Review Article

Supercritical water gasification of microalgal biomass for hydrogen production-A review

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HIGHLIGHTS

- A high carbohydrate and low protein content usually favour high H_2 yield.
- Catalysts (alkali salts, ruthenium, nickel) increase conversion and H_2 yield.
- High temperatures, low biomass concentrations increase conversion and H_2 yield.
- Operating conditions have a significant impact but must consider the whole system.
- The inorganic salts remaining after gasification can be used to grow microalgae.

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ABSTRACT

Due to their potential for a high growth rate microalgae are seen as promising feedstocks for hydrogen production, but their high-water content makes them unsuitable for traditional gasification. An alternative method, such as supercritical water gasification, is required to maximise this potential. This review assesses the literature involving the supercritical water gasification of microalgae and other relevant feedstocks. The impact on hydrogen yield, of biomass composition, catalysts, operating conditions, and the integration of the reactor into larger systems are considered. A high carbohydrate and low protein feed is usually preferable for maximum hydrogen yield. Homogeneous alkali metal salts and heterogeneous transition metals are desirable as catalysts. Issues such as recyclability, deactivation, and poor selectivity towards hydrogen production of these catalysts remain problematic. High temperatures and low biomass concentrations are suitable for high yields but require high energy inputs, so may not be advantageous when considering a whole system energy balance.

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Contents

Abbreviations

Abbreviation	Meaning
SCW	Supercritical Water
WGS	Water Gas Shift Reaction
CGE	Carbon Gasification Efficiency
HGE	Hydrogen Gasification Efficiency
SCWG	Supercritical Water Gasification
5-HMF	(5-(hydroxymethyl)furfural)

1.   Introduction

The release of greenhouse gases, largely through the burning of fossil fuels, has significantly increased the average global temperature to 1.2 °C above pre-industrial levels. Unless this warming is limited to 1.5 °C, irreversible environmental tipping points could be crossed and devastating consequences for global ecosystems and communities are foreseen. To prevent the crossing of environmental tipping points, net greenhouse gas emissions must be zero by 2050 [1]. Hydrogen could replace fossil fuels in many applications where electrification is difficult, such as heavy industry and long-distance transport. However, to be carbon neutral, highly polluting methods of hydrogen production that currently produce most of the hydrogen today, such as steam methane reforming, must be replaced. Within these alternatives, biomass-derived hydrogen is an attractive option as it has the advantage of not increasing the strain on renewable electricity production, which would occur with widespread production of hydrogen through electrolysis, while also possessing the potential to be carbon negative if combined with carbon capture and storage [2].

Amongst potential biomass feedstocks, microalgae have excellent potential. A much higher photosynthetic efficiency than terrestrial plants [3] results in a growth rate up to tenfold greater [4] and a correspondingly greater rate of carbon sequestration [5]. This allows more efficient use of the land available, a significant advantage because land use is an area of major concern of bioenergy [6]. Microalgae can also

simultaneously remove harmful metals from the environment [7]. However, the high-water content of algae has an adverse effect on traditional thermal gasification processes due to the significant energy required for drying [8]. Therefore, it is important to consider conversion processes that can handle feedstocks with a high-water content.

Supercritical water gasification (SCWG) involves the conversion of organic compounds to gaseous products in water under conditions above its critical point (374 °C and 22.1 MPa) [9]. The use of water as the reaction medium makes it appropriate for high moisture feeds (like microalgae), while the thermophysical properties of supercritical water (SCW) bring a variety of other advantages. Beyond the critical point, the density and viscosity fall, increasing the diffusivity, thus reducing transport limitations, and increasing reaction rates [10]. Furthermore, the dielectric constant of SCW is significantly lower than that of subcritical water, making it a universal solvent for all organics, polymers and gases whereas the solubility of polar compounds decreases [10]. This allows the organic intermediates formed from the degradation of biomass to dissolve into the water, reducing their chance of recombining to form longer chain tars and chars [11]. Such compounds are usually undesirable as they reduce gasification yield and can block the reactor. Although, the biochar has the potential to be used in Electrochemical Double Layer Capacitors, so may be of value if reactors are designed to capture the solid product [12].

This review aims to summarise the work up to date on the supercritical water gasification of microalgal biomass. It identifies key areas that affect hydrogen production and biomass conversion, drawing on work done on algae as well as other relevant biomass feedstocks. It also looks at potential systems that incorporate SCWG of algae, while maximising their efficiency and reducing waste. This will help to identify areas of further work required to address existing technical challenges and increase the feasibility of this technology.
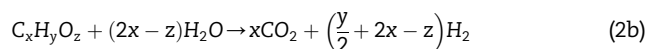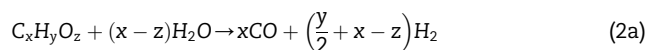
2. Supercritical water gasification reactions

2.1. Main reactions

In SCWG, several reactions occur, both in series and in parallel with each other. The first reaction is the hydrolysis of the longer chain molecules within the biomass into smaller intermediates, as shown B and I in equation (1) respectively. For example, starch is broken down into glucose and protein is broken down into its constituent amino acids [13].

