely thermodynamic, and relates to the thermodynamic anomalies in the fluid's critical behavior. For instance, various thermodynamic quantities, such as the heat capacity, compressibility coefficient, thermal expansion coefficient, and the density fluctuations go through maxima upon varying pressure or temperature. The locations of those maxima form a whole set of 'lines of maxima' in the supercritical region and all these lines merge asymptotically into a single line when approaching the critical point [38]. In particular, the Widom line depends on the used quantity and has an upper pressure limit between 3 and 10 times higher than the critical pressure [44].

Across the Widom line at which is located the maxima of isobaric heat capacity, the phenomenon of supercritical pseudo-boiling (PB) occurs when the fluid changes its state from LL to GL phase [45]. Therefore, this transitional line is referred to as PB-Widom line [19]. The PB transition obeys similar laws to sub-critical boiling [46] having associated with it a large heat capacity and a steep decay in fluid's density. However, the PB is a continuous transition, happening at a finite temperature interval in which the energy supplied to the system is used to both increase the temperature of the fluid and change its structure from LL to GL states [45]. It was demonstrated that, during isobaric heating in the supercritical region closed to the critical point, while the water density drops by a factor of three in the PB transitional region, the system needs more than 16 times less energy to increase its temperature by 1 K than to overcome the molecular attractions at the structural change from LL to GL phase [19].

In Figure 1 we present the water density variation in the supercritical region, along isobars and in the temperature interval from 600 to 800 K that includes the PB transitional region. We use the density values reported in the NIST database [47]. It is to note in Figure 1, that the density decay within the PB region is smothering as the pressure increases. Additionally, Figure 1 shows how the water density varies along the PB-Widom line (red line) that is determined based on Banuti's theory of PB [45] and using NIST reference data for water heat capacity [47] (see Experimental section in [19]). It can be seen that the water density value at the PB-Widom line increases as pressure increase, however, it is always close to the critical density of 322 kg m<sup>-3</sup>. It is important to remember that water has LL densities above the PB-Widom line, while below this line, GL water density values are recorded [19].



**Figure 1.** Water density variation with temperature along isobars in the PB region; the red line corresponds to the density values at the PB-Widom line calculated based on Banuti's theory [45]; Water's density values on the blue curves have been obtained from publicly available NIST database at https://webbook.nist.gov/chemistry/fluid (last accessed on 28 October 2021).

Maxim et al. studied the PB phenomenon by neutron imaging [19,48], which is a sensitive experimental technique for water density analysis. Results presented in [48] are the first reporting on the experimental visualization of SCW pseudo-boiling, providing

evidence of how the system evolves rapidly from the LL to the GL phase of water as the PB-Widom line is crossed during isobaric heating. Moreover, it is shown from the reported neutron imaging density maps that the LL and GL states can be identified macroscopically when SCW interacts with microporous carbon with a monolithic structure [48]. The main results of this study are presented as a summary in Figure 2 that shows the water density fluctuations in the presence of carbon porous monolith when the SCW reactor is heated at 225 bar. It is visible that the LL and GL phases can be separated at the time of PB. Moreover, in a temperature range of a few K, which is the PB region, the density of water changes from LL values, of about 650 kg m<sup>-3</sup>, to values for GL close to 150 kg m<sup>-3</sup> [48].



**Figure 2.** Water density fluctuations in the presence of carbon porous monolith; from left to right: the carbon monolith inside the SCW reactor, the color scaled water density map and the density variation over time; it is visible the LL/GL phase separation at the time of PB (adapted from [48]).

The findings reported in studies by Maxim et al. [19,48] are very important as they managed to finely tune the properties of water, which is of great interest for the optimization of SCW reactors' operating parameters. Water properties strongly affect the reaction rates and selectivity of the organic reactions in SCW. For example, it is reported that the catalytic gasification of lignin is enhanced at 673 K by the increase in water density. After 180 min, the total gas yield reaches 100% when the water density is above 330 kg m<sup>-3</sup> (LL SCW), compared to only 60–70% when the water density is below 200 kg m<sup>-3</sup>, although the composition of the gas product is independent of the SCW density [49]. At a water density of 330 kg m<sup>-3</sup> (the value at the PB-Widom line), and at 673 K, after 15 min of reaction over the catalyst, the carbon yield of the gas products from sugarcane bagasse, cellulose, and lignin was 50.3, 74.4, and 31.1 C %, respectively [50]. The amount of sulfur that remained on the catalyst surface after gasification of lignin at 673 K for 180 min decreased with increasing water density from 500 kg m<sup>-3</sup> to 650 kg m<sup>-3</sup> [27]. In the case of catalytic gasification of alkylphenols as lignin model compounds at 673 K, for 15 min, the ratio of methane increased with increasing water density in the GL region, from 100 to 300 kg m<sup>-3</sup> [51]. The water density significantly affects the carbon gasification efficiency of catalytic SCWG at 873 K with wastewater obtained from the hydrothermal liquefaction of microalgae. It is reported that by increasing the density from 107 kg m<sup>-3</sup> to 263 kg m<sup>-3</sup>, the carbon gasification efficiency increased from 25.43% to 97.63%, respectively. The authors claim that the release of more  $H\bullet$  and  $OH\bullet$  radicals over the Ru/C catalyst with the water density increase, provides a more effective medium for the decomposition of the organic matter [52]. The acid catalytic properties of metal oxides in SCW depend on the water properties. At 673 K, it was found that the water density has two different effects on model organic reactions rates catalyzed by TiO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub>, and NbO<sub>X</sub>/TiO<sub>2</sub>. One is a suppression effect with increasing water density from 167 kg m<sup>-3</sup> to 626 kg m<sup>-3</sup> caused by competitive adsorption between water and the reactants on acid sites. The other is a promotion effect of Brønsted acidity with increasing water density caused by water dissociation on acid sites due to a large ionic product of water [53]. Screening the literature reporting results on

SCWO, it is notable that the oxidation in SCW is mainly performed in the GL region, with water densities lower than 200 kg m<sup>-3</sup> [54].

### 3. Supercritical Water Processes Relevant for Waste Treatment

As stated above, gasification and oxidation performed in water under supercritical conditions are the most applicable processes for waste treatment.

A system working under SCW conditions can be operated only in batches at the lab-scale, or in continuous/plug flow mode, applicable at both lab-scale and at pilot or industrial plants. The advantage of the flow systems over batch processing is the possibility to include engineered mixers for the water and feedstock streams. Comparative studies of waste SCWO experiments have revealed that continuous flow reactors outperform batch reactors in terms of treatment capacity, waste destruction efficiency and reproducibility [15,55].

Schematically, a continuous SCW system can be presented as containing six main sections (Figure 3): (1) feeding, (2) pressurization/depressurization, (3) heating/heat exchange/heat recovery, (4) reactor, (5) phase separation, (6) sampling and characterization.



Figure 3. Schematic representation of a continuous flow SCW system.

