

Article

Hydrogen Production by Catalytic Supercritical Water Gasification of Black Liquor-Based Wastewater

Hary Demey ^{*}, Gilles Ratel, Bruno Lacaze, Olivier Delattre, Geert Haarlemmer and Anne Roubaud 

CEA, LITEN, DTCH, Laboratoire Réacteurs et Procédés (LRP), University Grenoble Alpes, F-38000 Grenoble, France

^{*} Correspondence: hary.demeycedeno@cea.fr; Tel.: +33-438-78-5650

Abstract: In this work, the wastewater obtained from the hydrothermal liquefaction of black liquor was treated and valorized for hydrogen production by supercritical water gasification (SCWG). The influence of the main process parameters on the conversion yield was studied. The experiments were conducted at three different temperatures (below and above the critical point of water): 350 °C, 450 °C and 600 °C. The results showed that by increasing the temperature from 350 °C to 600 °C, the total gas yield was highly improved (from 1.9 mol gas/kg of dried feedstock to 13.1 mol gas/kg of dried feedstock). The H₂ composition was higher than that of CH₄ and CO₂ at 600 °C, and the HHV of the obtained gas was 61.2 MJ/kg. The total organic carbon (TOC) removal efficiency was also improved by increasing the temperature, indicating that the SCWG process could be used for both applications: (i) for wastewater treatment; (ii) for producing a high calorific gas. The experiments with the Raney-nickel catalyst were performed in order to study the catalyst's influence on the conversion yield. The results indicated that the catalyst enhances carbon conversion and gas production from mild to higher temperatures. The maximum total gas yield obtained with this catalyst was 32.4 mol gas/kg of dried feedstock at 600 °C, which is 2.5 times higher than that obtained at the same operating conditions without a catalyst. The H₂ yield and the HHV of the obtained gas with the catalyst were 20.98 mol gas/kg dried feedstock and 80.2 MJ/kg, respectively. However, the major contribution of the catalytic SCWG process was the improvement of the total gas yield at mild operating temperatures (450 °C), and the obtained performance was even higher than that obtained at 600 °C without catalyst (17.81 mol gas/kg dried feedstock and 13.1 mol gas/kg dried feedstock, respectively). This is a sustainable approach for treating wastewater at mild temperatures by catalytic SCWG.

Keywords: black liquor; catalyst; supercritical water gasification (SCWG); wastewater treatment; hydrogen production



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1. Introduction

The waste valorization from industrial processes for sustainable applications (including bio-energy production) is one of the major concerns of this decade. The research on pulp and paper industry wastes is a hot topic since it involves the valorization of more than 500 million tons of concentrated black liquor per year (10% of which is in the European Union), according to Dafinov et al. [1]

The pulp and paper process includes the cooking of wood chips at high pressure and temperature using a white liquor to dissolve lignin. The spent cooking liquor (so-called black liquor) contains organic residues, which can be used as an energy source [2]. Some operating plants around the world employ recovery boilers to process spent pulping liquors and to produce steam for electrical co-generation. However, this technology has many shortcomings, which are related to (i) relatively low energy efficiency; (ii) relatively poor environmental performance; (iii) challenging boiler control; (iv) technical problems for controlling the sulfur balance, corrosion of the materials, etc. [2].

The energy content in the black liquor effluent is around 12.3 MJ/kg [3], and several authors have studied the feasibility of the gasification process (instead of combustion in a boiler) for producing a synthesis gas in order to be reused in the pulp and paper industry. The greater advantage of gasification over the combustion process is the flexibility offered by a gaseous fuel [2].

Supercritical water gasification (SCWG) is a thermochemical conversion process that employs water at supercritical conditions (i.e., $p > 221$ bar, $T > 374$ °C). The goal is to convert the maximum amount of organic carbon contained in the feedstock into a gaseous phase (containing hydrogen and methane, mainly). A solid (char) and an oily liquid (aromatic hydrocarbons) are also produced. These by-products could decrease the gas yield of the process, depending on the feedstock composition and the operating conditions (Figure 1).

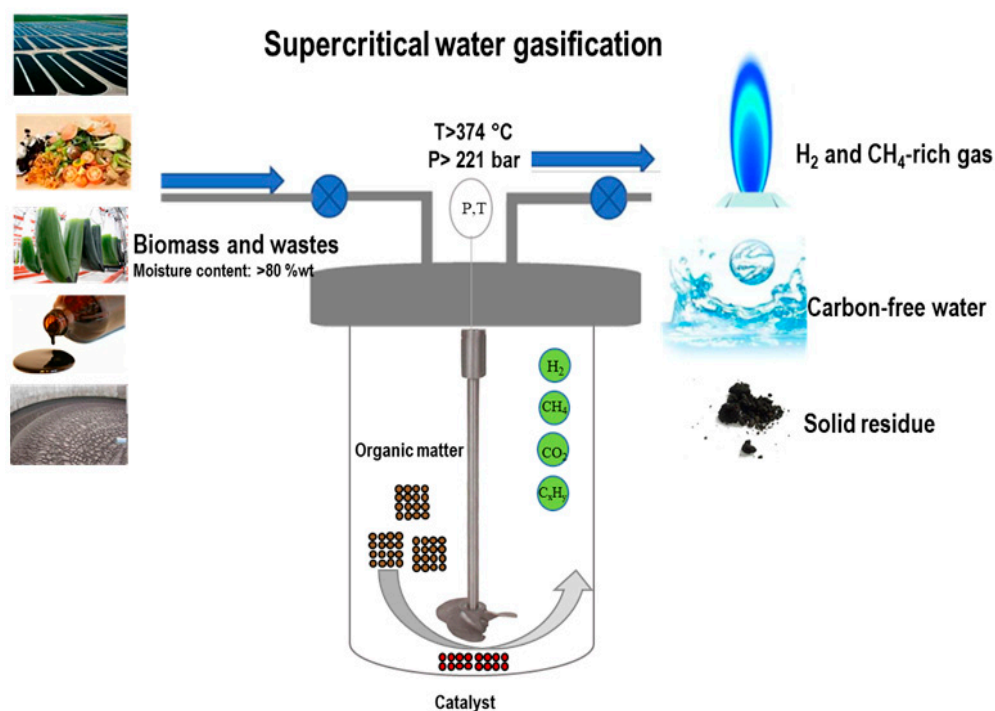


Figure 1. Supercritical water gasification process (so-called hydrothermal gasification).