$$B + H_2O \rightarrow I_1 + I_2 \tag{1}$$

The main reactions considered for the gasification of these intermediates are steam reforming, water gas shift (WGS) and methanation reactions, as shown by equations (2)–(4) respectively [14]. The gaseous products are hydrogen (H_2), carbon dioxide (CO_2), carbon monoxide (CO) and methane (CH_4),

$$C_xH_yO_z + (x - z)H_2O \rightarrow xCO + \left(\frac{y}{2} + x - z\right)H_2 \tag{2a}$$

$$C_xH_yO_z + (2x - z)H_2O \rightarrow xCO_2 + \left(\frac{y}{2} + 2x - z\right)H_2 \tag{2b}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{3}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{4a}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{4b}$$

The steam reforming reaction can produce CO (Equation (2a)) [13], CO_2 (Equation (2b)) [9] or both as potential reaction pathways [15,16]. As equation (2b) is equal to 2a followed by the water gas shift reaction, it would be difficult to tell whether the CO_2 arose directly from the steam reforming reaction or via a two-step reaction. Hence, either of them could be the correct pathway. However, equation (2a) must occur as CO is often found as a product if a catalyst is not used [17]. Hence, it is likely that equation (2b) is this combined with the water gas shift reaction. Similarly, a direct formation of CH_4 and CO_2 has also been outlined as a potential reaction [13], which can be explained by reaction 2b followed by 4b, so is not considered here. In some cases, glucose for example, equation (2a) does not contain water at all, which suggests that water is also a product of the reaction which in those cases, is produced at the same rate it is used up. Indicating a catalytic effect of the water.

In practice, SCWG involves several other possible side/intermediate reactions, some of which are discussed in more detail in section 2.2. Multiple sources have reported that at low temperatures, when gasifying different algal strains without the presence of a catalyst, the gas product consists almost entirely of CO_2 [4,18]. Thhydris means that decarboxylation reactions must predominate. The occurrence of short chain alkanes such as ethane or propane, gives evidence of cracking reactions [15], while the formation of chars shows polymerisation reactions are present [16]. A variety of other molecular rearrangements can also occur in the reactor; particularly problematic being dehydration and ring closure reactions to form phenols [19]. Phenols are very difficult to gasify, reducing the gasification of other compounds around them and can polymerise into highly toxic compounds [20,21].

2.2. Reaction pathways

The potential reaction pathways in SCWG for some compounds commonly found in biomass have been studied and evaluated in the literature mainly focusing on lignocellulosic biomass, but some of it is relevant to algal biomass. Microalgae consist mainly of proteins, lipids, and carbohydrates [22], with the total products being a result of their breakdown and the interactions between breakdown products. Reaction pathways of model compounds have been studied and, while the real system will be more complex, this helps to understand some of the reactions that describe the SCWG process.

2.2.1. Carbohydrate gasification

Glucose is commonly used as a model compound for studying the gasification of carbohydrates as it the 'building unit' of carbohydrates and thus is the decomposition product of many major carbohydrates [9]. Fig. 1 shows the reaction pathways in SCWG of glucose outlined in the literature [23,24]. One pathway forms phenols and other aromatics, either directly or through electrocyclic reaction of furans. These are difficult to gasify due to the stability of the benzene ring in SCW, thus are much more likely to form chars, making this route undesirable. To maximise the gas produced, the formation of readily gasified short chain acids, alcohols and ketones, formed through C−C scission of larger ketones, aldehydes, and furans, is preferred. This can be achieved through the addition of catalysts, as discussed later in section 3.2. Despite this, furans such as 5-Hydroxymethylfurfural or furfural are useful chemical precursors in biorefinery processes [25], so the formation of these may be preferred in some cases.

2.2.2. Protein gasification

Proteins commonly hydrolyse in supercritical water to form amino acids and peptides which subsequently undergo further reactions [26] but, compared with carbohydrates, the hydrolysis of proteins is up to 12 times slower and proteins are hydrolysed from the microalgae at approximately half the rate [27]. Possible pathways include the decarboxylation route to form amines and carbon dioxide or deamination to form ammonia and organic acids. These have both been noted extensively in the subcritical region [28−30] and remain the main pathways in the supercritical region [31], and hence are likely to occur in SCWG both during heating and in the reactor.

The stable nature of amines makes that pathway undesirable and the formation of ammonia and organic acids, the favourable pathway for hydrogen production. Additionally, amino acids can react with carbonyl intermediates in the Maillard reaction to form N-heterocyclic compounds such as pyridine [32,33], which are also stable and thus undesirable for gas production. The peptides can hydrolyse into amino acids or decompose into aromatic hydrocarbons, diketopiperazine, aliphatic amines or aldehydes [33]. Many of these are undesirable as they can polymerise into tar and chars [26], which are difficult to gasify and can block the reactor. This pathway is summarised in Fig. 2.

2.2.3. Lipid gasification

Literature on the mechanisms for lipid gasification has been studied less than that for carbohydrates or proteins, however, some work on model compounds to represent lipids has been carried out. Lipids hydrolyse rapidly in sub or supercritical water, to form fatty acids and glycerol. Oleic acid, a model fatty acid, initially decomposes either through decarboxylation or decarbonylation to large aliphatic hydrocarbons, or through the cracking of C−C bonds to form shorter fatty acids. Some of the aliphatic hydrocarbons can rearrange to form cycloalkanes, precursors to aromatic compounds [34], which are undesirable as they can polymerise into tar and chars [26]. Further decompositions of both oxygenated and aliphatic hydrocarbon intermediates into gaseous products also occur, particularly at longer reaction times, at higher temperatures and in the presence of a catalyst [34,35].