In the first three sections the operating parameters, such as feed concentration, time, pressure, and temperature are established. The flow rate is an important parameter to be set in the feeding section. Based on the amount of feedstock, water and the flow rate, the time parameter is established and is reported as reaction time, residence time, space time or contact time. The pressure inside the batch reactor is auto generated and can be estimated based on pressure-volume-temperature relations [56] taking into account the operating temperature and the reactor's degree of filling [5]. In continuous flow systems pressure control and depressurization are ensured by a back-pressure regulator valve, as for example in SCWG [57], or in SCWO [58–60]. The fourth part, the reactor, is the main component of the SCW system. Reactors must be made of materials able to withstand the high-temperature and high-pressure conditions and to be corrosive resistant. The materials used for SCW systems' reactors are most commonly stainless steel [61–68], Inconel [69], or Hastelloy [70]. At lab scale, for batch SCW systems, quartz bas also been used as a reactor material [71–74]. A ceramic inlay of aluminum oxide has also been proposed for use in SCWG reactors [75]. For continuous systems, tubular reactors with different orientations have been proposed. In the horizontal position [24,76,77], the reactants mixture is more uniformly exposed to the reaction conditions, while the vertical orientation [17,28,78–82] of the reactor is better for salts removal. For the same issue of salts removal, an inclined plug-flow reactor was recently used for the SCWO process [55]. Microchannel reactors (coiled) are also used for SCWG experiments [83,84] and also for SCWO studies [15,54]. In the catalytic processes the catalyst is loaded in the reactor as fixed/packed [85] or fluidized bed [86]. In the fifth section, the process products in gaseous, liquid and solid phases are separated. The last part of the SCW system helps for process performance evaluation

which is based on sampling and characterization of gas, liquid, and solid products. Most commonly, the products' characterization is performed by on-line techniques, such as gas chromatography (GC), liquid chromatography (LC), total organic carbon (TOC) analysis, etc. The process performance is evaluated in terms of total gas yields, the selectivity towards desirable gas products and the carbon gasification efficiency in the case of SCWG, while for the SCWO the degree of conversion, the total organic carbon, and chemical oxygen demand removal efficiencies can be reported.

#### 3.1. Supercritical Water Gasification

The SCWG is a complex process which includes the structural breakdown of the organic matter into low-molecular weight compounds, and the reactions in SCW with the formation of gaseous fraction containing H<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and other light hydrocarbons, of the water-soluble compounds contained in the liquid fraction and of the solid byproducts, such char, tar, and salts. The overall gasification reaction is endothermic and therefore the SCW system should be operated at high temperature for process efficiency. Three main categories of reactions are studied for the optimization of operating parameters in the SCWG systems. These are the reforming and the water-gas shift reactions for an  $H_2$ -rich gas product, and the methanation reactions for the formation of  $CH_4$  [26]. The reforming reactions are endothermic; the water-gas shift reaction is mildly exothermic, and the methanation reactions are exothermic [87], suggesting that they are thermodynamically favored at high, moderate, and low temperatures, respectively. For the energy cycle optimization and heat recovery it is important to know the energy of these reactions. The thermodynamic studies of the SCWG process are well reported in the literature by Fiori & Castello [88] and Hantoko [87]. Their thermodynamic equilibrium calculations are carried out based on Gibbs free energy minimization by using Aspen Plus software. Rorrer and Goodwin group studied the gasification of glucose in SCW at 1023 K and estimated the standard enthalpy of reforming reaction by Hess' Law to be equal to 114 kJ mol<sup>-1</sup> based on gas-phase water or 246 kJ mol<sup>-1</sup> based on liquid-phase water [83]. The same group, performed thermodynamic calculations using ChemCad 6.1 for the enthalpy of phenol and xylose reforming at the same 1023 K, and report values of  $472 \text{ kJ} \text{ mol}^{-1}$  and 335 kJ mol<sup>-1</sup>, respectively [84]. Using Aspen Plus software, Guiterez Ortiz et al., estimated the enthalpy variation for glycerol reforming in SCW at 1073 K and 243 bar to a value of 192 kJ mol<sup>-1</sup> [89].

As the overall gasification reaction is endothermic, the energy recovery within the gasification process is a key issue for cost-efficient operation of SCW systems. The energy recovery is possible only for systems operated in continuous/plug flow mode [17,79], for example, the VERENA plant used for SCWG of agricultural matter [16]. It was demonstrated that energy yield can reach 85% if the energy is recovered from hot water at 300 bar and 873 K, while assuming the ideal scenario of no external heat loss [78]. Energy savings of about 15.58% were achieved when gasification of food waste was performed by a two-step heating process, initiated by a hydrothermal pretreatment for a short time, followed by the SCWG reaction [70].

## 3.2. Supercritical Water Oxidation

The SCWO process is a single-phase reaction between the organic compounds and the oxidant, with the formation of  $CO_2$  and  $H_2O$ . The heteroatoms, such as chlorine, sulfur, and phosphorus are transformed in inorganic compounds, typically acids, salts, or oxides, while the organic bounded nitrogen usually converts to  $N_2$  and  $N_2O$ . Unwanted compounds, like dioxins or  $NO_x$  are not normally formed [14,90,91].

Historically, the SCWO emerged as a further development of the wet-air oxidation technology, and as an alternative to the incineration process of the non-biodegradable organic wastes. The main advantages of SCWO over the two above-mentioned processes are the residence time of seconds compared to hours for wet-air oxidation, and lower operating temperature than a typical incinerator. The development of the SCWO technology

started practically in the early 80s with the work of Modell for the treatment of sewage sludge [92], and it is based on the MODAR process proposed initially for the treatment of human wastes on NASA' space facilities [13].

As the corrosion and salts deposition are even more challenging issues in the SCWO process, it is mandatory to have a very short reaction/residence time in the reactor and a salt separator section. For this, the SCWO systems differ from SCWGs in the feeding section, as proper mixing and preheating of the feed, water, and oxidant streams should be achieved before the reaction. In this view, feeding systems based on oxidant multiinjection at different reactor points has been proposed to avoid the corrosion and salt deposition problems [93–95]. It was found that oxidant dosage in a SCWO reactor is also an aspect in energy management [93]. Moreover, the multi-injection oxidant feeding systems showed enhanced total organic removal efficiency [94]. In order to overcome corrosion and salt deposition problems, the multi-feed injection technology was coupled with dynamic gas seal wall reactor [95]. An innovative feed system was proposed by Vadillo et al. in 2012 for the treatment of water-insoluble organics and wastewaters with a wide range of concentrations by SCWO at 823 K and 250 bar. The feed system of the pilot plant located at the University of Cadiz includes three independent feed streams: water, water-insoluble waste and air. The first two streams were mixed under the SCW conditions that allowed complete dissolution of the organic compounds before entering the reactor. The oxidation reactions took place at a high rate and released a significant amount of heat after the addition to the reactor of the third stream, the oxidant. This feed system allows the SCWO process to remain energy self-sufficient [96].

Oxygen is the most used oxidant agent in SCWO [90,92,97–101], which is supplied to the system at various concentrations. Another oxidant used is  $H_2O_2$  [13,15,34,54,55,59,93, 94,102–108] which during the preheating decomposes and yield molecular oxygen [98,108].

