

# Supercritical water gasification of microalgae: The impact of the algal growth water

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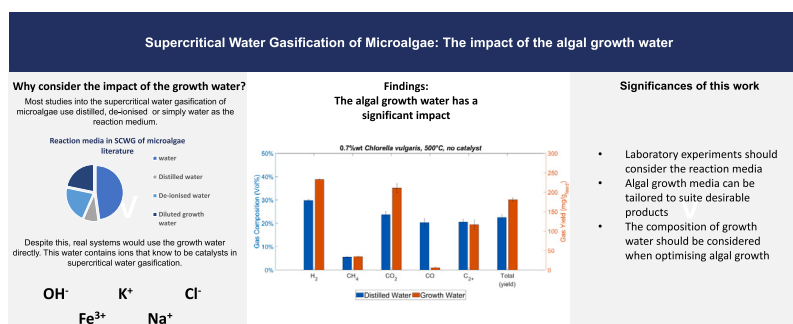
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## HIGHLIGHTS

- Algal growth water has a significant impact on supercritical water gasification.
- CO<sub>2</sub> content in the gas is increased and CO is decreased.
- Effect is likely to be due the presence of potassium ions and a high pH.
- The effect is masked when KOH catalyst is used.
- The impact of the growth water should be considered in future research.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Investigation into the supercritical water gasification (SCWG) of microalgae has largely used deionized water as the reaction medium. However, real systems would use the algal growth water directly, containing ions that have been known to catalyse SCWG (K<sup>+</sup>, Na<sup>+</sup>, OH<sup>-</sup>, Fe<sup>3+</sup>, Cl<sup>-</sup>). Investigation into the effect of the growth water on SCWG was carried out for a range of temperatures (450–550), biomass concentrations (1–3wt%) and catalysts (KOH, Ru/C), using glucose or *Chlorella vulgaris* as the feedstock was performed. A significant increase in CO<sub>2</sub> and reduction in CO content in the gas was observed without a catalyst and with a Ru/C catalyst. An increase in char/tar was also observed without a catalyst. As a result, the impact of the growth water should be considered for the SCWG of microalgae, in laboratory experiments and the selection of algal growth media in industrial applications.

**Abbreviations:** BECCS, Bioenergy with carbon capture and storage; SCWG, Supercritical water gasification; GW, Algal growth water; DW, Distilled water; SCW, Supercritical water; WGS, Water gas shift reaction.

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## 1. Introduction

To achieve decarbonisation targets and limit global warming to 1.5 °C above pre-industrial levels, carbon removal technologies are expected to be key achieving this, of which bioenergy with carbon capture and storage (BECCS) is expected to be a significant contributor [1]. As a result, deployment of new bioenergy projects is rapidly required. However, the production of many biomass sources can come with negative environmental and social impacts. The use of fertilizers causing eutrophication in waterways [2], the use of pesticides [3] and large monocultures [4] are all damaging to biodiversity. Additionally, the

competition for land and fertilizers can have negative impacts on food prices [5].

Microalgae offer an alternative biomass source that can grow 10 times faster than terrestrial plants [6], thus far less land is required. Additionally, they are grown in man-made ponds, meaning arable land or the use of pesticides are not required, and nutrients used are contained so they do not enter waterway. Despite these advantages, the high-water content of microalgae has an adverse effect on the efficiency of conventional energy conversion processes such as thermal gasification or pyrolysis [7]. Therefore, alternative methods of extracting the energy and carbon from the algae is required.

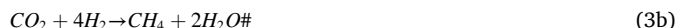
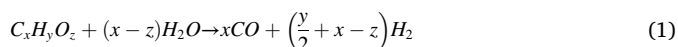
**Table 1**  
Supercritical water gasification of microalgae literature summary.