The degradation of glycerol in hydrothermal conditions can occur through competing ionic or free radical pathways,
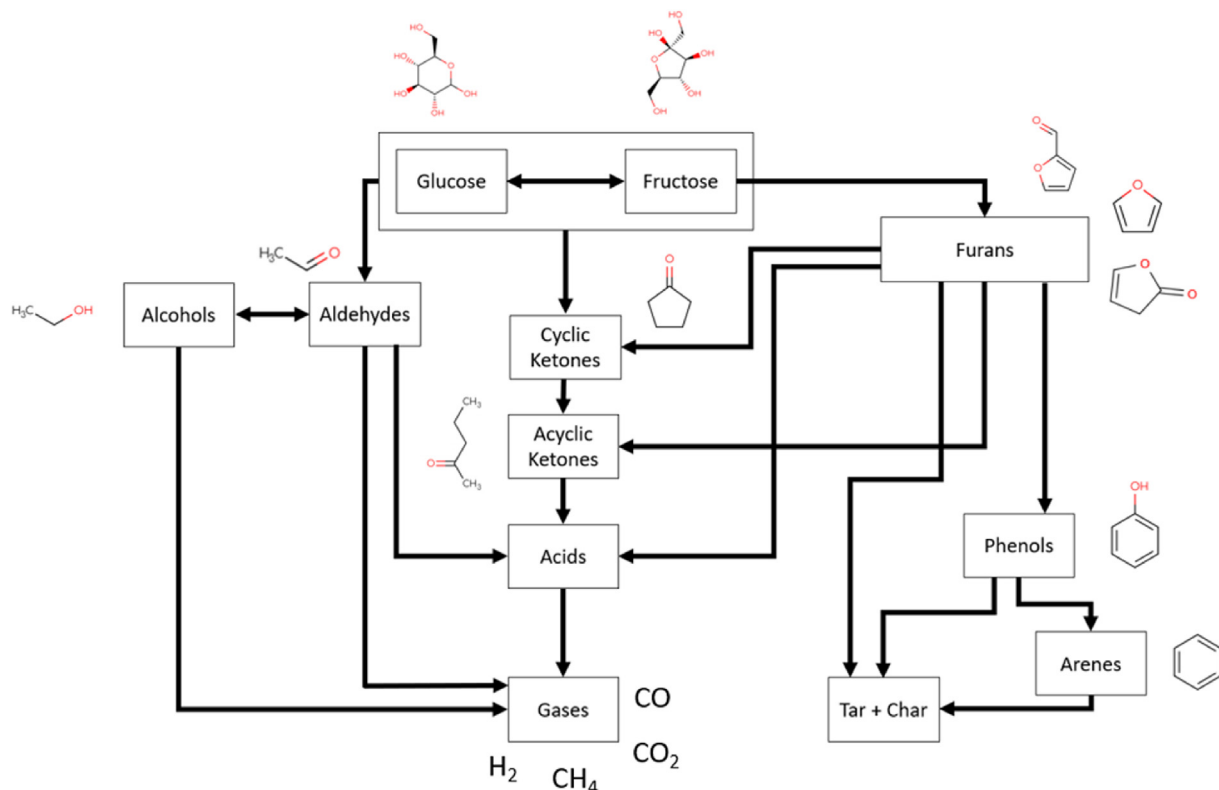

Fig. 1 − Reaction pathways for the supercritical water gasification of glucose [23,26].
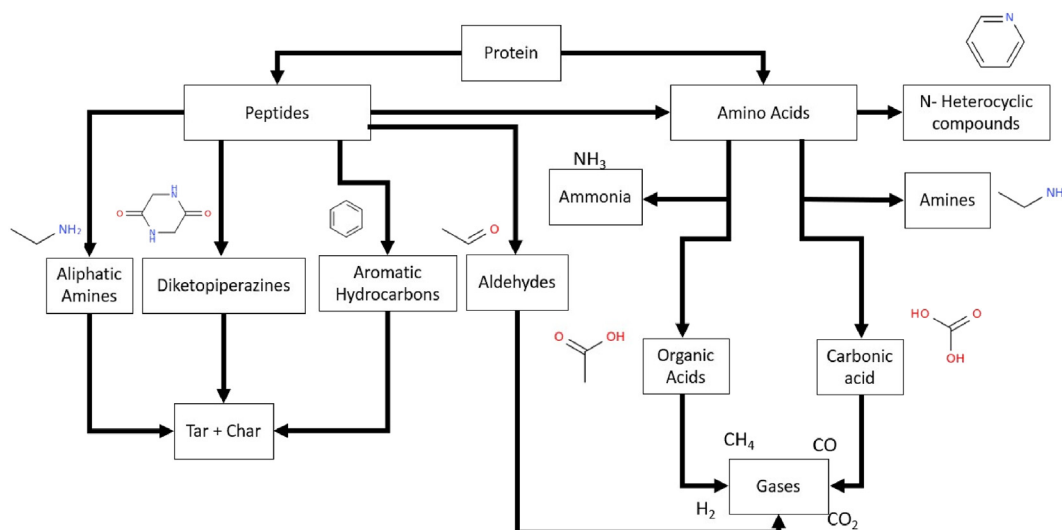
Fig. 2 – Protein gasification reaction pathway. Adapted from [26].