Comparative studies for wastewater treatment by both SCWO and SCWG revealed that the former can be performed in a shorter reaction time [109,110]. For instance, from industrial pharmaceutical wastewater treated by SCWG at 673 K, the maximum H<sub>2</sub> yield of 126.5 mmol/L was obtained after 45 min., while after only 5 min, near-complete conversion of 99.5% was reached by SCWO using H<sub>2</sub>O<sub>2</sub> and an oxidation coefficient of 4, at the same operating temperature [110].

#### 4. Functional Materials for SCW Processes

The functional materials employed in the SCW processes for waste treatment are manly with catalytic and adsorption activity. This review focuses on metal and metal oxide functional materials for gasification and oxidation in water under supercritical conditions.

#### 4.1. Metal-Based Catalysts for SCWG

Catalytic gasification in SCW of different waste feedstocks using metals as the active material is a common practice nowadays for producing combustible gas. This is mainly due to the ability of metals to selectively catalyze the reactions through which  $H_2$  is produced, by reforming and water gas shift reactions [111,112] at relatively high temperatures, or by methanation reactions at low SCW temperatures with CH<sub>4</sub> production [50,113,114].

Ni-based materials [66,115,116], noble metals [50,117], and some bimetallic catalysts [112,118,119] have been tested for the gasification of various sources of real waste, such as pinewood [111,120] and straw [68,121] biomass, food waste [122], waste cooking oil [123], waste tires [66], and sugarcane bagasse [50]. Table 1 presents a selection of results obtained from the waste gasification experiments under various SCW conditions reported in studies, mostly in recent years.

It was found that Raney Ni increased the  $H_2$  yield by enhancing the water gas shift reaction during the gasification of lignocellulosic biomass, such as sunflower stalk and corncob. At 773 K, 314 bar and after 60 min reaction time, the fraction of  $H_2$  obtained from sunflower stalk is two times higher than that produced when corncob is used as feedstock. The catalyst affected both the deamination and the decarboxylation of the amino acids during the biomass structural breakdown, as well as degradation of the organic acids to produce mainly CO,  $CO_2$ ,  $H_2$ , and water [115].

**Table 1.** Metal-based catalysts used for SCWG of waste; there are three categories of metal-based materials included in this table, namely Ni-based, noble metals and bimetallic catalysts.

Metal Catalyst	Feed	Optimal Operation Conditions <sup>1</sup>		Efficiency and Selectivity	Reference
	Raney Ni	Sunflower stalk	773 K, 314 bar, $\rho_{\rm H2O} = 123 \text{ kg m}^{-3}$ , 60 min residence time 8.3 g biomass, 0.8 g catalyst	477.3 g gas/kg biomass 7.9 mol $H_2/kg$ biomass	Yanik et al. 2008 [115]
		Corncob		448.1 g gas/kg biomass 3.47 mol $H_2/kg$ biomass	
	Ni/CeO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> 7.2 wt. % Ni loading	cellulose	823 K, 30 min residence time water to biomass 7:1, 0.65 g catalyst	24.5% carbon efficiency 1.63 mmol H <sub>2</sub> /g biomass	Ding et al. 2014 [111]
		pinewood		25.2% carbon efficiency 1.3 mmol $H_2/g$ biomass	
Ni-based	Ni nanoparticles (obtained by Ni precursor impregnation into feedstock material)	Pinewood biomass 8996 ppm Ni	773 K, ~230 bar, $\rho_{H2O} = 81 \text{ kg m}^{-3}$ , 45 min residence time,2 water-to-biomass ratio 10:1	19.6% carbon gasification efficiency 9.5 mmol/g total gas yield 2.8 mmol H <sub>2</sub> /g biomass	Nanda et al. 2016 [120]
		Wheat straw biomass 12,358 ppm Ni		32.6% carbon gasification efficiency 5.8 mmol H <sub>2</sub> /g biomass	
	Ni/Si-Al <sub>2</sub> O <sub>3</sub>	Wheat straw biomass	823 K, 230 bar, $\rho_{\rm H2O}$ = 71 kg m <sup>-3</sup> , 60 min reaction time 20 wt. % feed concentration, 5 wt.% catalyst loading	18.2 mmol/g total gas yield 5.1 mmol H <sub>2</sub> /g biomass	Nanda et al. 2018 [121]
	Ni/ZrO <sub>2</sub> modified 10 wt. % Ni loading; Co promoter	Oil-containing wastewater	823 K, 30 min retention time 5 wt.% feed concentration; Ni addition rate of 10%	98.8% carbon gasification efficiency 63.2 mol H <sub>2</sub> /kg feed	Kou et al. 2018 [124]
	Ni/Si-Al <sub>2</sub> O <sub>3</sub>	Bitumen	973 K, 230 bar, $\rho_{\rm H2O}$ = 55 kg m <sup>-3</sup> , 60 min reaction time 20 wt. % feed concentration, 5 wt. % catalyst loading	7.1 mmol/g total gas yield 2.71 mmol H <sub>2</sub> /g bitumen	Rana et al. 2018 [125]
	Ni/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	Waste tires	898 K, 230 bar, $\rho_{\rm H2O}$ = 62 kg m <sup>-3</sup> , 60 min reaction time 5 wt. % feed concentration, 2 wt.% catalyst loading	43.4% carbon gasification efficiency 83.1% H <sub>2</sub> selectivity	Nanda, Reddy, et al. 2019 [66]
	Ni/Si-Al <sub>2</sub> O <sub>3</sub>	Waste cooking oil	948 K, 230 bar, $\rho_{\rm H2O}$ = 57 kg m <sup>-3</sup> , 60 min reaction time 25 wt. % feed concentration, 5 wt.% catalyst loading	21.71 mol/kg total gas yield 74% H <sub>2</sub> selectivity	Nanda, Rana, et al. 2019 [123]
	Ni/La-Al <sub>2</sub> O <sub>3</sub> 15 wt.% Ni on support with 9 wt.% La-Al <sub>2</sub> O <sub>3</sub>	Food waste	753 K, 280 bar, $\rho_{H2O} = 113 \text{ kg m}^{-3}$ , 40 min residence time, stirring at 80 rpm 8 wt.% feed concentration	20.7% carbon gasification efficiency 8.03 mol H <sub>2</sub> /kg food waste 42.46% H <sub>2</sub> mole fraction	Su et al. 2020 [122]