The main advantage of SCWG over conventional gasification is that wet feedstock (>80% moisture) can be directly gasified without an energy-intensive drying step [4]. The main drawback is that most interesting conversion yields have been reported in the literature at high temperature/pressure conditions (>600 °C, >300 bar). This is the cause of the expensive reactor costs, since at severe temperature and pressure conditions special alloy materials are required.

Recently, it has been reported in the literature that the presence of a suitable heterogeneous catalyst could improve the gas yield at moderate temperatures (400–500 °C) and enhance the selectivity of species for obtaining a hydrogen-rich gas [5]. However, further research is required in order to optimize the management of the catalytic material in the reactor and to avoid faster deactivation.

According to Correa and Kruse [6], nickel-based catalysts have been used in SCWG since these are low-cost and their efficiency is comparable to that of noble metals. Sinag et al. [7] found that the Raney nickel catalyst promoted the degradation of intermediate compounds (such as phenols, acetic, and formic acids), leading to a higher CH₄ production. This was also supported by Sheikhdavoodi et al. [8] in their experiments with sugarcane bagasse. They observed that Raney nickel showed the highest carbon conversion and low hydrogen production compared to the results obtained with KOH and NaOH catalysts. Azadi et al. [9] reported that nickel catalysts contribute to promoting

the C-O bond cleavage and the hydrogenation of the produced CO₂. This leads to higher methane production and lower hydrogen selectivity.

Thus, carbon-based materials have been studied in the literature for enhancing H₂ production in the SCWG process. Sheikhdavoodi et al. [8] reported that activated carbon improves the H₂ yield in comparison to Raney nickel, but not as high as alkali metals. Catalysts based on noble metals have also been studied and compared to nickel-based catalysts. Yamaguchi et al. [10] investigated the impact of noble metals on hydrogen production. The authors reported the following sequence, according to the H₂ yield: Pd > Ru > Pt > Rh > Ni; however, the high price per kg of noble metals and their deactivation during SCWG makes it difficult for a large industrial-scale application. Yamaguchi et al. [10] revealed that the catalyst support plays an important role in the stability of the catalyst for being reused in several gasification cycles; they reported that Ru/Al₂O₃ catalyst is rapidly deactivated after two utilization cycles.

This work is in the frame of the Waste2Road European project, which aims to develop a new generation of cost-effective biofuels from a carefully selected range of low-cost and abundant biogenic residues and waste fractions, aiming to achieve high overall carbon yields > 45% while reducing greenhouse gases emissions (GHG) > 80%. The hydrothermal liquefaction (HTL) process has been previously used to convert sulfur-free black liquor to an intermediate liquid product (bio-oil), which allows easier and cheaper processing into existing oil refineries. However, HTL processes also generate an aqueous phase that contains organic matter that should be integrated into the overall value chain.

In a previous work, Huet et al. [11] reported the aqueous phase composition obtained at different temperatures from hydrothermal liquefaction (HTL) of black liquor (from the soda pulping process). The main monomeric compounds identified in the aqueous phase were phenol, catechol, guaiacol, and syringol. The results indicated an increase in phenol concentration by increasing the temperature from 250 °C to 310 °C. The results reported recently by Curmi et al. [12] also confirmed this trend, and it was found that HTL treatment at 280 °C allows increasing the concentration of guaiacol, but from temperatures higher than 350 °C, the most significant compound was phenol with a concentration around 0.3 g/L.

The goal of this work is to valorize the black liquor- HTL effluent for producing a gas rich in hydrogen for energy applications. The catalytic and non-catalytic SCWG processes were studied in order to convert and remove the carbon contained in this wastewater. The influence of the main process parameters was studied in order to find the best operating conditions for obtaining a higher gas yield with a higher carbon conversion.

2. Materials and Methods

2.1. Materials

The feedstock used in this work is the aqueous phase generated during the thermal-conversion of black liquor by hydrothermal liquefaction (HTL) process at 350 °C. The feedstock was placed in a batch autoclave reactor (manufactured by TOP Industrie, Vaux-le-Pénil, France) and injected in the heated reactor with/without Raney nickel catalyst (provided by Sigma Aldrich, St. Louis, MO, USA). The amount of catalysts was set as 0.1 g of catalyst per gram of wet feedstock.

2.2. Methods

The gas composition was analyzed by a Micro-GC Fusion (provided by INFICON, Bad Ragaz, Switzerland), and the elemental analyses of the remaining solid biochar were performed with a Vario EL cube instrument (provided by ELEMENTAR, Langenselbold, Germany). The anions/cations concentrations from aqueous phase were analyzed by ion chromatography (ICS-3000, provided by DIONEX, Sunnyvale, CA, USA) and the total organic carbon by TOC-L equipment (provided by SHIMADZU, Kyoto, Japan). The thermodynamic yields were calculated at different temperatures by GEMINI 2 software (provided by Thermodata, Saint Martin d'Hères, France).

2.3. Supercritical Water Gasification Process

The tests were carried out in a 500 mL batch reactor (provided by Top-Industrie, Vaux-le-Pénil, France, Figure 2). The reactor is made of 1.4571 stainless steel (containing between 16–18% of Cr and 10.5–13% of Ni). The maximum operating temperature of the reactor is 650 °C, and its maximum operating pressure is 400 bar. The temperature inside the reactor is measured by a type K thermocouple; the pressure is monitored by a sensor and a manometer. A known mass of feedstock (~10 g) is introduced into the reactor. Then, it is closed, and the tightness is tested three times (each test takes ~10 min with 70 bar of nitrogen). After sweeping with nitrogen to an inert atmosphere, the pressure is adjusted to 7–8 bar with nitrogen. The reactor is then heated (~5 °C/min), and the stirrer is set at 300 rpm.