where the reactions are driven by charged ions and molecules with unpaired electrons respectively. Above the critical point, the low ionic product means that there are few ionic compounds available, so the free radical pathways dominate [36]. This makes these the most relevant pathways for SCWG, although some intermediates from the ionic pathways may be present in smaller quantities due to the subcritical conditions during heating. Buhler et al. [36] and Ortiz et al. [37] both outlined the dehydration pathway for free radical dominated gasification. In this, glycerol is dehydrated to either hydroxy acetone or 3-hydroxypropanal. The former then undergoes C—C bond scission, to acetaldehyde and formaldehyde, which decompose further into gas under supercritical conditions, while 3-hydroxypropanal dehydrates further to form acrolein, which decomposes further into ethylene and CO. However, the dehydrogenation pathway, another free radical pathway, would also fit the data observed by Ortiz et al. [37], so further work is needed to fully understand whether either or perhaps

a combination of the two is correct. For hydrogen production, the dehydrogenation pathway would be preferable, as 6 mol of hydrogen are produced per mole of glycerol, compared to just one in the dehydration pathway. These are shown in Fig. 3.

3. Influential factors

The operating conditions and catalysts can all have a significant impact on the reaction pathways discussed in section two and other reactions in a SCWG system, thus impacting upon the composition of the product streams [38], as outlined in sections 3.2-3.6. Moreover, different biomass types have different mixes of biochemical components, all of which react differently in SCW and can have significant interactions with each other, thereby having a substantial impact on the final product [9,22].To produce hydrogen, it is important to maximise selectivity by increasing hydrogen producing reactions
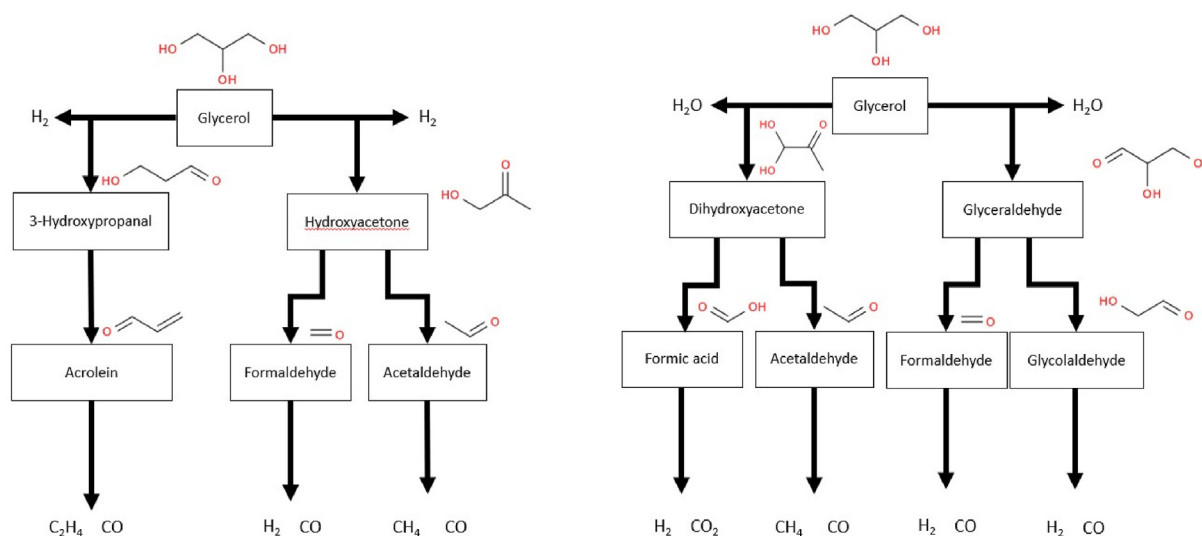

Fig. 3 – Potential free radical reaction pathways for the gasification of glycerol as a model compound for lipids. Adapted from [37].

like steam reforming and WGS, while limiting hydrogen consuming reactions like methanation. It is also important to avoid unwanted, stable compounds, such as char or phenol, that reduce the overall yield and can block the reactor.

3.1. Biomass composition

Microalgae mostly consists of the three groups of compounds: carbohydrates, proteins, and lipids. The precise composition is a function of both the strain and the growth conditions [39], meaning that a wide range of compositions can be found, as shown Table 1. Advantageously, microalgae do not contain lignin, which is known to be particularly difficult to gasify, reducing the conversion and yield of hydrogen in both real biomass and mixtures of model compounds [20,38,40,41].

3.1.1. Effect of protein

As shown in Table 1, some of these strains, such as *Chlorella vulgaris* or *Spirulina,* contain very high levels of protein and are therefore used as a potential alternative protein source in food supplements [46]. For *Chlorella vulgaris*, this protein content was maximised in the fastest growing (exponential) phase of growth [47]. However, this high protein content can be detrimental to the gasification performance. Kruse et al. [48] observed that a high protein feed, mostly chicken and rice, resulted in a significantly lower gas yield than glucose or a plant-based feedstock of carrots and onions. They hypothesised that the amines and aldose sugars formed in protein decomposition react in the Maillard reaction to form relatively stable free radical ions (cyclic N compounds such as pyridine or pyridium [49]), which act as free-radical scavengers, inhibiting the free radical reactions involved in gasification. This same effect was also found in their subsequent experiments when the amino acid alanine or urea were added to glucose both of which form free radical scavenging compounds [50]. Other amino acids, proline and histidine were found to decompose into stable free radical compounds, which would have a similar negative effect on gasification [51,52].