Metal Catalyst	Feed	<b>Optimal Operation Conditions</b> <sup>1</sup>		Efficiency and Selectivity	Reference
	Ni/functionalized carbon nanotubes 10% Ni loading	Light gas oil (LGO)	948 K, 230 bar, $\rho_{H2O} = 57 \text{ kg m}^{-3}$	4.46 mol H <sub>2</sub> /kg gas oil 94% H <sub>2</sub> selectivity	_ Rana et al. 2020 [116]
		Heavy gas oil (HGO)	20 wt. % feed concentration, 5 wt. % catalyst dosage	3.68 mol H <sub>2</sub> /kg gas oil 78% H <sub>2</sub> selectivity	
	Ni/Ce-ZrO <sub>2</sub> 10 wt % Ni loading	Soybean straw	773 K, 230–250 bar, $\rho_{\text{H2O}} = 81-90 \text{ kg m}^{-3}$ , 45 min residence time 1.11 g biomass, 1 g catalyst, water to feedstock 1:10	31.6% gasification efficiency 10.9 mmol H <sub>2</sub> /g biomass 81.7% H <sub>2</sub> selectivity	Okolie et al. 2021 [68]
M	Metal Catalyst		Optimal Operation Conditions <sup>1</sup>	Efficiency and Selectivity	Reference
	Ru/C 2% Ru on C	Spirulina platensis algae	$\begin{array}{c} 675 \text{ K}, 315 \text{ bar},\\ \rho_{\text{H2O}} = 390 \text{ kg m}^{-3}, 361 \text{ min}\\ \text{reaction time}\\ 2.5 \text{ wt. }\% \text{ feed concentration},\\ 8.1 \text{ g catalyst/g dry matter} \end{array}$	109% carbon gasification 41.7 vol. % CH <sub>4</sub> , 8 vol. % H <sub>2</sub>	Stucki et al. 2009 [79]
	Ru/TiO <sub>2</sub> 2 wt.% Ru on TiO <sub>2</sub>	Sugarcane bagasse	673 K, 300 bar, $\rho_{\rm H2O}$ = 359 kg m <sup>-3</sup> , 15 min reaction time 0.1 g feed, 0.38 g catalyst	50.3% carbon yield 39.4% CH <sub>4</sub> , 14.4% H <sub>2</sub>	Osada et al. 2012 [50]
	Ru/Al <sub>2</sub> O <sub>3</sub>	Wheat straw biomass	823 K, 230 bar, $\rho_{H2O}$ = 71 kg m <sup>-3</sup> , 60 min reaction time 20 wt. % feed concentration, 5 wt. % catalyst loading	15 mmol/g total gas yield 4.18 mmol H <sub>2</sub> /g biomass	Nanda et al. 2018 [121]
Noble metals	Ru/Al <sub>2</sub> O <sub>3</sub>	Bitumen	973 K, 230 bar, $\rho_{H2O} = 55 \text{ kg m}^{-3}$ , 60 min reaction time 20 wt. % feedstock concentration, 5 wt. % catalyst	6.8 mmol/g total gas yield 2.94 mmol H <sub>2</sub> /g bitumen	Rana et al. 2018 [125]
	Ru/Al <sub>2</sub> O <sub>3</sub>	Waste tires	898 K, 230–250 bar, $\rho_{\rm H2O}$ = 61.59–67.60 kg m <sup>-3</sup> , 60 min reaction time 5 wt. % feed concentration, 2 wt. % catalyst	40.4% carbon gasification efficiency 79.9% H <sub>2</sub> selectivity	Nanda, Reddy, et al. 2019 [66]
	Ru/Al <sub>2</sub> O <sub>3</sub>	Waste cooking oil	948 K ~230 bar, $\rho_{\rm H2O}$ =57 kg m <sup>-3</sup> , 60 min reaction time 25 wt. % feed concentration, 5 wt. % catalyst	21.4 mol/kg total gas yield 90% H <sub>2</sub> selectivity	Nanda, Rana, et al. 2019 [123]
	Ru/C 1 wt. % Ru on C	Wastewater from hydrothermal liquefaction of microalgae biomass	873 K ~460 bar, $\rho_{\rm H2O} = 146$ kg m <sup>-3</sup> , 60 min reaction time 12 mg catalyst/mL <sub>(aq·)</sub>	97.63% carbon gasification efficiency 2.10 mmol $H_2/g_{(aq\cdot)}$	Shan et al. 2021 [52]

# Table 1. Cont.

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Metal Catalyst	Feed	Optimal C	peration Conditions <sup>1</sup>	Efficiency and Selectivity	Reference
	K <sub>2</sub> CO <sub>3</sub> + Ru/Al <sub>2</sub> O <sub>3</sub> 1:1	Depolymerizing slag	723 K, 10 min residence time 5% feed concentration, depolymerizing slag, K <sub>2</sub> CO <sub>3</sub> and Ru/Al <sub>2</sub> O <sub>3</sub> 2:1:1	66.46% H <sub>2</sub> efficiency 13.22 mmol H <sub>2</sub> /g biomass	Wang et al. 2021 [74]
Bimetallics	Ni–Ru/CeO <sub>2</sub> 30 wt. % Ni–Ru on CeO <sub>2</sub> Ni to Ru 1:0.1	Indole, nitrogen- containing compound	773 K, 300 bar, $\rho_{\rm H2O}$ = 115 kg m <sup>-3</sup> , 30 min reaction time 0.3 mol/L feed concentration, 25 wt. % catalyst	13.9% carbon gasification efficiency 75% C selectivity, 202% H selectivity	Guo et al. 2015 [118]
	Fe-Ni/Ru-Al <sub>2</sub> O <sub>3</sub> (γ) 12 wt. % of Ni and 6 wt.% of Fe in the active phase on support with 2 wt. % of Ru-Al <sub>2</sub> O <sub>3</sub> (γ)	Enteromorpha intestinalis algal biomass	713 K, 250 bars, $\rho_{\rm H2O}$ = 115 kg m <sup>-3</sup> , 10 min reaction time 0.06 g feed, 6 g water	39% carbon gasification efficiency 12.288 mmol H <sub>2</sub> /g biomass 74% H <sub>2</sub> selectivity	Norouzi et al. 2017 [112]
	Ni-Ru/Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub> 10 wt. % Ni and	Biocrude from corn husk	973 K, 250 bar, – $\rho_{\text{H2O}} = 60 \text{ kg m}^{-3}$ , 300 min run time	~90% carbon gasification efficiency 2 mol H <sub>2</sub> /mol C in feed	Tushar - et al. 2020 [126]
	0.08 wt.% Ru on Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	Biocrude from cattle manure		~90% carbon gasification efficiency 1 mol H <sub>2</sub> /mol C in feed	
	Raney-Ni-Mo 93.57 wt.% Raney-Ni 0.31 wt. % Mo	Sewage sludge	723 K, 286 bar, $\rho_{\text{H2O}} = 136 \text{ kg m}^{-3}$ , 25 min residence time 8.9 wt. % feed concentration, 1.4 g catalyst/g dry sludge	92% gasification efficiency 18.13 mol H <sub>2</sub> /kg dry sludge	Chen et al. 2020 [119]

Table 1. Cont.

<sup>1</sup> Water density values from NIST database at https://webbook.nist.gov/chemistry/fluid/ (accessed on 28 October 2021).

Ni nanoparticles impregnated on the feedstock material were used as catalyst in the gasification reaction of pinewood and wheat straw biomass. The  $H_2$  yield was doubled when the SCWG reaction at 773 K used wheat straw as the feedstock compared to pinewood [120].