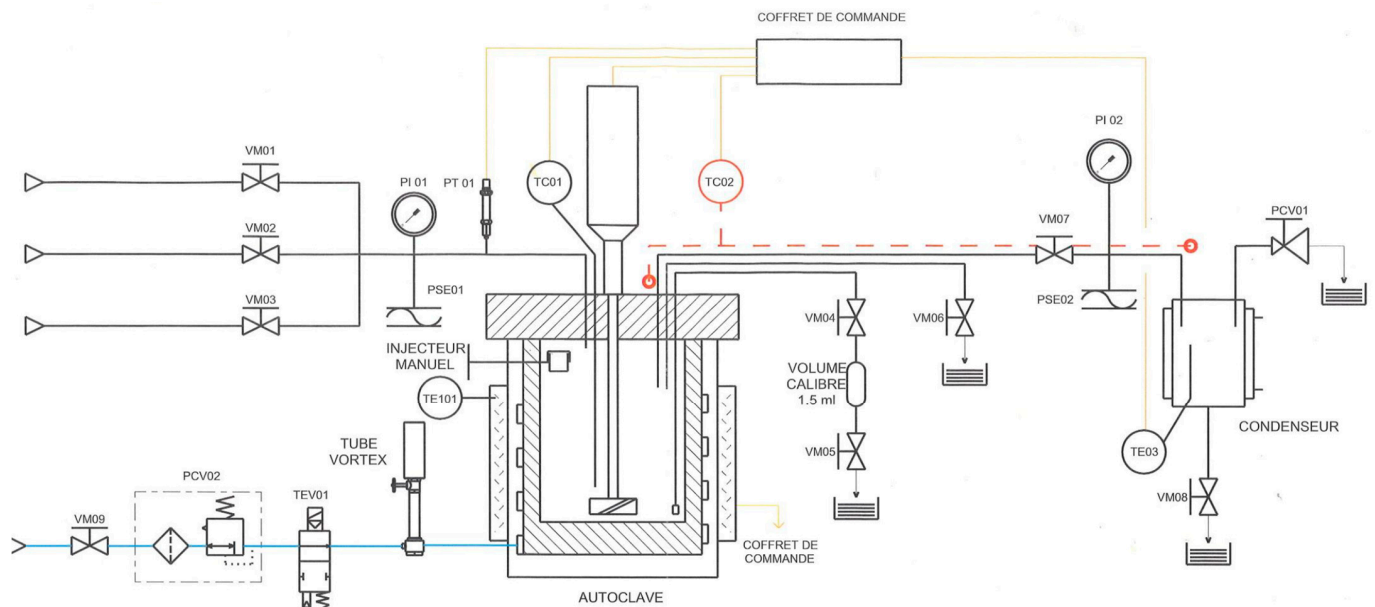


Figure 2. Supercritical water gasification reactor provided by Top-Industrie (France).

Once the reactor reaches the set temperature, 50 g of feedstock is injected with a piston cylinder. During the injection of the feedstock, the temperature in the reactor decreases, and after injection, the temperature increases rapidly (in less than 3–5 min) until the set-point at supercritical conditions (this time represents the beginning of the holding time $t = t_0$, Figure 3).

Once the reactor reaches the set temperature, the plateau (holding time) begins. At the end of the reaction, the reactor is cooled (~10 °C/min) until room temperature (Figure 3). The phases present in the reactor are subsequently analyzed (gaseous, and a solid phase). The composition of the gas is analyzed (by μ GC), followed by the purge of the remaining gas. The reactor is then opened, and the aqueous and solid phases are recovered, separated (by Buchner filtration), weighed, and analyzed.

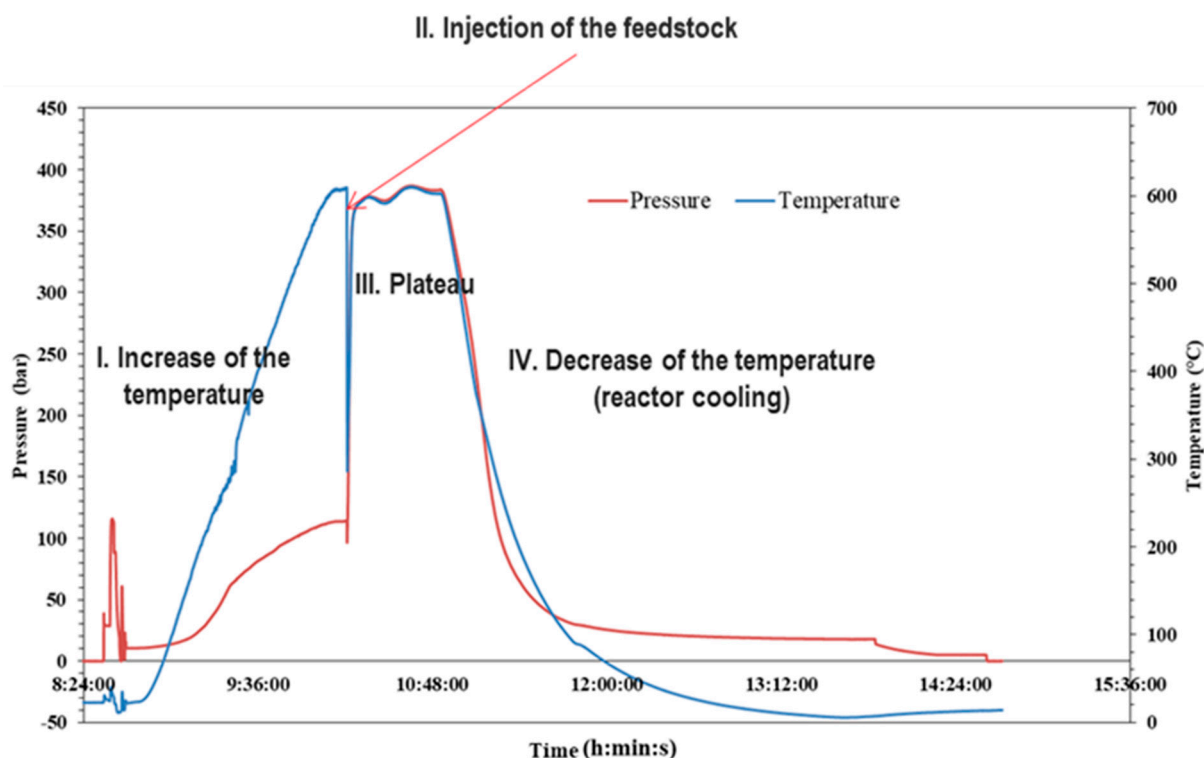


Figure 3. Temperature and pressure profiles of the SCWG process.