Chakinala et al. [4] found that adding the amino acid alanine to glycerol actually increased the gas produced, though this does not disprove the theory proposed by Kruse

et al. [48]. In the second case, the alanine was added without the addition of an alkali metal salt catalyst. This is significant as the release of ammonia from amino acid degradation catalyses the reaction and can increase gas yield in the same way as the salts [22]. This effect would be lost when the salts are already present, so only the negative effect of the free radical scavenging is observed. In a real system, these catalysts are likely to be present, so the effect of proteins would be negative overall and should be avoided if possible. Moreover, the slower hydrolysis of proteins to the amino acids, compared to carbohydrates and lipids [9], should result in real proteins having a more significant negative impact of gasification than their constituents at shorter reaction times.

As with alanine, Chakinala et al. [4] noted that the addition of another amino acid, glycine, to glycerol increased gas yield. This is a contradiction with Caputo et al. [22] who found that gasifying glycine in its pure form and with glucose, both produced a lower gas yield than pure glucose or the microalga *Nannochloropsis gaditana*. Both had similar reactor setups, with the latter being at a higher temperature (550−650 °C vs 663 °C) and longer residence time (3−12s vs 128s), which are known to increase the gas yield (as discussed in sections 3.3 and 3.5). The main difference appears to be the reactor feedstock. In the first example, a small amount of glycine (0.5%wt) was added to a feed of 10%wt glycerol, while the second was 3% glycine with 1% glucose. As a result, the contribution to the gas from the glycine was small in the first instance, so the difficulty gasifying the latter could be masked by the glycerol and the potential increase in gas produced due to the catalytic effect of the ammonia. Additionally, glucose and glycerol could interact with the amino acid differently and a study with comparable concentrations would be required to determine the extent of this factor.

Despite this discrepancy both papers showed that under the same conditions different impacts can occur from different amino acids. Proline, known for being a free radical scavenger in plant tissue, had a much larger detrimental effect on glycerol gasification than glycine or alanine [4], while glycine was much harder to gasify than leucine or glutamic acid [22]. Under different conditions, this may alter, as some amino acids are less affected by these changes, for example, proline is less

Table 1 − Microalgae compositions.

| Strain	Alga Type	Composition (wt%)			Source
		Carbohydrate	Lipids	Protein	
Chlorella vulgaris	Chlorophyceae (Green)	15	13	50	[4]
Chlorella vulgaris	Chlorophyceae (Green)	10	7	67	[42]
Chlorella vulgaris	Chlorophyceae (Green)	10.	12	65	[18]
Chlorella vulgaris (under light and nutrient stresses)	Chlorophyceae (Green)	61	9	7	[42]
Scenedesmus quadricauda	Chlorophyceae (Green)	43	20	27	[18]
Auxenochlorella pyrenoidosa	Chlorophyceae (Green)	19	21	55	[43]
Porphyridium cruentum	Porphyridiophyceae (Red)	40	8	43	[44]
Nannochloropsis oculata	Eutomatophyceae	8	32	57	[44]
Nannochloropsis gaditana	Eutomatophyceae	12	32	38	[22]
Nannochloropsis oceanica	Eutomatophyceae	28	21	41	[43]
Spirulina	Cyanophyceae (Blue-Green/Cyanobacterium)	20	5	65	[44]
Arthrospira platensis	Cyanophyceae (Blue-Green/Cyanobacterium)	15	6	67	[43]
Synechocystis sp.(low dilution rate)	Cyanophyceae (Blue-Green/Cyanobacterium)	11	66	20	[45]
Synechocystis sp.(high dilution rate)	Cyanophyceae (Blue-Green/Cyanobacterium)	10	62	11	[45]
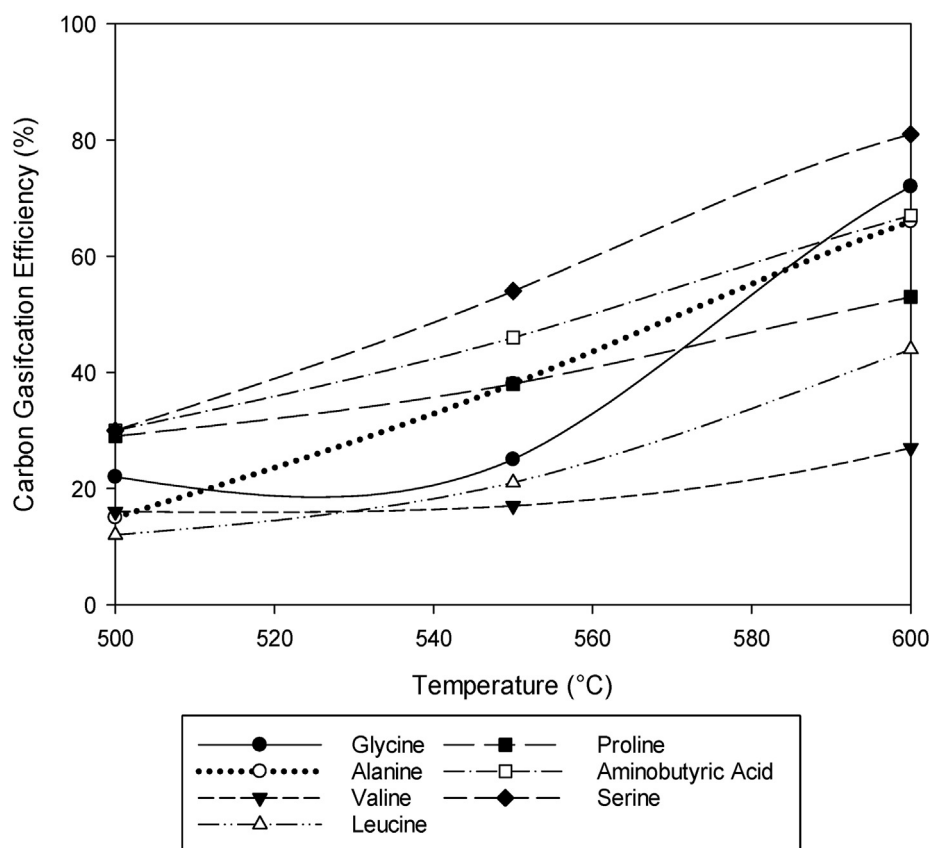
Fig. 4 – Carbon gasification efficiency of different amino acids at varying temperatures. Adapted from [53].