Feedstocks	Reactor type	Catalysts	Temp (°C)	Pressure (MPa)	Time (min)	Biomass Conc (wt%)	Reaction Media	Source
<i>Spirulina platensis</i>	Batch	Ru/C	399–409	30.8–34.5	60–360	2.5–20 %	Water	[10]
<i>Chlorella vulgaris Scenedesmus quadricauda</i>	Batch	Ru/ZrO <sub>2</sub> Ni/α-Al <sub>2</sub> O <sub>3</sub> Raney nickel	385	26	10–60	5 %	Distilled water	[11]
<i>Chlorella vulgaris Spirulina platensis Saccharina latissimi</i>	Batch	NaOH Nickel/ Al <sub>2</sub> O <sub>3</sub>	500	36	30	5 %	De-ionised water	[12]
<i>Botryococcus braunii Nannochloropsis oculata Tetraselmis chuii</i>	Batch	Nickel NaCl	400	25	10	4.3 %k	De-ionised water	[13]
<i>Chlorella vulgaris</i> Glycerol Amino Acids	Batch and continuous	Ru/TiO <sub>2</sub> NiMo/Al <sub>2</sub> O <sub>3</sub> PtPd/Al <sub>2</sub> O <sub>3</sub> CoMo/Al <sub>2</sub> O <sub>3</sub> Inconel Ni wire K <sub>2</sub> CO <sub>3</sub>	400–650	24–25	0.067–2	7.3–10 %	Diluted growth water	[14]
<i>Acutodesmus obliquus</i>	Continuous	K <sub>2</sub> CO <sub>3</sub>	600–690	28	2.33–2.5	2–20 %	Diluted growth water	[15]
<i>Acutodesmus obliquus</i>	Continuous	None	600–650	28	NS	2.5–5 %	Growth water	[16]
<i>Nannochloropsis gaditana</i>	Continuous	K <sub>2</sub> CO <sub>3</sub> Na <sub>2</sub> CO <sub>3</sub>	663	24	2.13	1,1.16 %	Water	[17]
<i>Chlorella pyrenoidosa</i>	Batch	Ni (Various supports)	430	13–22	60	16.67 %	Water	[18]
<i>Chlorella</i> sp.	Batch, stainless steel	Ni Cu Co Mn Cr All on reduced graphene oxide	380		30	1.4 %	De-ionised water	[19]
<i>Chlorella pyrenoidosa</i>	Batch	Ru/C and Rh/C	380–600	22–55	60	26.6–50 %	Water	[20]
<i>Nannochloropsis oculata</i>	Batch	Ni/γAl <sub>2</sub> O <sub>3</sub> Ni/La-γAl <sub>2</sub> O <sub>3</sub>	400–500	28	15	NS	De-ionised water	[21]
<i>Chlorella vulgaris</i>	Batch	Ru (Various supports)	385	26.2	15–120	5.06–10.12 %	Distilled water	[22]
<i>Chlorella S.P (Increased Carbohydrate content)</i>	Batch	NiO/SiO <sub>2</sub> MnO <sub>2</sub> /SiO <sub>2</sub>	355–405	17.5–26.5	15–45	1–8 %	Water	[23]
<i>Phaeodactylum tricornutumpr</i>	Continuous	Ru/C	425	30	NS	6.5 %	Water	[24]
<i>Chlorella vulgaris</i>	Continuous	None	550	30	2	1.5 %	Diluted growth water	[25]
<i>Chlorella S.P</i> <i>Chlorella S.P (Increased Carbohydrate content)</i>	Batch	None	380	22.5	30	4.9 %	De-ionised water	[26]
<i>Chlorella vulgaris</i> <i>Chlorella vulgaris</i> (oil removed)	Continuous	None	600	25	0.117–1	1 %	Water	[27]
<i>Chlorella pyrenoidosa</i> <i>S. platensis Schizochytrium limacinum</i> <i>Nannochloropsis species</i>	Batch	Pd/C Ru/C Pt/C Rh/C Ir/C	430 °C	22–55	60	25–100 %	Water	[28]
<i>Spirulina</i>	Continuous	None	550–600	23.5	0.067–0.15	17.5–25 %	Water	[29]
<i>Chlorella vulgaris</i>	Continuous	Ru/C	394–420	26–30	Not stated	2.8–14.8 %	Diluted growth water	[30]
<i>Chlorella vulgaris</i> hydrochar	Continuous	None	650	30	2	2.5 %	Diluted growth water	[31]
Various Cyanobacteria	Batch	None	400–500	22	30	NS	Lake Water	[32]
Various Cyanobacteria	Batch	None	350–450	23	0–60	NS	Lake Water	[33]

Supercritical water gasification (SCWG) uses water above its critical point (374 °C and 22.1 MPa) as the reaction medium to form gaseous products ( $H_2$ ,  $CH_4$ ,  $CO$ ,  $CO_2$ , and short chain hydrocarbons). The  $CO_2$  can then be captured, leaving a highly combustible gas stream, which can be used for a variety of energy applications. The use of water makes it appropriate for high moisture feeds such as microalgae and the thermophysical properties of supercritical water (SCW) brings other advantages. The low density and viscosity of SCW increases the diffusivity, thus increasing reaction rates [8]. Additionally, the weakened hydrogen bonds, and low dielectric constant allow organic intermediates formed during the reaction, to dissolve and thus prevent recombination to form undesirable tars and chars [9], which limit operability and reduce gas yield.

The SCWG of microalgal biomass has been widely studied for a range of reaction conditions, catalysts, algal strains, and reactor types. These are summarised in Table 1. However, in most of these cases, the reactor feedstock is prepared by adding distilled, deionised or what is listed as simply water to dry or concentrated feedstocks to produce the desired concentration. This is not representative of a real-life situation as the addition of deionised water would greatly increase the energy requirement and thus reduce the efficiency of the process. The use of the water used to grow the algae as the reaction medium is a far more realistic scenario. The growth water contains ions remaining from the original growth media, many of which have been known to catalyse SCWG ( $K^+$ ,  $Na^+$ ,  $OH^-$ ,  $Fe^{3+}$ ,  $Cl^-$ ) and other ions for which the effect has not been studied. Therefore, this could have a significant impact on the results of the SCWG reaction.

The main gas forming reaction in SCWG are steam reforming, water gas shift (WGS) and methanation [34], outlined in Eqs. (1)–(3) below. Steam reforming and WGS are highly desired as they increase the gas yield and produce more hydrogen in place of carbon monoxide, which is toxic and less desirable as a fuel. Methanation is also less desirable as methane contains carbon, so it is more difficult to apply BECCS to this, though it still remains a useful fuel. At mild conditions, decarboxylation reactions are also significant, producing a gas stream of predominantly  $CO_2$  [11,35].



In addition to these, a number of other reactions occur in the liquid phase, which produce a range of intermediates and can have a strong influence on the gas produced. Using real biomass, such as microalgae, these reactions are complex due to the variety of compounds available. However, analysis has been done on model compounds to help understand these reactions. Glucose is a key compound as it forms the building block of many carbohydrates, which are key components in all biomasses (including microalgae). In SCWG, SCW can break down glucose through C-C bond scission into straight chain or cyclic ketones and aldehydes, which are readily broken down into gas, which is desirable. Alternatively, it can easily dehydrate into furfural and other furans, which can dehydrate further into phenol. Both of these are known to be refractory in SCW and have a greater tendency to polymerise into undesirable tar/char [36,37]. This is summarised in Fig. 1.