3. Results and Discussion

3.1. Characterization of the Feedstock

The feedstock characterization results are presented in Table 1. As expected, the aqueous phase generated during the thermal conversion of black liquor by the hydrothermal liquefaction (HTL) process has a high carbon content (23.7 g/L), which can be valorized for gas production.

The high ash content of the feedstock (32% *w/w*) can be explained by the high amount of sodium contained in the black liquor (obtained from the soda pulping process). For a continuous industrial process, this inorganic content represents a drawback since the salts could precipitate as a function of the operating temperature, clogging the pipes and the reactor. Thus, a previous treatment for removing it from the feedstock is required, which is a scope of ongoing work.

3.2. Effect of the Temperature on the Conversion Yield

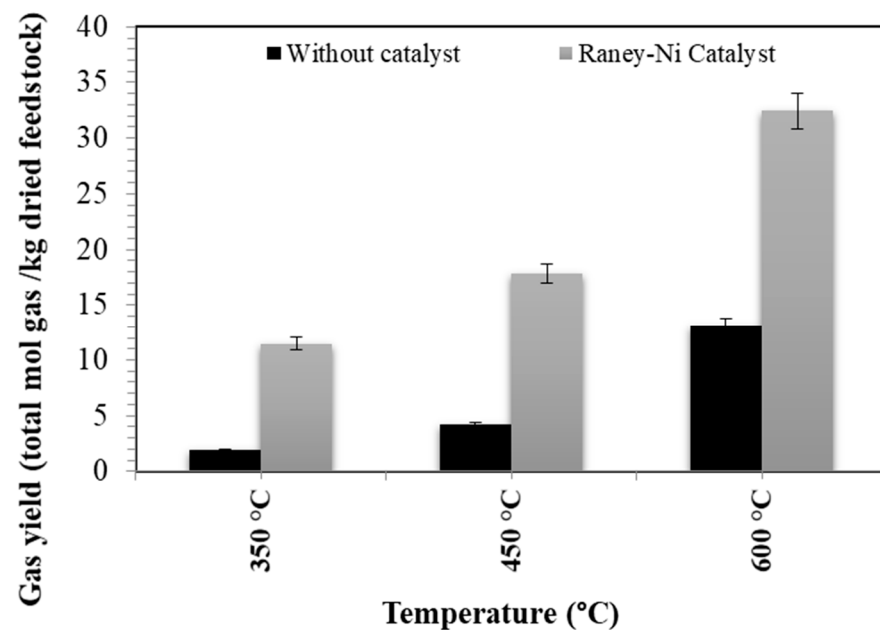
Temperature is an important parameter affecting the conversion yield of the feedstock in the process. The effect of temperature has been studied at three different levels (350 °C, 450 °C, and 600 °C) with and without catalyst at the same holding time (30 min). The results in Figure 4 confirm that at higher temperatures, a major conversion of the organic matter into gas molecules was obtained. The results without catalyst indicated that by increasing the temperature from 350 °C to 600 °C, the gas yield is enhanced (from 1.9 mol gas/kg of dried feedstock to 13.1 mol gas/kg of dried feedstock). This represents an improvement of the gas production of six times higher at 600 °C (without catalyst). These findings are in agreement with those reported in the literature [5,13,14].

The results obtained with the Raney nickel catalyst follow the same trend as those without catalysts (Figure 4). It means that by increasing the temperature, the gas yield is highly improved from 11.5 mol gas/kg of dried feedstock at 350 °C to 32.4 mol gas/kg of dried feedstock at 600 °C, which represents an improvement of the gas production of 2.5 times higher in comparison to non-catalytic process at 600 °C.

Table 1. Characterization analyses of the feedstock.

Parameter	Unit	Feedstock
pH		10.8
Dry matter	% w/w	9.8
Ash content (815 °C)	% w/w db *	32
C	% w/w db *	28.4
H	% w/w db *	2.52
N	% w/w db *	0.22
S	% w/w db *	0.31
Total organic carbon content (TOC)	mg/L	23,692
Total inorganic carbon content (TIC)	mg/L	4658
Total carbon content (TC)	mg/L	28,350
HHV	MJ/kg db *	7.42
Na ⁺ content	mg/L	29,279
NH ₄ ⁺ content	mg/L	24
Mg ²⁺ content	mg/L	2
K ⁺ content	mg/L	149
Ca ²⁺ content	mg/L	5
Cl [−] content	mg/L	160
NO ₃ [−] content	mg/L	<LOD
SO ₄ ^{2−} content	mg/L	546
PO ₄ ^{3−} content	mg/L	27

* db: Dry basis; LOD: Limit of Detection.

**Figure 4.** Effect of the temperature on total gas yield.

Additionally, the gas yield obtained at 450 °C with a catalyst (17.8 mol gas/kg) is higher than that obtained at 600 °C without a catalyst (13.1 mol gas/kg). This means that the catalytic SCWG process allows improved gas production at mild temperature conditions, which is promising for developing this technology on a larger scale.

The gas yields of the experiments are reported in Figure 5, which are compared to those obtained by theoretical calculations (thermodynamic equilibrium). The major species present in the gas are hydrogen, methane, and carbon dioxide. As expected, all yields increase with temperature. Particularly, for the non-catalytic SCWG process, some minor species, such as ethane, carbon monoxide, and ethylene, have been detected and measured in trace concentrations (Figure 5a). The H_2/CH_4 molar ratio is higher at lower temperatures, indicating that hydrogen production is favored from this feedstock; however, the total amount of gas produced at 350 °C and 450 °C is very low (<5 mol gas/kg of dried feedstock). The best gas composition was obtained at 600 °C (5.8 mol H_2 /kg, 4.4 mol CH_4 /kg, and 1.1 mol C_2H_6 /kg).