sensitive to an increase in the temperature [53], as shown in Fig. 4. Moreover, the akyl group, which forms the backbone of amino acid valine, caused an increase in hydrocarbon intermediates with more than two carbons, when compared with other amino acids or glucose. These intermediates were effectively converted to hydrogen and methane in the presence of a catalyst [54], resulting in a positive impact on the gas yield. This outlines further complexities that show the effect on the gasification of the protein content will also depend on the composition of the proteins. So, while in general, protein will decrease gas yield, there may be some cases (small amounts of protein, without the presence of alkali metal salts [4]) that 'break the rule' and some that have a larger impact.

3.1.2.   Effect of carbohydrates
When gasifying glucose, albumin and canola oil, at low temperatures without a catalyst, as model compounds for carbohydrates, protein, and lipids respectively, glucose had the highest carbon conversion to gas [18]. The carbon conversion is often stated as carbon gasification efficiency (CGE), defined as moles of carbon in gas/moles of carbon in feed. Without a

catalyst, glucose had a CGE of close to 100% much higher than the three amino acids glycine, leucine and glutamic acid (40−75%) or *Nannochloropsis gaditana* (82%) [22]. This indicates that a higher carbohydrate content in the algae may increase the conversion of biomass into gas and therefore facilitate high hydrogen yields.

Samiee-Zafarghandi et al. [42] found that increasing the carbohydrate content at the expense of protein by altering the growth conditions on *Chlorella vulgaris* increased both conversion and hydrogen content in the gas significantly, as shown in Table 2. Fozer et al. [55] confirmed increasing the carbohydrate content of *Chlorella vulgaris,* through altering the light intensity and dilution rate, increased hydrogen content and total gas yield. Similarly, when comparing *Chlorella vulgaris, Spirulina platensis* and *Saccharina latissimi,* the higher carbohydrate content (in *Saccharina latissimi*) gave a higher CGE and hydrogen content [17]. However, this is not always the case, *Chlorella vulgaris* (high protein) and *Scenedesmus quadricauda* (high carbohydrate) had a similar conversion, with the latter having a higher hydrogen content in the product stream [18]. Jiao et al. [56] found that *Nannochloropsis* sp. had the lowest

Table 2 – Comparison of gas composition, gas yield and gasification efficiency for supercritical water gasification of Chlorella vulgaris with or without increased carbohydrate content. Taken from [42].

Biomass	Gas Composition (mole%)				Gas Yield (mmol/g)	Hydrogen Yield (mmol/g)	Gasification Efficiency
	H_2	CO	CH_4	CO_2			
Chlorella vulgaris with a high protein content	3.95	18.97	1.9	75.18	1.46	0.0577	5.67%
Chlorella vulgaris with a high carbohydrate content	9.42	11.7	0.83	78.05	2.7	0.254	10.25%

carbon conversion despite the highest carbohydrate content, when compared with *Chlorella pyrenoidosa, S. platensis and Schizochytrium limacinum*, but again gave the highest hydrogen content.

There could be several reasons for this disparity. Firstly, as with the proteins, different carbohydrates can also have different CGE and hydrogen yields under similar reaction conditions. Williams and Onwudili [57] found that glucose, starch, cellulose, and a starchy real biomass (cassava) all gave very different conversions and hydrogen yields, even though the materials were all based on glucose. Secondly, Tiong et al. [18] stated the lower tenacity of the cell membrane in *Chlorella vulgaris* than *Scenedesmus quadricauda* as the reason for a higher conversion at short residence times. Factors like this can also be influential, particularly under milder conditions and shorter timeframes, where it may be harder to overcome these effects and break down the biomass. This was the case with the low temperature and residence time in that example or the very high biomass concentration used by Jiao et al. [56]. Finally, in some cases the carbohydrate content is lower, but lipid content might be higher. Lipids are less problematic to gasify than protein, so should not have as great an impact on conversion but may impact gas composition (as noted in section 3.1.3). In all these cases the hydrogen content was increased, and in many cases, conversion was also increased, therefore a higher carbohydrate content is likely to increase the hydrogen yield. Consequently, a higher carbohydrate content is usually preferred for hydrogen production, but not in every case.