This paper investigates the impact of using algal growth water (GW) compared with distilled water (DW) as the reaction medium in the SCWG of glucose and *Chlorella vulgaris*. Glucose gasification was performed without a catalyst for a range of temperatures (450–550 °C) and concentrations (1–3wt%). Glucose gasification was conducted at 500 °C and 2wt% used a KOH and Ru/C catalysts, to study the effect under catalytic SCWG. These were selected as they represent the most common types of homogenous and heterogenous catalysts [38]. Additionally, non-catalytic SCWG of *Chlorella vulgaris* was performed to ensure the effect of using the growth water still applied to algal biomass.

## 2. Materials and methods

### 2.1. Materials

The microalga (*Chlorella vulgaris*) was grown in two parallel 5 L stirred tank vessels, with a working volume of 4 L each (8 L in total). The whole system was sparged with 4 L  $min^{-1}$  of air ( $\sim 0.04\%$   $CO_2$ ). The reactors are constantly illuminated by two panels of white LED lights with a light intensity at the wall of the reactors of 25  $W\ m^{-2}$ . The growth medium used is chu13, which is prepared to the specifications shown in Appendix A, with the pH adjusted to 7.5 using 2 M sodium hydroxide.

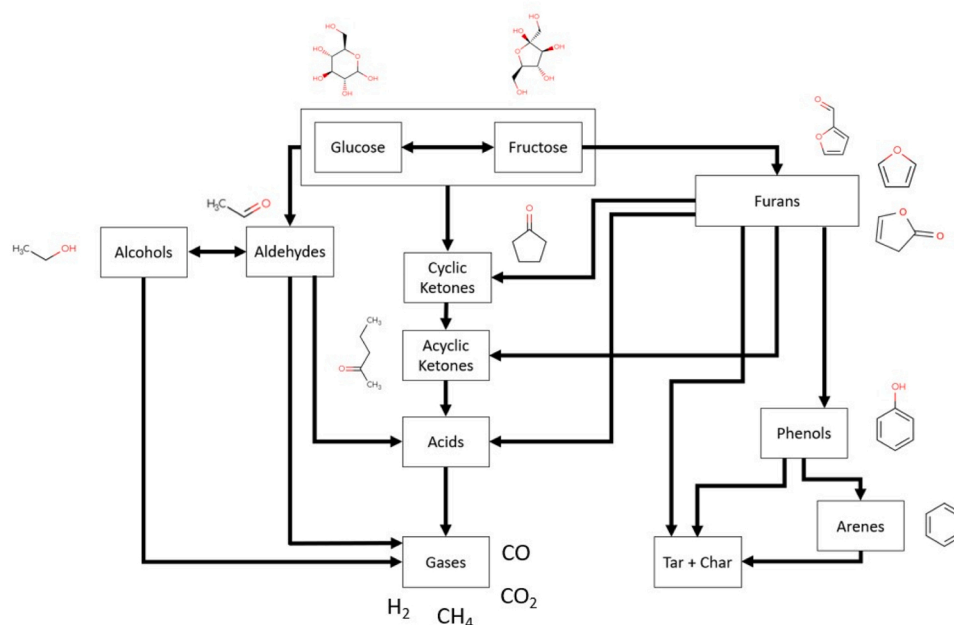


Fig. 1. Reaction pathways of the supercritical water gasification of glucose [38].

The culture was grown for two weeks, with centrifugal separation of algae from the growth medium. The algae was then stored at 4 °C until required and the residual liquid (the growth water (GW)) is autoclaved at 120 °C for 20 min, before storing in darkness at room temperature. No further precipitation of the medium was observed, and the composition of the resulting GW was analysed by ALS Laboratories Ltd. The GW had an average pH of 9.200 mg/l of organic carbon and the composition of ions displayed in Table 2.

The carbohydrate content of the microalgae was measured using the Anthrone method and proteins content was measured using the lowry method both outlined in [39]. The lipid content was measured gravimetrically, following sonication for 1 h at and extraction using a 2:1 mixture of chloroform and methanol. The results of this are displayed in Table 3.

Dry D-glucose (99.5 %) powder was obtained from sigma Aldrich. Potassium hydroxide > 85 % (KOH) was obtained from VWR. Ruthenium (5wt%) catalyst supported on activated carbon (Ru/C) was obtained from Sigma-Aldrich, with an average particle size of 105.6 nm (range of 68.7–169.9). Distilled water (DW) was produced by double distilling tap water in a Cole-Parmer Aquatron A4000D automatic still. Double-lined supeliner gas bags were obtained from Sigma-Aldridge.

## 2.2. Supercritical Water Gasification Reactor Set-Up

The reactor consists of a 25 m coiled stainless-steel 316 pipe with an internal diameter of 3.87 mm (nominal 1/4"), located within a Carbolite Gero LHT oven (max temperature 600 °C), which is maintained at the desired reaction temperature. The feedstock solution is kept suspended using a magnetic stirrer to ensure heterogenous elements (algae or Ru/C catalyst) do not settle and the feedstock is homogenous for the whole experiment. This feed is supplied by 2 Jasco Pu-2086 HPLC pumps, which maintain the desired flowrate to ensure a residence time of 32 s. The flowrate used was 19.4, 20 and 20.914 ml/min for 450, 500 and 550 °C respectively. The reactor exit stream passes through a shell-and-tube heat exchanger to cool it to ambient temperature before flowing through a back pressure regulator (BPR) to maintain the pressure in the reactor and reduce the stream to ambient pressure. The pressure is maintained between 23 and 25 MPa. The fluid stream is filtered before and after the BPR using a 2 µm and 0.5 µm filters respectively, to prevent blockages and solid material entering the liquid product. The filtered stream is admitted to a gas/liquid separator. The gas stream can then be either passed through a bubble column to measure flowrate or collected in a gas sampling bags for analysis. This is shown in Fig. 2.