Catalytic activity of Ni supported on Si-Al<sub>2</sub>O<sub>3</sub>, was tested at SCW conditions in the gasification reaction of wheat straw biomass [121], bitumen [125], and waste cooking oil [123]. After 60 min of reaction time at 230 bar, the highest total gas yield was obtained when waste cooking oil was gasified over Ni/Si-Al<sub>2</sub>O<sub>3</sub> at 948 K [123]. Ni on SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support also exhibited catalytic activity for the SCWG of waste tires at 898 K, with a carbon gasification efficiency as high as 43.4% [66]. Nearly complete conversion of glycerol (a waste compound from biofuel production) to an H<sub>2</sub>-rich gas was achieved when commercial Ni/Al<sub>2</sub>O<sub>3</sub>- SiO<sub>2</sub>, was used in the SCW reforming process [23].

Alumina supported Ni catalysts, promoted with rare-earth Ce/La, were used as catalysts in the gasification reaction of pinewood [111] and food waste [122] at 823 K and 753 K, respectively. The carbon gasification efficiency was around 20% in both cases, with higher H<sub>2</sub> selectivity when an La-promoted Ni catalyst was used for the food-waste gasification [122] than in the gasification of pinewood over a Ce-promoted Ni catalyst [111]. In the last case, it was found that the small amount of nitrogen and sulfur in the pinewood, contributed to the deactivation of the catalyst and, therefore, low gas yields were obtained [111].

A Ce-promoted Ni catalyst on ZrO<sub>2</sub> support was used for the SCWG of soybean straw at 773 K, and pressure around 240 bar. Compared with the performances of other tested

catalysts in this study, after 45 min residence time, the highest gasification efficiency was obtained with the Ce-promoted Ni/ZrO<sub>2</sub>. Moreover, the results highlighted that, besides surface area, coke formation, active metal dispersion, and metal—support interactions are also determining factors in improving product yield and selectivity [68]. The catalytic activity of Ni/ZrO<sub>2</sub> with Co promoters was tested for the gasification of oil-containing wastewater at 823 K. Carbon gasification efficiency as high as 98.8% was obtained after 30 min. Actually, it was found that all tested Ni-based catalysts are highly active for the C-C cleavage and water gas shift reaction [124].

The catalytic activity of Ni supported on functionalized carbon nanotubes was evaluated during the gasification in SCW of light and heavy gas oils at 948 K and 230 bar. It was found that the catalyst improved the  $H_2$  gas yield by promoting the cracking and reforming reactions, particularly in the treatment of light gas oil due to the easy accessibility to the active sites [116].

Various noble metals, such as Ru, Rh, Pt, and Pd were tested in catalytic gasification of different feedstocks [50,117]. Among these, the Ru-based catalysts were the most active catalysts in the SCWG processes starting from microalgae sources [71,86], sugarcane bagasse [50], or depolymerizing slag [74].

Ru on an Al<sub>2</sub>O<sub>3</sub> support demonstrated catalytic activity in the SCWG of wheat straw biomass [121], Canadian Athabasca bitumen [125], waste tires [66], and waste cooking oil [123] at 823 K, 973 K, 898 K, and 948 K, respectively. The selectivity towards the reactions with H<sub>2</sub> as gas product varied from almost 30%, in the case of straw feed [121], to the 90% achieved when waste cooking oil was the source [123]. The combined use of K<sub>2</sub>CO<sub>3</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> for the SCWG of depolymerizing slag (produced during the process of converting biomass into aircraft fuel, mainly composed of lignin and bits of cellulose and hemicellulose) increased the hydrogen efficiency compared with the non-catalytic process. This is due to a synergetic effect as the active materials act on different reaction stages, the combination performing better together than any of the single catalysts. The K<sub>2</sub>CO<sub>3</sub> promoted the swelling and hydrolysis of lignocellulose and increased the amounts of phenolic intermediates while Ru/Al<sub>2</sub>O<sub>3</sub> facilitated the hydrogenation reaction of hydrolyzed products, ring-opening reactions, and the cleavage of carbon-carbon bonds [74].

Ru supported on C-based materials was more active for gasification reactions in SCW with formation of  $CH_4$  as the main fraction in the gas product. At relatively low temperatures, such as 673 K and 683 K, Ru/C catalyzed the methanation reaction during the SCWG of *Spirulina platensis algae* [79] and *Nannochloropsis* sp. *marine microalgae* [113], respectively. Complete conversion of sugarcane bagasse to a  $CH_4$ -rich gas product was achieved when SCWG was performed at 673 K and 300 bar [50]. A Ru/C catalyst was used for the SCWG processing of wastewater from hydrothermal liquefaction of microalgae biomass at 873 K. With increasing water density and catalyst loading, the production of  $CH_4$  and  $H_2$  was promoted, with the  $H_2$  yield always exceeding the  $CH_4$  fraction [52].

The bimetallic Ni–Ru on a CeO<sub>2</sub> support showed high efficiency and gas yields in producing CO<sub>2</sub>, CH<sub>4</sub>, and H<sub>2</sub> from indole, a recalcitrant nitrogen-containing compound related to algal biomass processing. Operating above the critical pressure of water at 723 K for 30 min is a prerequisite for the Ni–Ru composite catalyst to reach a high conversion of indole [118]. Ni-Ru/Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst showed significant increase in H<sub>2</sub> yield compared to the non-catalytic process in the SCWG of corn husk biocrude at 973 K and 250 bar. Steep deactivation of the catalyst was observed after 2 h of steam time. In the same conditions, when used for cattle manure biocrude gasification, it produced much lower and rather steady H<sub>2</sub> yield comparing to cornhusk feed. In the 773–973 K temperature range at 250 bar, the catalyst achieved a gasification efficiency of ~90% in corn husk and cattle manure biocrude treatment regardless of temperature, producing H<sub>2</sub>-rich gas [126].

For the SCWG of *Enteromorpha intestinalis algae* biomass at 713 K and 250 bar a Rupromoted Fe–Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> nanocatalyst performed better than the un-promoted reference in increasing H<sub>2</sub> selectivity and only slightly reduced the gasification efficiency by decreasing

the amount of CH<sub>4</sub>, CO, and C<sub>2</sub> hydrocarbons. The Ru-promoted catalyst showed increased dispersion and smaller size Ni crystallite size (~ 3.2 nm) on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support [112].

High hydrogen yield and gasification efficiency was obtained with the Raney-Ni-Mo as catalyst in the SCWG of sewage sludge at 723 K. Compared to other catalysts tested in similar conditions, this bimetallic catalyst had a higher surface area and favorable pore distribution [119].

## 4.2. Metal Oxides for SCW Processes

Table 2 summarizes the main findings of studies reporting results on catalytic SCW processes using metal oxides as the active material.