3.1.3. Effect of lipids

There is far less literature available assessing the effect of lipids in microalgal gasification or the gasification of lipids in general. This is likely to be a result of the potential for biodiesel production from the high lipid content of some microalgae [58], leading to more research into that area. However, as a key component in most algal strains, it is important to know the impact of lipids on gasification. Nurcahyani et al. [59] compared the gasification of *Chlorella vulgaris* with and without its lipids component, which was extracted using hexane. They found that the original algae had a higher gas yield and lower solid residue, with more methane and less hydrogen than the residual algae (without lipid). A subsequent kinetic study, in the same paper, revealed that when gasifying *Chlorella vulgaris*, the part of the algae extractable with hexane (lipids) produced gas 3.5 times faster than the remaining biomass (mostly carbohydrate and protein). This was confirmed by Jiao et al. [56] who gasified the extracted oil and residual solids from *Chlorella pyrenoidosa*. They found that the oil extracted gave a higher gas yield than the residuals and higher methane content than either the residuals or the original algae. The total methane yield was also higher than the total for the algae or any other algae tested.

These show that the lipid proportion is less resistant to gasification than the remaining solids, which consist of mostly carbohydrates and protein. As discussed earlier, it is likely that protein is the main cause of this lower production, meaning lipids are less resistant to gasification than proteins, being more comparable to carbohydrates. Lipids also have the tendency to produce a large amount of methane, which can be undesirable for a hydrogen production system as it would reduce the selectivity to hydrogen. However, in a system where the methane is used for heating the reactor or chemical looping is used to purify the syngas (as mentioned in section 5), some methane will not be problematic and in that case higher lipid contents would be acceptable. In some cases, a mixture of hydrogen and methane (Hythane), is seen as advantageous when compared with the individual gases [60].

3.1.4. Tailoring growth conditions for gasification

The information detailed above outlines the composition of biomass that would be most suitable for hydrogen production through SCWG. This will influence the choice of algal strain and the growth conditions as both are can significantly affect the final biomass composition. One way in which the composition of the algae can be altered is through nutrient limitation; the way in which an alga responds depends on the strain. As nitrogen is a vital component of proteins, limiting this reduces the protein content [39] and, depending on the strain, increases the content of carbohydrate and lipids in some cases [61,62] but only the carbohydrate content in others [63,64]. Similarly, phosphorus limitation alters the algal composition, but less predictably, reducing the protein in some cases [65,66] and reducing the lipids content in others [67]. In addition to these, limiting micronutrients like iron [68], silicon [63] and sulphur [66], can alter the composition. However, in all these cases, especially under nitrogen and phosphorus limitation, the algal growth was reduced. This would mean a larger area is required to grow the same quantity of algae, creating issues with land use and capital cost. A balance of the growth and composition of the algae, potentially using a two-stage system, should be considered.

One case where the growth wasn't limited was the limiting of calcium, which increased biomass productivity in both the green alga *Chlorella sorokiniana str* [61] and the blue green alga (Cyanobacterium) *Spirulina platensis* [69], while increasing carbohydrate and lipid content. The increased productivity is due to weaker cell walls [61], which facilitated easier gasification of *Chlorella vulgaris* at short residence times [18], which could be beneficial to gasification. Hence, calcium limitation offers the potential double benefit of increased growth and increased gas production, so should be further investigated. The effect of salinity also has potential because for *Spirulina platensis,* increasing salinity increased the carbohydrate content without reducing the growth [69]. However, this is not the case for all strains as the growth can be reduced in some cases [68,70]. Likewise, an increased pH can increase the availability of inorganic carbon which increases growth of strains that can use bicarbonate as a source of carbon [71] but high pH levels are detrimental to the growth of other algal strains that cannot [72]. Being able to operate at higher pH is desirable as the higher solubility of bicarbonate allows a higher uptake of CO_2 from the gas stream [73] and reduces the chance of contamination from other organisms [74]. This should be considered when selecting the alga strain.

Variations in the light intensity can also be used [55], however in outdoor settings the light source is often sunlight so is difficult to control. The use of artificial lights can be used to overcome this but that requires additional input of energy, which will reduce the benefits of the increased hydrogen

production. Considering how to optimise the suitability of a feedstock and the growth of the algae is an important area that can help increase the hydrogen yield per unit of area needed to growth the algae. It should therefore be a key area of further research into the SCWG of microalgae.
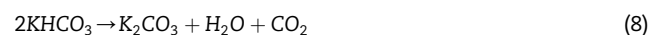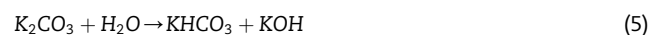
3.2. Catalysts

Catalysts can be used to reduce the activation energy of reactions, hence reducing the operating temperatures and increasing the biomass concentration ranges that could still achieve high conversion and high hydrogen selectivity [75]. A lower temperature can reduce the potential corrosive effects of the medium, reducing the cost of equipment [76], while lower temperatures and higher biomass concentrations reduce the energy losses upon heating the water [77]. Heat recovery systems can reduce the heat losses but not entirely remove them [78]; minimising the heating requirements is still vital. The high costs, both capital and operating, are major barriers to commercialisation of supercritical technologies [79], and hence catalysts will be key to overcoming them. To achieve this, the catalysts should increase the $C-C$ bond cleavage, increasing reactions like hydrolysis and steam reforming that break down the biomass, hence increasing the carbon conversion. They should also increase the WGS reaction, while suppressing $C-O$ bond cleavage (reactions such as methanation), increasing hydrogen selectivity [80] as shown in Fig. 5.