Initially the oven is allowed to reach the desired temperature; the system is then fed with DW only and the pressure is gradually increased until the required pressure has been met. The correct quantity of feedstock (glucose or microalgae) is mixed with 500 ml of either DW or GW, along with the correct quantity of catalyst (if required) and shaken vigorously to obtain a homogenous mixture is achieved. If microalgae or the Ru/C catalyst is used, the solution is kept homogenous using a

**Table 2**  
Growth water ion composition.

Ion	Average Concentration (mg/l)	Standard deviation
Potassium	220.00	14.14
Sulphate	163.50	189.01
Sodium	68.50	10.79
Chloride	53.75	16.19
Calcium	23.03	3.77
Magnesium	22.25	3.86
Phosphate	4.40	3.29
Iron	2.33	0.36
Zinc	0.21	0.07
Molybdate	0.108	0.013
Copper	0.038	0.008
Cobalt	0.003	0.001
Nitrate	< 7	n/a

**Table 3**  
Chlorella vulgaris composition.

Component	wt%
Carbohydrates	15 %
Proteins	52 %
Lipids	33 %

magnetic stirrer. The feedstock is then fed into the system until noticeable product is seen in the gas/liquid separator. Three flowrate measurements are taken over the 6 min following this, before switching to fill the gas bag until it is sufficiently filled. Samples of the liquid product are withdrawn regularly throughout. Following the reaction, the reactor is flushed with DW for 30 min at reaction temperature before being allowed to cool. All experiments are repeated for each datapoint.

## 2.3. Analysis

The gas product is analysed using a Shimadzu 2014 Gas chromatography with a thermal conductivity detector (GC-TCD) and a 0.35 mm internal diameter, 20 m Shim Carbon ST column to determine the composition of the gas. The liquid product is analysed for total organic carbon (TOC) and which organic compounds were present. TOC was calculated using Spectroquant® TOC Cell test, following a 10x dilution with distilled water. To analyse the organic compounds in the liquid product, they were extracted overnight using a 4:1 ratio of dichloromethane: sample. The extract was passed through a Thermo Scientific Trace1600-ISQ7610 Gas chromatography-mass spectrometer (GC-MS), using helium as the carrier gas and a Restek Rxi-35Sil MS column with a 0.5 µm film thickness, a 0.25 mm inner diameter and 30 m length. The carbon that forms char or tar is calculated for the following equation, where C is the mass of carbon.

$$C_{\frac{char}{tar}} = C_{Feed} - C_{Liquid} - C_{Gas} \quad (1)$$

Inorganic carbon produced through reaction of CO<sub>2</sub> with an alkaline media has been significant in experiments with hydroxide catalysts previously [40]. However, CO<sub>2</sub> absorbed due to the increased pH of the GW was found to be negligible, so was not considered in the carbon balance. Analysis of the iron content in the liquid effluent was analysed using Inductively coupled plasma atomic emission spectroscopy (ICP).

The growth water composition (displayed in Table 2) was analysed by ICP-MS and colorimetric techniques which were performed by ALS Laboratories (UK) Limited, following dilution 10x with deionised water. All tests are repeated once and a two tailed t-test was performed to compare the gas composition (H<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub> vol %) and carbon distribution (carbon in gas, liquid, tar/char) results between DW and GW across the whole data set. A p-value is produced for each output variable, which indicates the probability that the two data sets are different. This identifies if the differences observed when GW is used are significant or can be explained by the error observed in the data. A p-value < 0.05 is seen as significant.

## 3. Results and discussion

### 3.1. Glucose gasification without a catalyst

SCWG of glucose was performed without a catalyst for a range of temperatures (450, 500, 550 °C) at 2 wt% glucose and a range of glucose concentrations (1wt%, 2wt%, 3wt%) at 500 °C. These were completed with either (DW) or (GW) to evaluate the difference effect of the GW at a range of temperatures and glucose concentrations. The composition of the gas product, total gas yield and distribution of carbon in the products are shown in Fig. 3.

These results show a clear decrease in quantity of CO and increase of CO<sub>2</sub> in the gas stream across all the chosen temperatures and glucose concentrations when the GW is used. This is most pronounced when

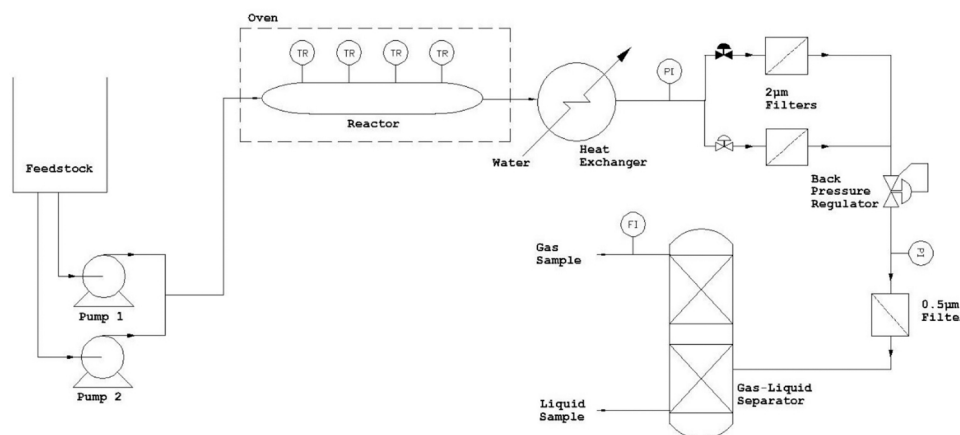


Fig. 2. Experimental set-up. Process flow diagram showing equipment used in the experiments.