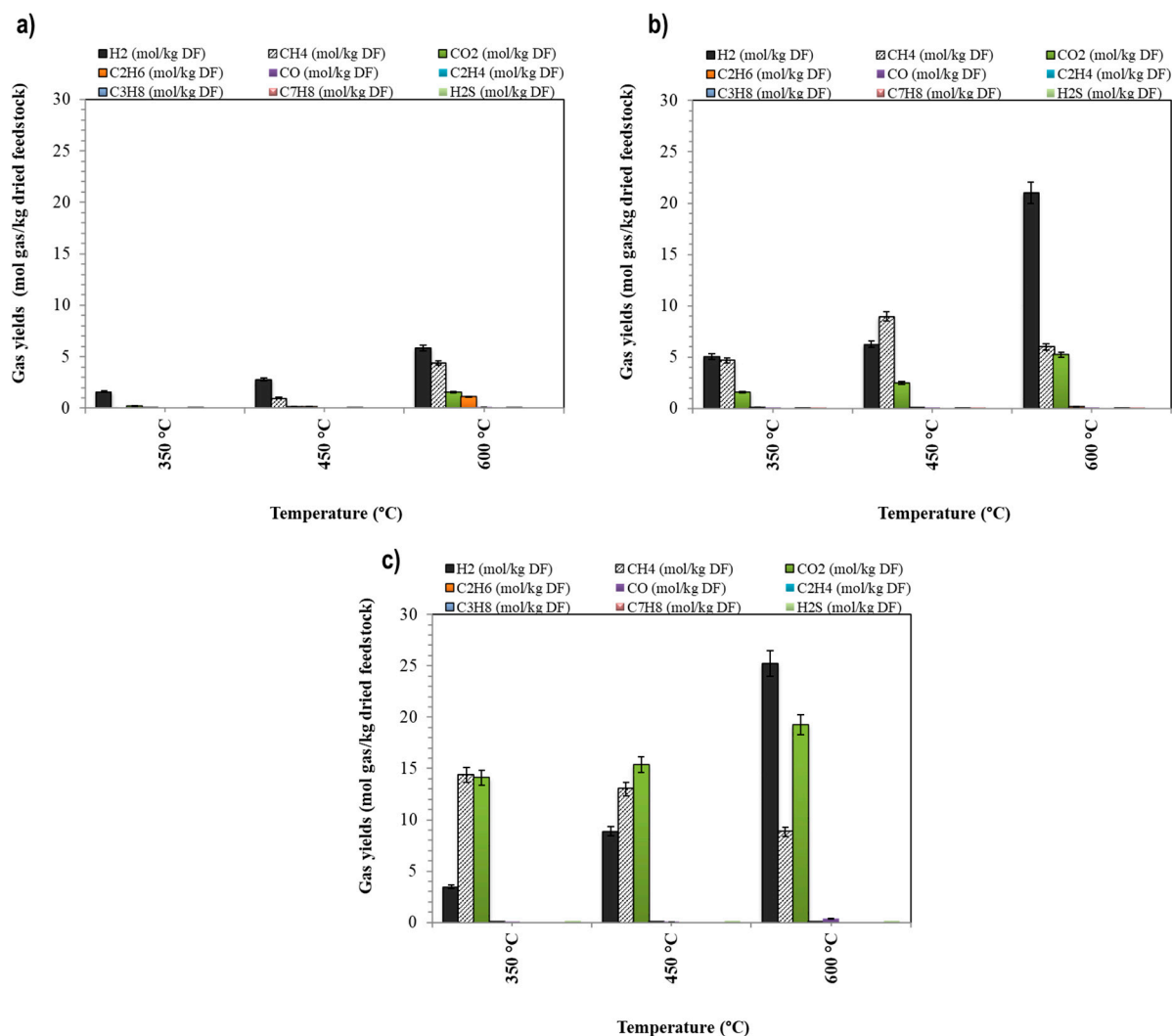


Figure 5. Gas yields: (a) non-catalytic experiments; (b) catalytic experiments; (c) thermodynamic equilibrium calculations.

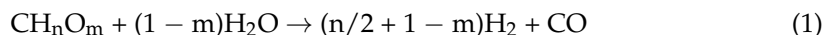
The results obtained by the catalytic process (Figure 5b) are promising since a higher gas amount is produced, containing a greater H_2 concentration. At 600 °C, the compositions are closer to those of the thermodynamic equilibrium (Figure 5c), especially hydrogen and methane compositions. The higher heating value (HHV) of this gas was estimated as 80.2 MJ/kg (excluding CO_2), and the H_2/CH_4 molar ratio was 3.5 (i.e., 21 mol H_2 /kg and 6 mol CH_4 /kg), which is largely greater than that obtained without catalyst at the same operating conditions.

Interestingly, at 450 °C, the H_2/CH_4 molar ratio decreases slightly, and the predominant species is CH_4 (i.e., 6.2 mol H_2 /kg and 8.9 mol CH_4 /kg), which could be due to the

equilibrium shift of the methane reforming reaction. These results (at 450 °C) are also higher than those obtained at 600 °C without a catalyst.

The main reactions involved in the process can be summarized as follows [15]:

Steam reforming



Water–Gas shift (WGS)



Methane reforming



Additionally, many other reactions, such as cracking, chain rearrangements, condensation, decarboxylation, and polymerization reactions, may occur. The decrease of CO formation at increasing temperatures implies that the water–gas shift reaction occurs, and it contributes to the increase in H₂ production. At higher temperatures, endothermic reactions are favored. The biomass reforming reaction is endothermic, and therefore, an increased temperature could enhance the formation of H₂ molecules. Another possible way of H₂ formation is the thermal decomposition of the intermediate compounds [14].

However, the CO₂ concentrations of the experiments do not correspond by far to those obtained by thermodynamic equilibrium calculations (Figure 5c). Gong et al. [15] studied the synergistic effect of NaOH and nickel-based catalysts on hydrogen production from the supercritical water gasification of dewatered sewage sludge. It was reported that NaOH contributes to CO₂ capture, producing sodium carbonate, which shifts the equilibrium of methane reforming reaction and WGS reactions to the production of H₂ molecules. It was reported that the largest hydrogen yield obtained was almost five times as much as without a catalyst. The maximum H₂ yield (4.8 mol H₂ per kilogram of organic matter) was achieved at 400 °C and with a catalyst mix of 3.33% *w/w* of Ni and 1.67 % *w/w* of NaOH. The CO₂-capture reactions reported by Gong et al. [15] are:

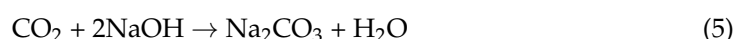


Table 2 shows several H₂ yields reported in the literature obtained by SCWG of different biomasses and wastes. Gokkaya et al. [16] studied the influence of 10% *w/w* K₂CO₃ catalyst on hydrothermal gasification of xylose; they obtained a maximum H₂ yield of 18 mol H₂/kg at 600 °C, 21 MPa, and 60 min of holding time. However, at the same operating conditions without a catalyst, they reported 15 mol H₂/kg, which is a low gain in terms of hydrogen production with a K₂CO₃ catalyst. A similar trend was reported by Chen et al. [17] by catalytic hydrothermal gasification of sewage sludge with a mix of 50% *w/w* K₂CO₃ and 25% *w/w* Raney Ni/Mo₂ at 750 °C, 30 min of holding time; they reported that catalysts have an influence with reaction times but did not contribute to improving the H₂ yield. The maximum H₂ yield obtained was 20.6 mol H₂/kg.