SCW Process Functionality	Metal Oxide	Feed	Optimal Reaction Conditions <sup>1</sup>	Efficiency and Selectivity	Reference
	Red mud (Fe-oxide containing residue from Al-production)	Sunflower stalk	773 K, 314 bar, $ ho_{ m H2O}$ = 123 kg m <sup>-3</sup> , 60 min 8.3 g feed, 0.8 g catalyst	446.8 g gas/kg sunflower stalk 8.09 mol H <sub>2</sub> /kg sunflower stalk 2.95 mol CH <sub>4</sub> /kg sunflower stalk	Yanik et al. 2008 [115]
		Corncob		426.0 g gas/kg corncob 5.65 mol H <sub>2</sub> /kg corncob 3.33 mol CH <sub>4</sub> /kg corncob	
	Cubic CeO <sub>2</sub> nanocatalyst	Black liquor	723 K, 250 bar, $\rho_{\rm H2O} = 109 \text{ kg m}^{-3}$ , 60 min reaction time 10 wt. % feed concentration, 5 g catalyst/g feed	~20% carbon conversion 360 µmol H <sub>2</sub>	Boucard et al. 2015 [127]
SCWG catalyst	$\begin{array}{c} \text{RuO}_2/\gamma\text{-Al}_2\text{O}_3\\ \text{20 wt.} \ \% \ \text{RuO}_2 \ \text{on}\\ \gamma\text{-Al}_2\text{O}_3 \end{array}$	Refuse derived fuel from municipal solid waste	723 K, 290 bar, $\rho_{\rm H2O}$ = 140 kg m <sup>-3</sup> , 60 min reaction time 1.0 g of feed, 0.5 g catalyst	93% carbon gasification efficiency 36.9 vol. % H <sub>2</sub> , 23.2 vol. % CH <sub>4</sub>	Yildirir, Onwudili, and Williams 2017 [65]
	ZnO-doped Ni–CaO 5 wt. % ZnO with 5 wt. % Ni-CaO	Biomass- empty palm fruit bunches (EFBs)	653 K, 8 min reaction time 0.3 g feed, 5 wt. % catalyst, 8 mL deionized water	17.1% conversion 105.7 mmol H <sub>2</sub> /mL feed	Taufiq-Yap, Sivasangar, and Surahim 2019 [67]
	Co <sub>2</sub> O <sub>3</sub>	Soda black liquor	873 K, 240–260 bar, $\rho_{\rm H2O}$ = 67–74 kg m <sup>-3</sup> , 30 min reaction time the mass ratio of catalyst to feed 1:1	71.05% gasification efficiency 54.8% H <sub>2</sub> fractions	Cao et al. 2020 [128]
	NiFe <sub>2</sub> O <sub>4</sub>	Eucalyptus wood chips	723 K, 60 min reaction time 2.2 g feed, 2.0 g catalyst	95.49% biomass conversion 25.05 mol. % H <sub>2</sub>	Borges et al. 2020 [129]
SCWO catalyst	MnO <sub>2</sub> powder	NH <sub>3</sub> + phenol model solution	773 K, 247 bar, $\rho_{\rm H2O}$ = 88 kg m <sup>-3</sup> , 0.03 min contact time $C_{\rm NH3,0}$ = 1.67 mol/m <sup>3</sup> $C_{\rm Ph,0}$ = 0.107 mol/m <sup>3</sup> $C_{\rm O2,0}$ = 11.0 mol/m <sup>3</sup>	>90% NH3 conversion >90% TOC conversion	Oshima, Inaba, and Koda 2001 [98]

Table 2. Metal oxide materials for SCW processes.

SCW Process Functionality	Metal Oxide	Feed	Optimal Reaction Conditions <sup>1</sup>	Efficiency and Selectivity	Reference
	Mn <sub>2</sub> O <sub>3</sub> /Ti-Al	p-nitrophenol wastewater	693 K, 260 bar, $\rho_{\rm H2O}$ = 143 kg m <sup>-3</sup> , 0.1 min residence time 1000 mg/L feed concentration, 6.5 g of catalyst	99% conversion	Dong et al. 2015 [130]
SCW S-removal	ZnO	refractory sulfur compound from crude oil	673 K, 250 bar, $\rho_{\rm H2O}$ = 167 kg m <sup>-3</sup> , 60 min reaction time 1:1 wt./wt. of oil/water, 0.35 g catalyst	25% efficiency of sulfur removal	Ates et al. 2014 [131]
Sorbent -	ZnO Katalco	Chlorella vulgaris	673 K, 280 bar, $ ho_{ m H2O}$ = 261 kg m <sup>-3</sup> , 6000 min stream time 31 g S in feed	8% efficiency of sulfur removal	Peng et al. 2017 [132]

Table 2. Cont.

<sup>1</sup> Water density values from NIST database at https://webbook.nist.gov/chemistry/fluid/ (accessed on 28 October 2021).

Various transition metal oxides have been tested for the gasification of biomass and biomass related model compounds, and for gas production from industrial and municipal wastes under different SCW conditions [67,72,128,133].

At 773 K, 314 bar for 60 min, the gasification of sunflower stalk and corncob as lignocellulosic feedstock and leather waste as a proteinous biomass was highly efficient when using red mud, an Fe-oxide-containing residue from Al production by the Bayer process, as the catalyst. This catalyst exhibits good selectivity for  $H_2$  and  $CO_2$  production. It is notable that a very small amount of coke was generated when gasification was started from corncob and leather waste. This study proved that iron-based materials exhibit catalytic activity for the production of  $H_2$  from biomass [115].

Gasification of soda black liquor was tested in SCW at 873 K and pressures ranging from 240 to 260 bar, over various transition metal oxides, such as  $V_2O_5$ ,  $Cr_2O_3$ ,  $MnO_2$ ,  $Fe_2O_3$ ,  $Co_2O_3$ , CuO, ZnO,  $ZrO_2$ ,  $MoO_3$ ,  $WO_3$ ,  $TiO_2$ , and  $Fe_3O_4$ . The highest gasification efficiency was achieved when  $V_2O_5$  was used as catalyst, however with low  $H_2$  selectivity. The highest  $H_2$  fraction in the gas product was obtained when ZnO and  $Co_2O_3$  were used as catalysts in the gasification reaction [128]. When the same metal oxides were tested for the gasification of glucose model compound, all the metal oxides improved the  $CH_4$  fractions except  $V_2O_5$ , CuO, and  $ZrO_2$  [72]. Under the investigated processing conditions, the least stable catalysts were found to be CuO and  $Fe_2O_3$  which reduced to metal or lower-valence metal oxides (Cu, Cu<sub>2</sub>O, or FeO) without catalytic activity [128].

A ZnO-doped Ni–CaO catalyst, specifically at 5 wt. % ZnO with a Ni loading of 5 wt. % on CaO showed high feedstock conversion and H<sub>2</sub> production by empty palm fruit bunch biomass gasification at 653 K and 8 min reaction time. Hydrogen made up the largest proportion in the resulting gas which consisted mainly of H<sub>2</sub> and CO<sub>2</sub>, CH<sub>4</sub>, and CO. It was suggested that the formation of an Ni<sub>0.8</sub>Zn<sub>0.2</sub>O phase from the strong interaction between the dopants actively promoted the water-gas shift reaction [67].

An RuO<sub>2</sub> catalyst supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was used for the gasification of refuse-derived fuel from municipal solid waste at 773 K, and 290 bar. With an Ru loading of 20 wt. % on the support, the attained carbon gasification efficiency was 93% after 60 min residence time. Although the largest fraction in the gas product was CO<sub>2</sub>, almost 37% H<sub>2</sub> and 23% of CH<sub>4</sub> were obtained under optimal reaction conditions. However, the CO<sub>2</sub> fraction decreased with increasing reaction time [65].