conditions favour gasification (low biomass concentration and high temperature), in which the CO concentration falls from  $\sim 30$  vol% with deionised water to  $< 8$  % with the growth water. These differences were shown to have statistical significance as the results of the T-test gave p-values of 0.00001 and 0.0001 for CO and CO<sub>2</sub> concentrations respectively. Increases in H<sub>2</sub>, CH<sub>4</sub>, and total gas were also observed, but they proved not to be significant in these results (p values of 0.54, 0.08 and 0.22 respectively).

A significant increase in CO<sub>2</sub> and decrease in CO with a less significant increase in total gas yield suggests gas phase reactions being catalysed, namely the water gas shift reaction (WGS). Potassium, sodium, and hydroxide ions are all present in the GW, which have been known to catalyse the WGS reaction in SCWG [12,41–43] hence their catalytic influence may be present here. However, an increased WGS would also increase the hydrogen more significantly. Therefore, either the hydrogen is being consumed in subsequent reactions or a different ion in the medium is the cause of this phenomena, or a combination of the two. There are many ions present, many of which have never been specifically studied in SCWG, therefore it is difficult to be certain without further investigation.

There is also a clear decrease in the carbon remaining in the liquid following the reaction and a clear increase in the tar/char produced, when using growth water compared with distilled water. This difference was significant with p values of 0.01 being observed for both carbons remaining in liquid and in the tar/char. A notable increase in tar was observed visually on the filters when growth water is used, indicating the increase in tar/char is predominantly due to an increase in tar. However, further work is needed to quantify the tar and char product separately, as this was not possible with the reactor set-up used for these reactions. An increase in the carbon in the gas was also observed but this increase was found to be insignificant (p value of 0.46).

Analysis of the liquid phase at 2 wt% glucose and 500 °C showed that the quantity of furans (furfural, furones and furaldehydes) was reduced by 85 % in growth water SCWG compared to distilled water. The use of KOH on xylose, a similar compound to glucose, also showed a large reduction furfural compared with non-catalytic runs [44]. However, in that case the tar/char was lower than the non-catalytic example. Additionally, the quantity of phenols in the liquid product increased by 128 % when using GW. Sinag et al. [45], observed similar effect when using KOH as a catalyst in the SCWG of glucose. This shows again, a similar impact to alkali catalysts, indicating the potassium and/or hydroxide ions contribute to the GW effect. However, as outlined later (Section 3.2), this is not the case when using KOH in study.

Furans such as furfural, and phenols are both known to be refractory in SCWG and precursors to the formation of tars and chars [36,37]. Therefore, it would be expected that a decrease in furans observed when GW was used would increase the gas and reduce the tars/chars.

However, an increase in phenols would have the opposite effect. Consequently, the increase in phenols counteracted most of the positive impact achieved through reduced furans. Additionally, the impact on tars/chars from the phenol increase is greater than from the furan decrease. This indicates that phenols are the main precursors for char formation in the SCWG of glucose. This is likely to be a result of the benzene ring being harder to break than the furan ring [46]. This should be considered when selecting a catalyst to minimise residue and thus reduce the potential for blockages in the reactor.