Su et al. [18] reported the study of hydrogen production through SCWG of food wastes, including the influence of different food additives (such as NaOH, NaHCO₃, and NaCl) on the gas yield. The results showed that the increase in temperature improved the gasification efficiency, and the addition of Na⁺ promoted the gas yield and hydrogen production. The maximum H₂ yield obtained was 12.7 mol H₂/kg and a total gas yield of 14 mol/kg at 450 °C by using 5% *w/w* of NaOH. In this work, the maximum H₂ yield was obtained with Raney nickel catalyst at 600 °C and 30 min of holding time, representing 20.98 mol H₂/kg.

It is possible that sodium hydroxide available in the feedstock contributed via a synergetic effect with Raney nickel catalysts towards H₂ production, which is in agreement with Gong et al. [15]. However, a deep study with model compounds for simulating the real feedstock, such as black liquor or agricultural biomasses (with and without NaOH), is being performed to demonstrate the NaOH contribution to the process and will be the scope of a future work.

Table 2. Different biomasses and wastes tested in SCWG.

Feedstock	Operating Conditions	Catalyst	H ₂ yield	Reference
Kraft lignin	651 °C, 25 MPa	Without catalyst	1.60 mol H ₂ /kg lignin	Kang et al. [19]
Paper waste sludge	450 °C, 60 min	Ni/Al ₂ O ₃ -SiO ₂	5.8 mol H ₂ /kg	Louw et al. [20]
Paper waste sludge	450 °C, 60 min	K ₂ CO ₃	7.5 mol H ₂ /kg	Louw et al. [20]
Glucose	750 °C, 28 MPa	Without catalyst	4.78 mol H ₂ /mol glucose	Lee et al. [21]
Xylose	600 °C, 21 MPa, 60 min	Without catalyst	15 mol H ₂ /kg	Gokkaya et al. [16]
Xylose	600 °C, 21 MPa, 60 min	K ₂ CO ₃	18 mol H ₂ /kg	Gokkaya et al. [16]
Timothy grass	650 °C, 23–25 MPa, 45 min	Without catalyst	5.15 mol H ₂ /kg	Nanda et al. [22]
Timothy grass	650 °C, 23–25 MPa, 45 min	3% <i>w/w</i> KOH	8.91 mol H ₂ /kg	Nanda et al. [22]
Alkaline black liquor from wheat straw	650 °C, 25 MPa, 12.4 min	Without catalyst	11.3 mol H ₂ /kg	Cao et al. [23]
Coconut shell	650 °C, 23–25 MPa, 45 min	2% <i>w/w</i> K ₂ CO ₃	4.78 mol H ₂ /kg	Nanda et al. [24]
Dewatered sewage sludge	400 °C, 10 min	3.33% <i>w/w</i> Ni and 1.67% <i>w/w</i> NaOH	4.8 mol H ₂ /kg of organic matter	Gong et al. [15]
Sewage sludge	750 °C, 30 min	Without catalyst	20.66 mol H ₂ /kg	Chen et al. [17]
Sewage sludge	750 °C, 30 min	50% <i>w/w</i> K ₂ CO ₃ 25% <i>w/w</i> Raney Ni/Mo ₂	20.03 mol H ₂ /kg	Chen et al. [17]
Food waste	450 °C, 25 MPa, 60 min	5% <i>w/w</i> NaOH	12.73 mol H ₂ /kg	Su et al. [18]
HTL effluent based on Black liquor	450 °C, 30 min	Raney Ni	6.25 mol H ₂ /kg	This work
HTL effluent based on Black liquor	600 °C, 30 min	Raney Ni	20.98 mol H ₂ /kg	This work

3.3. Aqueous Phase Analyses

The experiments showed a significant reduction of the organic carbon in the remaining aqueous phase obtained after the SCWG process. As expected, the best results were obtained at 600 °C without a catalyst and at 450 °C with a catalyst. As presented in the previous section, the total organic carbon (TOC) content of the black liquor-based feedstock was 23.7 g/L. The results in Figure 6 show that TOC contained in the initial wastewater was almost totally removed/converted at 600 °C (non-catalytic process) and from temperatures above 450 °C in a catalytic process.

However, the total inorganic carbon (TIC) was also favored by increasing the temperatures from 5 g/L contained in the feedstock to 13 g/L at 600 °C. A fraction of this TIC could be attributed to the partial CO₂ dissolution in water, which leads to the formation of carbonate species. The pH of the remaining aqueous phase was slightly basic (between pH 8.3 and 9.3). The change in pH from pH 11 (initial feedstock) to pH 8–9 (aqueous phase) was also observed by Curmi et al. [12], and it was attributed to the partial dissolution of

CO₂ in water, which contributes to the formation of carbonates, increasing the inorganic carbon content (TIC).