Rare-earth metal oxides, such as CeO<sub>2</sub>, showed little catalytic activity within the gasification reaction of glucose at 873 K, 250 bar, and 10 min reaction time in a quartz capillary reactor [72] and the same for the gasification of soda black liquor at 873 K and

240–260 bar [128]. Cubic CeO<sub>2</sub> nanocatalyst was tested for the gasification of black liquor in sub- and supercritical conditions at 623 K and 723 K, 250 bar in a batch reactor for 15 min and 60 min. The carbon conversion of black liquor at sub and supercritical conditions improved over the catalyst. The selectivity for H<sub>2</sub> formation in SCW & 60 min was not high, as the amount of H<sub>2</sub> was only slightly affected by the catalyst compared to the non-catalytic conditions. It was shown that, at longer reaction times and in sub- rather than supercritical conditions of water, the CeO<sub>2</sub> catalyst improves the water gas shift reaction which increases the H<sub>2</sub> yield. The amount of coke produced without the catalyst was lower than that with the catalyst [127].

The activity of NiFe<sub>2</sub>O<sub>4</sub> spinel-type catalyst was examined, as a function of temperature, at 673, 723, and 773 K for 60 min in the gasification of eucalyptus wood chips. A conversion of 95% compared to 73% in the non-catalytic process was attained, with the highest  $H_2$  fraction formed at 723 K. Tests of recyclability under the operating conditions using recovered and recalcined catalysts indicated coke formation and significant deactivation after a third reaction cycle, leading to reduced biomass conversion and  $H_2$  yield [129].

Figure 4 shows a selection of optimal operation conditions in terms of temperature and pressure at which various catalysts performed best in SCWG processes of different waste feedstocks. We selected data from Tables 1 and 2 and present them in Figure 4 relative to the PB-Widom line as determined in [19]. The first thing to observe in Figure 4 is that all catalysts perform well at pressures below 350 bar. Secondly, it is interesting to note that Ru-based catalysts used for SCWG of biomass to obtain CH<sub>4</sub> as the main gas product have the best performance at conditions close to the PB-Widom line. The other selected catalysts show high catalytic activity in the GL supercritical region of water. However, Ni-based catalysts seem to show the highest selectivity for H<sub>2</sub> formation at relatively higher temperatures than bimetallic catalysts or metal oxides.



**Figure 4.** Selected optimal pressure-temperature conditions for SCWG processes over various catalysts; a selection taken from Tables 1 and 2 is presented relative to the PB-Widom line [19].

Screening the selected literature, we found that catalytic SCWO is not a common practice, especially in recent years. This could be because the SCW by itself is active in the oxidation of most organic compounds, which activity is enhanced by the addition of the oxidative agent. Moreover, in some cases, it was reported that the SCW holds back, for instance, the conversion of  $NH_3$  into  $N_2$  and  $N_2O$  products, due to adsorption inhibition by water during the oxidation reaction over bulk  $MnO_2$  catalyst [98].

Most of the experiments on the oxidative catalysis in SCW are performed starting from model solutions and using MnO<sub>2</sub>-based catalysts [25,98,108,130,134].

The commercial catalyst CARULITE 150 with a composition of 45–60%  $MnO_2$  and 1–3% CuO on amorphous  $Al_2O_3$  support was used for the oxidation of phenol under various operation conditions. Using this catalyst, much higher phenol conversion and

selectivity to  $CO_2$  formation was achieved compared to the non-catalytic process at 658 K and 253 bar in presence of  $O_2$ . The phenol conversion was always higher than 70%, achievable in 2 s of space time, defined here as the ratio between the catalyst mass to the fluid flow rate. In aged conditions, the catalyst maintained high activity even after several days of continuous operation [108]. The activity for the phenol oxidation of bulk TiO<sub>2</sub> and MnO<sub>2</sub> versus that of commercial CARULITE was compared at 654 K and 253 bar. Only over the CARULITE catalyst did the conversion of phenol reach 100%, after less than 1 s of space time. While, the bulk TiO<sub>2</sub> and MnO<sub>2</sub> provided CO<sub>2</sub> selectivity similar to the non-catalytic process, i.e., no more than 40%, the commercial catalyst exhibited high selectivity to CO<sub>2</sub> formation, approaching 60% when the phenol oxidation was complete [25].

 $MnO_2$ , prepared by compression molding with nitrocellulose as pore forming agent and calcinated afterwards, it was catalytically tested for the oxidation of nitrobenzene at 738 K, 280 bar. Under these conditions, the degradation efficiency was higher than 99% even after 18 h on stream, showing the stability of the catalyst in SCW [134]. Using bulk  $MnO_2$  catalyst and  $H_2O_2$  as oxidant, experiments on the oxidation of diluted coke-works waste, containing manly  $NH_3$  and phenol, were performed at 773 K and 247 bar. A high total organic carbon removal efficiency was achieved, and a high conversion to  $N_2$  and  $N_2O$ , as minor product, with a selectivity of up to 90% [98].

 $Mn_2O_3$  supported on Ti-Al oxide composite, prepared by incipient wet impregnation using  $Mg(NO_3)_2$ , has been tested as a catalyst for oxidation of p-nitrophenol-containing wastewater, using compressed air and  $H_2O_2$  as oxidants, in the temperature interval from 658 K to 718 K, at 260 bar and 1–2 s reaction time. Compared to the activity of unsupported  $MnO_2$  and  $Mn_2O_3$ , the supported catalysts showed the highest removal efficiency, close to 100%, at the optimal temperature for the catalytic process of 693 K [130].

Transition metal oxide materials were used also for sulfur removal from SCW streams. For instance, ZnO and MoO<sub>3</sub> materials promoted sulfur removal during the decomposition in SCW of the aliphatic sulfide compounds contained in crude oil. The SCW desulfurization performance of such compounds increased from 3 to 25% when using ZnO as the sorbent material at 673 K and 250 bar. In fact, the SCW alone removed 6–7% of the sulfur present in the investigated crude oil [131]. The sorption mechanism is related to the sulfidation reaction based on the ability of metal oxides to replace the O with S. Commercial ZnO exhibited good sulfur adsorption performance under SCW conditions in the catalytic gasification of microalgae at 673 K and 280 bar. The adsorbent bed, placed before the catalytic bed, was used to avoid the poisoning by S species of the Ru catalyst [132].

#### 4.3. Supporting Materials and Promoters

The supporting materials employed in SCW processes, should have chemical stability, high surface area and to allow good dispersion of the catalyst particles onto their surface, while offering easy accessibility to the active sites. Two main types of catalyst supports are used in processes undergoing in SCW conditions. These are the metal-oxides, such as Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>, and MgO [52,68,135] and carbon-based materials such as activated carbon (AC), CNTs, and functionalized CNTs [116]. The former are stable compounds, chemically inert, and exhibit strong mechanic properties. The latter materials are attractive as supports for catalytic processes due to their large specific surface areas of ~800–1500 m<sup>2</sup> g<sup>-1</sup> [31], high heat conductivity, porosity, and stability with regard to morphological, physicochemical and thermal properties [116]. Still, the activated carbon's relative instability in multiple utilizations may limit the practical applications of these supporting materials compared to the metal oxide-supported catalyst [52].