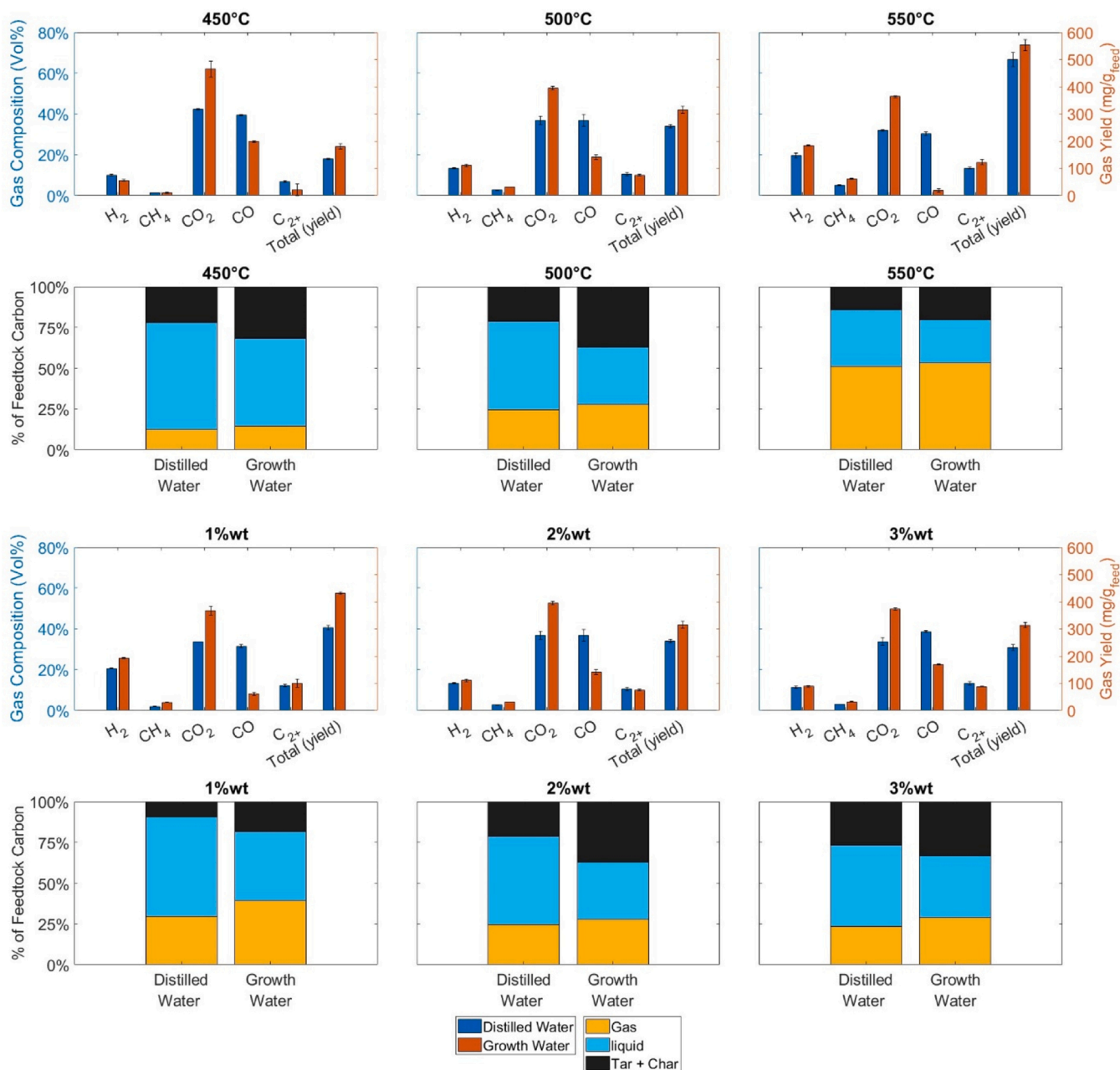
The formation of phenol in the SCWG of glucose has been proposed in two potential pathways. Through the dehydration and ring closure of furfural [47,48] or Diels–Alder cycloaddition of a conjugated diene and unsaturated furanone [49]. In both these cases, phenol is the degradation product of a furan (furfural or furanone), so it is likely the GW catalyses one of or both of these reactions, resulting in a lower quantity of furans. The quantity of furfural was reduced by 95 % but quantity of furone increased 4-fold. Indicating that the ring dehydration and ring closure of furfural was catalysed by the growth water. Additionally, Iron and chloride ions have been found to be effective dehydration catalysts when reacting pentose to form furfural at milder conditions [50]. Both of these are present in the GW and thus could contribute to this effect or the formation of furfural, thus further increasing the total phenol and tar/char.

The GW contains ions that are known to be corrosive to metals, such as OH<sup>-</sup> or Cl<sup>-</sup>, which would be expected to be most significant in the subcritical region when heating or cooling the reactor. In this experiment, no visual effects of corrosion were observed and ICP analysis of the liquid effluent showed a minimal increase in iron content when GW was present, thus the corrosion effects in this case were not noticeable. Nonetheless, the potential corrosive effects of the GW should be considered in reactor design, as differing concentrations of some ions and longer running times could make the effects more significant.

### 3.2. Glucose gasification with a catalyst

SCWG of glucose was performed with either a homogenous catalyst (KOH) or a heterogenous catalyst (Ru/C). The latter was suspended in the glucose solution to ensure a homogenous feedstock. This was carried out with GW or DW as the reaction media to understand if the effects outlined in Section 3.1 still applied when a catalyst is present. The results are shown in Fig. 4.

In the presence of the Ru/C catalyst a similar effect is observed as without a catalyst, a significant decrease in CO and increase in CO<sub>2</sub>. Although, in this case less significant than without a catalyst with p-values of 0.02 and 0.01 respectively. This similarly is due to the catalytic activity of Ru/C being a result of hydrogen affinity, allowing it to catalyse reactions such as hydrogenation and steam reforming [45]. This



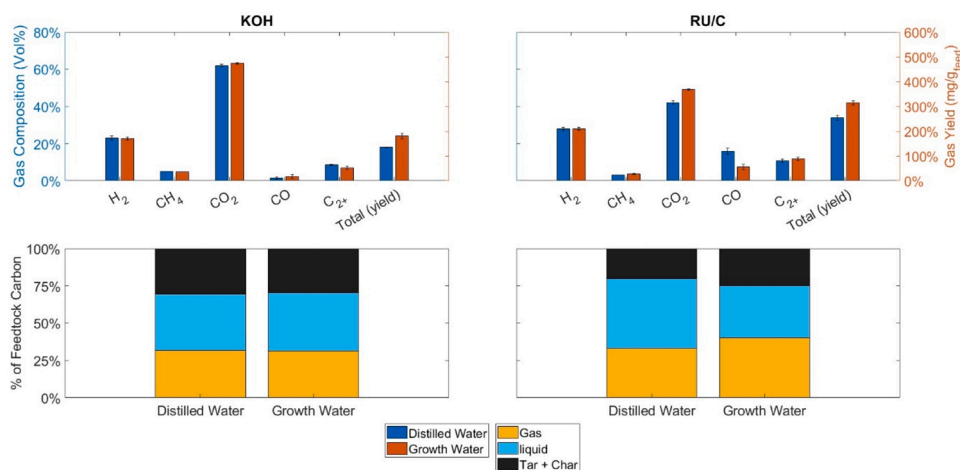
**Fig. 3.** Results of the supercritical water gasification of glucose without a catalyst. In all cases: 32 s residence time, 23–25 MPa pressure. Rows 1,2, 2wt% glucose, temperatures 450–550 °C. Rows 3,4, 1–3wt% glucose, temperature 500 °C.

effect of Ru/C catalysts breaks down the organic components but does not significantly catalyse the WGS reaction, resulting in large quantities of CO when DW was used. Therefore, the catalytic effect of the GW on the WGS reaction is still significant.