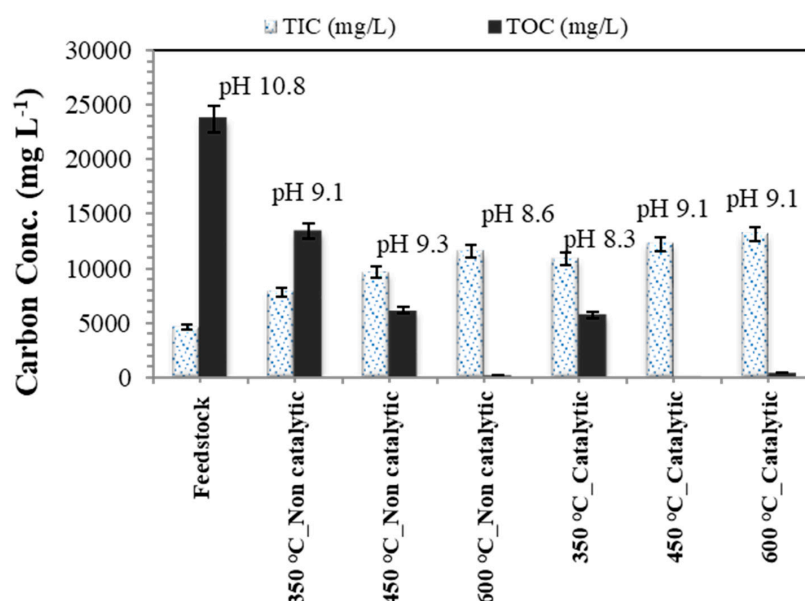


Figure 6. Organic and inorganic carbon contained in the feedstock and in the remaining aqueous phase (after SCWG process).

The removal/conversion of organic carbon (TOC) follows this trend:

Catalytic SCWG (600 °C) > Catalytic SCWG (450 °C) > non-catalytic SCWG (600 °C) > non-catalytic SCWG (450 °C) ~ Catalytic SCWG (350 °C) > non-catalytic SCWG (350 °C).

The carbon analyses on solid and gas phases revealed that at the best favorable conditions (i.e., catalytic SCWG from 450 °C), most of the carbon content was found in the gas composition, representing more than 50% *w/w*. It was found that the Raney nickel catalyst contributes to reducing the char formation at least three times lower in comparison to the non-catalytic process. Thus, the gas phase has a high calorific content since the reactions of methane and hydrogen production are also favored (Equations (1)–(4)). Figure 7 shows the black liquor feedstock before and after SCWG treatment. In summary, it was demonstrated that SCWG could be used as an alternative step for wastewater treatment since the carbon content can be valorized in gas, and the organic compounds in the residual water are converted.



Figure 7. Black liquor-based feedstock, before SCWG (left) after SCWG (right).

The cations and anions concentrations were determined by the ion-chromatography technique. The results in Figure 8 show that the main elements present in the feedstock (before the SCWG process) follow this trend $\text{Na}^+ \gg \text{Cl}^- > \text{K}^+ > \text{NH}_4^+ \sim \text{PO}_4^{3-} > \text{Mg}^{2+}$. It was found that ammonium ions concentration increased ten times, from 24 mg/L (initial feedstock) to 265 mg/L (at 600 °C in the presence of the catalyst). This can be explained by the possible deamination of amine compounds present in the black liquor-based effluent, which conduct the formation of ammonium. Another possible explanation is the so-called HABER process, which is related to the reaction of N_2 with hydrogen to form ammoniac in the presence of nickel and iron (reactor walls effect); this could conduct the formation of ammonium (Equations (7)–(9)):

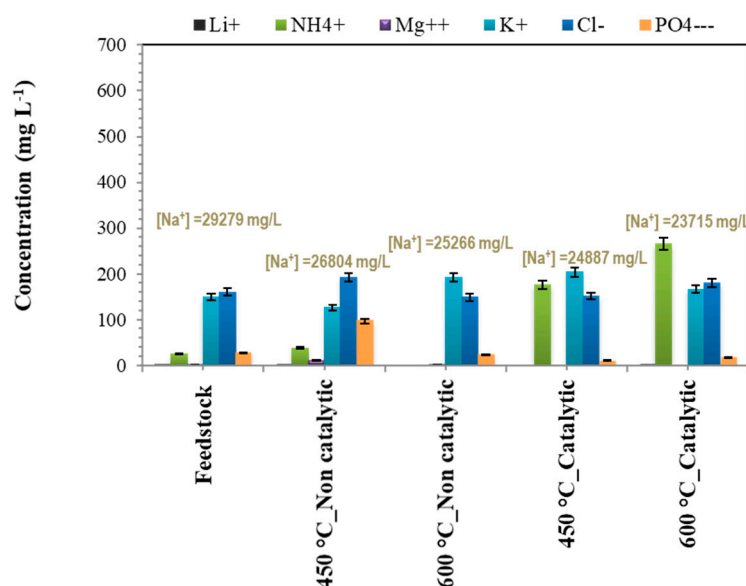
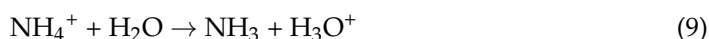


Figure 8. Aqueous phase analyses (cations and anions concentration).

4. Conclusions

This work demonstrates a sustainable approach to convert the carbon contained in the feedstock (aqueous phases from the HTL process) into fuel gases rich in hydrogen via the SCWG process. It was demonstrated that the SCWG process could be used for treating/cleaning the aqueous effluent of the HTL process, and the manufactured gas could be used for energy applications. It makes a significant contribution to the wastewater treatment industry and contributes to the valorization of these carbon resources. The main conclusions of this work are as follows:

- The results confirm that an increase in temperature conditions improves the conversion yield of the evaluated waste.
- The best operating conditions for valorizing the aqueous effluent (from the HTL process) were obtained at 600 °C with a Raney nickel catalyst. The gas yield obtained was 32.43 mol gas/kg of dried feedstock (containing 21 mol H_2 /kg dried feedstock and 6 mol CH_4 /kg dried feedstock). The higher heating value (HHV) of this gas was 80.2 MJ/kg.

- The utilization of a Raney nickel catalyst enhances the H_2/CH_4 molar ratio, which is advantageous for producing gas with a higher energy content (HHV) at lower temperatures (450 °C).
- The characterization results of the aqueous effluent after SCWG confirm the decrease of organic carbon concentration because of the conversion yield into gas molecules. The organic carbon concentration of the wastewater decreased notably after SCWG treatment from $T > 450$ °C with a catalyst.
- The Raney nickel catalyst improves the organic carbon conversion at lower temperatures (i.e., 450 °C), which is the major contribution of this work for decreasing the input of energy to the system and decreasing the process costs (linked to the special alloy materials conceived for operating at higher temperature and pressure conditions).