Various metal oxides, such as ZrO<sub>2</sub>, CeO<sub>2</sub>-ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO-Al<sub>2</sub>O<sub>3</sub> have been employed as supporting materials for the synthesis of Ni-based catalysts at 773 K and 230 bar [135]. The highest activity in the SCWG of glycerol was exhibited by the catalyst supported on MgO-Al<sub>2</sub>O<sub>3</sub>. This is due to the fact that the support allows high dispersion of the metallic component. Moreover, spinel-type oxides, e.g., NiAl<sub>2</sub>O<sub>4</sub> and MgAl<sub>2</sub>O<sub>4</sub> are formed with catalytic activity. In addition, the MgO-Al<sub>2</sub>O<sub>3</sub> support has an extremely stable

mesoporous structure in long-term SCW operations, an excellent coke resistance, and it is also easy to regenerate. The catalyst prepared on CeO<sub>2</sub>-ZrO<sub>2</sub> shows the lowest performance in the SCWG of glycerol due to low dispersion of active-Ni [135]. In another recent study on supported Ni catalysts for SCWG reaction it was found that the contribution of metal oxides as supporting materials for the formation of H<sub>2</sub> gas product decreased in the following order:  $ZrO_2 > Al_2O_3 > SiO_2 > Al_2O_3 - SiO_2$ . The study pointed out the importance of high surface area of catalysts during SCWG as well as the active metal dispersion within the support. Moreover, coke formation, and metal–support interactions played important role in the catalysts activity and selectivity [68]. Simple metal oxides were employed as supporting materials also for the Ru-based catalysts tested in the SCWG and it was found that the carbon gasification efficiency decreased in the following order:  $TiO_2 > CeO_2 >$  $ZrO_2 > Al_2O_3 > MgO$  [52].

The effect of carbon-based supports was evaluated in the SCWG of sugarcane bagasse over a Ru catalyst, and it was found that the support pore structure is modified due to blocking of the pores by the formation of carbonaceous products during the gasification process. The activity of the metallic catalyst drastically dropped during repetitive SCWG processes, therefore only fresh catalyst could be used [50]. Graphite and charcoal supporting materials for Ru catalysts employed in the SCWG of lignin were compared and it was found that the pore structure of the carbon supports played a crucial role in the catalytic activity [136]. When using graphite supported ruthenium catalysts, superior gasification yield was recorded, although the graphite has a six-times-smaller micropore volume than charcoal. The explanation is related to partially hydrolyzed lignin molecules that, due to their volume, were not able to reach the catalyst particles located within charcoal micropores [136]. The CNTs used as supports for Ni-based catalysts were found to be efficient in SCWG processes [116,135]. It was found that Ni/CNT catalyst prepared in SCW exhibited higher activity and increased stability compared to Ni/AC catalyst [135]. Moreover, functionalized CNTs, with increased surface area, proved to be efficient in obtaining  $H_2$ -rich gas from light gas oil and heavy gas oil by SCWG over an Ni-based catalyst. The support's high porosity facilitated the easy access of the waste/feedstock to the active sites of the catalyst [116].

In catalysis, promoters are substances that, added in small amounts to a given catalyst during preparation, work to improve its properties such as the activity (facilitate the desired reaction) and selectivity (suppress unwanted processes) as in the case of chemical promoters, or to improve stability (as in preventing sintering, physical promoters). By themselves, promoters have little or no activity. The effects of adding promoters such as Na, K, and Ce to Ni-supported catalysts on ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> catalysts were recently evaluated and the study showed an increased Ni dispersion which improved H<sub>2</sub> yields during SCWG [68]. It was found that CeO<sub>2</sub> can be used as promoter for coke removal from Ni catalyst surfaces by oxidizing the surface-deposited char due to its oxygen mobility and oxygen retaining ability [137]. Moreover, La promoter added to Al<sub>2</sub>O<sub>3</sub>-supported nickel catalyst diminished the carbon deposition and maintained catalyst activity over multiple cycles of food waste gasification experiments at 753 K [122].

## 5. Conclusions

In conclusion, we carefully screened the literature from recent decades reporting results related to waste treatment by SCWG and/or SCWO. We focused on functional materials, such as metal-based catalysts efficient for the gasification processes in SCW, and metal oxides with catalytic and sorption activity in both SCWG and SCWO. After processing the high amount of information on SCW processes starting from wastes and ending with energy-relevant products, we learned the following lessons:

 To overcome the issues related to the economic challenges coming from high operation costs of SCW systems and the technological problems caused by corrosion and salt deposition, it is necessary to optimize the operation parameters for enhanced energy efficiency and savings.

- Managing to finely tune the properties of SCW is the key towards the operating
  parameters optimization. For this, fundamental knowledge on the supercritical state
  of water is essential. During isobaric heating in the supercritical region of a fluid, the
  PB phenomenon occurs, which is reflected in the fluid structural changes from LL to
  GL phases, across the PB-Widom line. The water properties change drastically at this
  phase transition, and reaction mechanisms in LL water are different to those in the
  GL phase.
- Heterogeneous catalysis in SCW allows efficient treatment of various types of waste at relatively low temperatures, mostly in the GL region of water, with enhanced selectivity for the formation of desired products in a short time.
- Among metal functional materials for SCWG processes, the Ni-based catalysts are mostly active at temperatures higher than 773 K, enhancing the rates of reforming or water-gas shift reactions. Therefore, gasification over these catalysts results in the formation of an H<sub>2</sub>-rich gas product. Noble metals, such as Ru-based catalysts, are efficient at temperatures as low as 673 K and have high catalytic activity for reactions with CH<sub>4</sub> as main gas product, especially when the feedstock is based on microalgae biomass.
- Metal oxides are used as functional materials in both SCWG and SCWO treatment of wastes feedstock. Transition metal oxides mostly show catalytic activity in the gasification reactions of various types of wastes at temperatures of 763 K on average. For the SCWO only manganese-based oxides exhibit catalytic activity towards complete conversion of organic matter, obtained in seconds at temperatures not higher than 800 K. ZnO shows efficiency in the adsorption of sulfur from the SCW streams, and thus the poisoning and deactivation of catalysts is avoided.
- Supporting materials based on metal oxides prove to be more suitable for long term SCW operations, and more resistant to coke depositions than the carbon materials used as supports for catalysts, although the later provide higher surface area, and enhanced dispersibility of the catalyst particles can be achieved.
- Promoters such as rare earth-based materials increase the stability of catalysts under SCW conditions by reducing the coke/char deposition on the catalyst surface and thus avoiding the deactivation.

The information on waste-to-energy processes in SCW, selected and discussed here in correlation with fundamental water science, aims to be a practical guide for the selection of materials stable and functional under supercritical conditions.

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