With Ru/C catalyst the increase in total gas and carbon in the gas stream in GW compared with DW was significant, with the increase in the total tar/char not being significant. This indicates that the carbon that remained in the liquid phase when using DW as the reaction media, which polymerised to tar/char in GW when no catalyst was present, is converted to gas in GW when a ruthenium catalyst is present. As outlined in Section 3.1, this is expected to be largely made up of furans and phenols, which the hydrogenation activity of Ruthenium is known to be effective at breaking down [45]. A significant decrease in phenol content was observed when Ru/C was present as was established in Section 3.1, proved to be the main driver for char/tar production. Thus, the increased degradation of phenol reduced the effect of GW on the

tar/char. In this study, contrary to some literature [45], furan content increased in with the addition of Ru/C catalyst. Further evidencing phenol being the key driver in tar/char formation in the SCWG of glucose.

In the liquid product, when Ru/C was present, < 1 % of the furans were present when GW was used compared with DW, with an increased phenol content also being observed. However, the phenol content was still > 3 times lower than without the presence of the Ru/C catalyst. This effect was similar to that observed in non-catalytic runs, except with a greater conversion of furans the majority of which, was furfural. As outlined in Section 3.1, the GW catalyses the conversion of furfural to phenols. The greater extent to which the furans are reduced when Ru/C is present can be explained by Le Chatelier's principle as the increased conversion of phenol to gas pushes the equilibrium to the phenol side, thus reducing the quantity of furfural. This can explain why the organic carbon that remains in the liquid phase in DW, was converted to gas with



**Fig. 4.** Results of the supercritical water gasification of glucose with a catalyst. 32 s residence time, 23–25 MPa pressure, 500 °C temperature, 2 wt% glucose, 0.1 wt % catalyst concentration.

Ru/C present but to tar/char without a catalyst in GW. The GW catalyses the dehydration of furfural into phenol which, without a catalyst polymerises into char/tar but is readily gasified in the presence of Ru/C due to the strong hydrogenation activity of ruthenium.

In the presence of KOH, there is no significant difference to the gas composition, gas yield or carbon product distribution. This was carried out at the lowest catalyst concentration observed in the literature [13]. Therefore, in all cases where KOH was used as a catalyst, it is likely that the observed results would be an accurate representation of a real system, despite not including GW as the reaction medium. This concentration is still over 3 times that of the GW thus indicating that the effect of GW is similar to KOH but lower in magnitude, resulting in it being partially masked when both are present. This adds further evidence that the effect of hydroxide (high pH), and/or potassium and sodium ions in the salt are key in the effect of the GW, as proposed in Section 3.1.

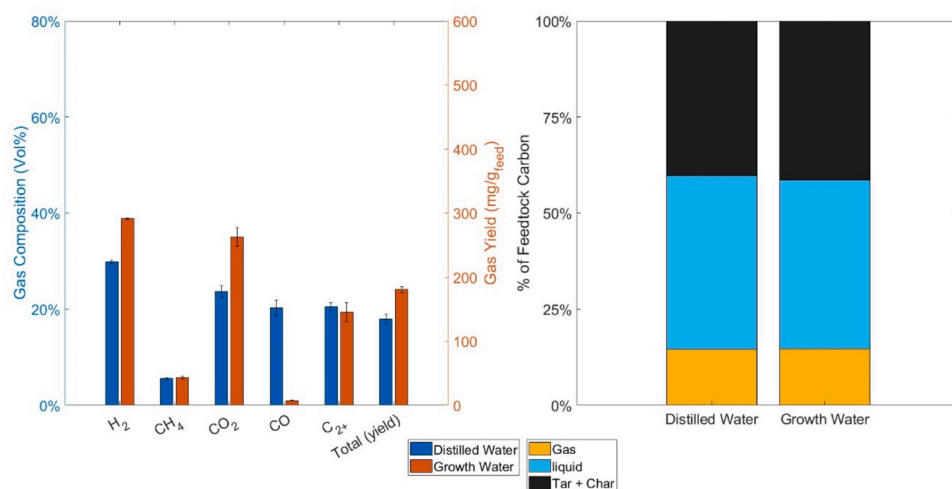
There is no significant quantity of furfural or furaldehyde present in the liquid product when KOH catalyst is used, with DW or GW. As a result, a decrease in both phenol and furan content is observed when using GW compared with DW. This indicates that the dominant driver in the catalysis of the dehydration of furfural to phenol is hydroxide or potassium ions in the GW. Despite this, the quantity of phenol was reduced in the presence of KOH, contrary to what was observed by Sinag et al. [45]. This could be explained by a shift from furfural formation,

towards formation of other intermediates such as aldehydes and ketones, which readily gasified so do not appear in significant quantities in the liquid product. This would explain the increased gas yield in the presence of KOH as they are more readily gasified. This may not have occurred in the experiments by Sinag et al. [45] as their set up was in a batch reactor, with a much slower heating rate, which would significantly affect the intermediates formed in the sub-critical phase.