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Abbreviations

Db	dry basis
DF	Dried feedstock
HHV	Higher heating value
LOD	Limit of detection
SCWG	Supercritical water gasification

References

1. Dafinov, A.; Font, J.; Garcia-Valls, R. Processing of black liquors by UF/NF ceramic membranes. *Desalination* **2005**, *173*, 83–90. [CrossRef]
2. Bajpai, P. *Black Liquor Gasification*; Elsevier: Amsterdam, The Netherlands, 2014.
3. Naqvi, M.; Yan, J.; Dahlquist, E. Black liquor gasification integrated in pulp and paper mills: A critical review. *Bioresour. Technol.* **2010**, *101*, 8001–8015. [CrossRef] [PubMed]
4. Lee, C.S.; Conradie, A.V.; 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. [CrossRef]
5. Chen, Y.; Yi, L.; Li, S.; Yin, J.; Jin, H. Catalytic gasification of sewage sludge in near and supercritical water with different catalysts. *Chem. Eng. J.* **2020**, *388*, 124292. [CrossRef]
6. Correa, C.R.; Kruse, A. Supercritical water gasification of biomass for hydrogen production—Review. *J. Supercrit. Fluids* **2018**, *133*, 573–590. [CrossRef]
7. Sinağ, A.; Kruse, A.; Rathert, J. Influence of the Heating Rate and the Type of Catalyst on the Formation of Key Intermediates and on the Generation of Gases During Hydropyrolysis of Glucose in Supercritical Water in a Batch Reactor. *Ind. Eng. Chem. Res.* **2004**, *43*, 502–508. [CrossRef]
8. Sheikhdavoodi, M.J.; Almassi, M.; Ebrahimi-Nik, M.; Kruse, A.; Bahrami, H. Gasification of sugarcane bagasse in supercritical water; evaluation of alkali catalysts for maximum hydrogen production. *J. Energy Inst.* **2015**, *88*, 450–458. [CrossRef]
9. Azadi, P.; Afif, E.; Foroughi, H.; Dai, T.; Azadi, F.; Farnood, R. Catalytic reforming of activated sludge model compounds in supercritical water using nickel and ruthenium catalysts. *Appl. Catal. B Environ.* **2013**, *134–135*, 265–273. [CrossRef]
10. Yamaguchi, A.; Hiyoshi, N.; Sato, O.; Bando, K.K.; Osada, M.; Shirai, M. Hydrogen production from woody biomass over supported metal catalysts in supercritical water. *Catal. Today* **2009**, *146*, 192–195. [CrossRef]
11. Huet, M.; Roubaud, A.; Chirat, C.; Lachenal, D. Hydrothermal treatment of black liquor for energy and phenolic platform molecules recovery in a pulp mill. *Biomass Bioenergy* **2016**, *89*, 105–112. [CrossRef]

12. Curmi, H.; Chirat, C.; Roubaud, A.; Peyrot, M.; Haarlemmer, G.; Lachenal, D. Extraction of phenolic compounds from sulfur-free black liquor thanks to hydrothermal treatment before the production of syngas for biofuels. *J. Supercrit. Fluids* **2022**, *181*, 105489. [[CrossRef](#)]
13. Yan, M.; Hantoko, D.; Kanchanatip, E.; Zheng, R.; Zhong, Y.; Mubeen, I. Valorization of sewage sludge through catalytic sub- and supercritical water gasification. *J. Energy Inst.* **2020**, *93*, 1419–1427. [[CrossRef](#)]
14. Acelas, N.Y.; López, D.P.; Brilman, D.W.; Kersten, S.R.; Kootstra, A.M. Supercritical water gasification of sewage sludge: Gas production and phosphorus recovery. *Bioresour. Technol.* **2014**, *174*, 167–175. [[CrossRef](#)]
15. Gong, M.; Zhu, W.; Zhang, H.W.; Ma, Q.; Su, Y.; Fan, Y.J. Influence of NaOH and Ni catalysts on hydrogen production from the supercritical water gasification of dewatered sewage sludge. *Int. J. Hydrogen Energy* **2014**, *39*, 19947–19954. [[CrossRef](#)]
16. Gökkaya, D.S.; Sağlam, M.; Yuksel, M.; Ballice, L. Hydrothermal gasification of xylose: Effects of reaction temperature, pressure, and K₂CO₃ as a catalyst on product distribution. *Biomass Bioenergy* **2016**, *91*, 26–36. [[CrossRef](#)]
17. 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. [[CrossRef](#)]
18. Su, W.; Cai, C.; Liu, P.; Lin, W.; Liang, B.; Zhang, H.; Ma, Z.; Ma, H.; Xing, Y.; Liu, W. Supercritical water gasification of food waste: Effect of parameters on hydrogen production. *Int. J. Hydrogen Energy* **2020**, *45*, 14744–14755. [[CrossRef](#)]
19. Kang, K.; Azargohar, R.; Dalai, A.K.; Wang, H. Noncatalytic Gasification of Lignin in Supercritical Water Using a Batch Reactor for Hydrogen Production: An Experimental and Modeling Study. *Energy Fuels* **2015**, *29*, 1776–1784. [[CrossRef](#)]
20. Louw, J.; Schwarz, C.E.; Burger, A.J. Catalytic supercritical water gasification of primary paper sludge using a homogeneous and heterogeneous catalyst: Experimental vs thermodynamic equilibrium results. *Bioresour. Technol.* **2016**, *201*, 111–120. [[CrossRef](#)]
21. Lee, I.G.; Kim, M.S.; Ihm, S.K. Gasification of Glucose in Supercritical Water. *Ind. Eng. Chem. Res.* **2002**, *41*, 1182–1188. [[CrossRef](#)]
22. Nanda, S.; Dalai, A.K.; Kozinski, J.A. Supercritical water gasification of timothy grass as an energy crop in the presence of alkali carbonate and hydroxide catalysts. *Biomass Bioenergy* **2016**, *95*, 378–387. [[CrossRef](#)]
23. Cao, C.; Guo, L.; Chen, Y.; Guo, S.; Lu, Y. Hydrogen production from supercritical water gasification of alkaline wheat straw pulping black liquor in continuous flow system. *Int. J. Hydrogen Energy* **2011**, *36*, 13528–13535. [[CrossRef](#)]
24. Nanda, S.; Isen, J.; Dalai, A.K.; Kozinski, J.A. Gasification of fruit wastes and agro-food residues in supercritical water. *Energy Convers. Manag.* **2016**, *110*, 296–306. [[CrossRef](#)]

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