### 3.3. Microalgae Gasification

Microalgal biomass contains a quantity of inorganic material (similar to that present in the GW) that is released during the SCWG process. Therefore, to verify the above results, gasification runs with microalgae must be conducted for comparison. An algal concentration of 0.7 wt% was suspended in either DW or GW with a temperature of 500 °C. All other conditions matched those in the glucose gasification experiments. The results are displayed in Fig. 5.

In the SCWG of microalgae, the difference between using GW and DW as the reaction media, was even greater than the glucose examples. As with glucose, the CO reduced and CO<sub>2</sub> increased significantly, with the CO almost completely removed when GW was used. Additionally, the impact on hydrogen and total gas yield was greater than glucose, resulting in a statistically significant increase in hydrogen yield (p-value



**Fig. 5.** Results of the supercritical water gasification of *Chlorella vulgaris* without a catalyst. 32 s residence time, 23–25 MPa pressure, 500 °C temperature, 0.7 wt % biomass.

0.001), even at this small sample size. However, unlike the glucose example, the carbon balance remained the same, with no significant change in the gas, liquid or tar/char. This indicates an increase in WGS reaction but minimal impact of the intermediate reaction pathway.

Glucose is a model compound representing carbohydrates, but that only typically represents a proportion (10–15 % [11,26,35]) of *Chlorella vulgaris*. Therefore, the impact on the protein and lipid proportions of the algae is still unclear. This could be explained by the impact on the protein/lipid intermediates being less significant than on the dehydration of furfural. Alternatively, interactions between intermediate products of proteins and carbohydrates are known to produce N-cyclic compounds that are difficult to gasify, form tar/char and are known to be free radical scavengers [36]. Therefore, a possible interpretation is that these reactions dominate in the intermediates and are less impacted by the contents of the GW, thus only the gas phase reactions are notable. This could explain the low gas and high tar/char yields. As a result, it would then be expected that algal strains with higher carbohydrate content would have a greater impact on the carbon distribution, as the impact of the furfural dehydration would be more significant.

Nonetheless, the large disparity in gas composition confirms the significant impact of the GW on the results of the SCWG of microalgae. Thus, it is important to consider when performing lab-based experiments to best understand the process in a real-life context. Furthermore, this analysis was only performed on one growth medium and one microalga, but different algal strains prefer different concentrations of ions, pH (Hydroxide ions) and growth period. Therefore, the impact of the GW on the reaction would vary. Additionally, the hydroxide ions are formed due to the removal of CO<sub>2</sub> by the alga hence may vary depending on gas feed rate, CO<sub>2</sub> % in gas, and growth rate. Therefore, this should be considered when choosing an alga and growth conditions for SCWG, as to maximise favourable products mainly hydrogen and reduce unwanted products, while minimising additional catalysts required. For example, some blue-green alga (cyanobacteria) can be grown at elevated pH [51], which increases hydroxide ions, which were outlined to have a significant impact on SCWG. Although the impact of the differing compositions of the algal strains [52], and impact on the algal growth must also be accounted for when selecting an alga and growth media.

#### 4. Conclusion

The use of algal growth water as the reaction medium has a significant impact on the SCWG of glucose and microalgae when no catalyst or

Ru/C catalyst are used. Specifically, the CO content in the gas is reduced and the CO<sub>2</sub> content is increased, due to the catalytic activity of potassium, sodium and hydroxide ions present in the media on the water gas shift reaction. Hence, when using an alkali catalyst such as KOH, no significant effect is observed when using the growth water. Additionally, the growth water catalysed the dehydration of furfural to phenol, which resulted in an increased tar/char yield in non-catalytic SCWG of glucose. However, in the presence of either catalyst this was not the case. This was due to the activity for the breakdown of phenols by Ru/C and the suppression of the formation of furfural by KOH. Consequently, it is important to consider the GW in laboratory experiments to accurately represent real systems, especially if no catalyst or heterogenous metal catalysts (such as Ru/C) are present. Additionally, this impact should be considered in choice of algal strain and growth media, as to maximise desirable products with reduced catalyst requirements.

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#### CRediT authorship contribution statement

**Bushra Al-Duri:** Supervision, Writing – review & editing. **John Love:** Supervision. **Lynne Macaskie:** Writing – review & editing. **Zain Shah:** Investigation, Visualization. **Rafael Orozco:** Supervision, Writing – review & editing. **Kieran Heeley:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Validation, Visualization, Writing – original draft, Writing – review & editing.

#### Declaration of Competing Interest

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

#### Data availability

Data will be made available on request.

#### Appendix. A-Chu13 composition

**Table 4**  
Ion content of Chu13 growth media.

Ion	Concentration (mg/l)
Potassium	190.60
Sulphate	77.13
Sodium	> 0.0093
Chloride	69.86
Calcium	38.67
Magnesium	20.24
Phosphate	43.61
Iron	4.57
Zinc	0.1
Molybdate	0.74
Copper	0.04
Cobalt	0.009
Nitrate	244.91



## B-Furan and phenol data

Table 5

Quantity of furans and phenols in liquid effluent. 500 °C, 2 wt% glucose.

Group	Compound	GC MS Area (counts)		Relative concentration when GW was used compared with DW (%)
		Distilled Water	Growth Water	
Phenols	phenol	241714	752705	311 %
	methyl phenols	1636312	3482440	213 %
	other phenols	0	37527.87	∞
	total	1878026	4272673	228 %
Furans	furones	88303.85075	447687	507 %
	furanaldehydes	4759544.382	887683.5	19 %
	furfural	6874268	371262.4	5 %
	total	11722115.95	1706633	15 %

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