3.2.1. Homogeneous catalysts

Homogeneous catalysts are catalysts that are in the same phase as the reaction media, in this case water. The most common of which for SCWG is alkali metal salts, which have widely been used in the SCWG of various feedstocks for both real biomass (including microalgae) and model compounds. An increase in the CGE is commonly observed, indicating an increase in carbon conversion and therefore increased $C-C$ bond cleavage. Onwudili et al. [17] suggest that nucleophilic attack of hydroxide ions in the subcritical region drives this increased degradation. However, Caputo et al. [22] observed significant increases in CGE with the addition of Na_2CO_3, despite a rapid heating rate and thus a very short time in the subcritical region, so this seems unlikely to be the main driver. More work is required to fully understand the driver behind this in the supercritical region.

Table 3 shows the wide range of biomass feedstocks for which alkali metal salts increase the conversion in SCWG, yet this is not always the case. Glutamic acid (an amino acid) was unaffected both in conversion and gas composition by the addition of the catalyst (Na_2CO_3) [22].This could be attributed to the ammonia being released during the reaction, as with the alkali metal salts, it can create an alkaline environment in water [90]. Consequently, further addition of alkali has a less significant effect on the reaction pathways and thus the gas yield. Onwudili et al. [17] found less gas was produced when gasifying algae in the presence of NaOH than without. This was due to the reaction of CO_2 with NaOH to form carbonates and bicarbonates. This is something that needs to be considered when comparing catalysts, as it could show a low CGE even though the reaction was successfully catalysed, as the carbon could remain in the liquid effluent in inorganic form.

Alkali salts also significantly enhance the WGS reaction, thus having a significant positive impact on hydrogen yield, as shown in Table 3. This is achieved through the reaction of the hydroxide such as KOH reacting with CO, to produce formate, which easily reacts with water to form hydrogen. This creates a more favourable route, thus accelerating the reaction. Equations (5)−(8) show the pathway when K_2CO_3 is added as catalyst, with KOH as an intermediate product. A similar pathway should be also found when other alkali metal carbonates and hydroxides are used [91].

$$K_2CO_3 + H_2O \rightarrow KHCO_3 + KOH \tag{5}$$

$$KOH + CO \rightarrow HCOOK \tag{6}$$

$$HCOOK + H_2O \rightarrow KHCO_3 + H_2 \tag{7}$$

$$2KHCO_3 \rightarrow K_2CO_3 + H_2O + CO_2 \tag{8}$$

Evidence of this is shown with the low (often negligible) CO content and high hydrogen content observed, when alkali metal salts are added to a wide range of biomass and model compounds [22,41,82,83,86,92]. One exception is some amino acids such as glycine and glutamic acid, where the impact of the released ammonia has already progressed the WGS reaction to such an extent that the catalyst has minimal effect on the gas yield or composition [17]. In the case of microalgae gasification, the concentration of ammonia released will be lower, due to biomass containing components (carbohydrates and lipids), making the ammonia produced more diluted
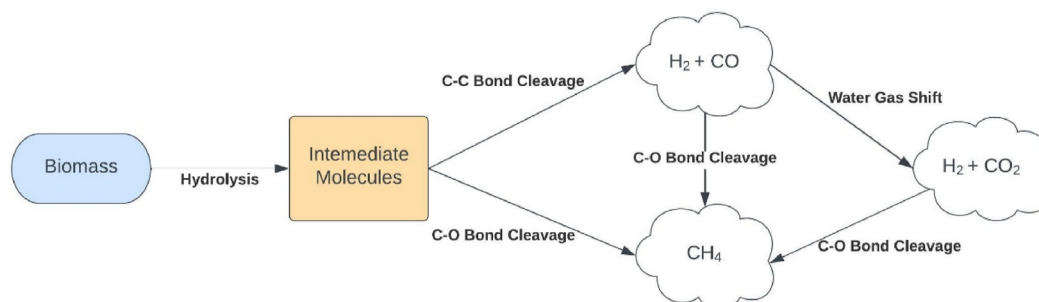

Fig. 5 − Potential products formed from different bond cleavages in supercritical water gasification. For hydrogen production, C−C bond cleavage and water gas shift are diesitable, C−O bond cleavage is undesirable. Adapted from [81].

Table 3 — Akali metal catalysts that increase the carbon gasification efficiency of the supercritical water gasification of biomass feedstocks.

Catalyst	Biomass or Model Compound	Increase in CGE?	Increase in Hydrogen Yield?	Increase in Hydrogen Content in Gas?	Sources
Potassium Hydroxide (KOH)	Sawdust, straw, sewage sludge, lignin, glycine, glucose, catechol, fructose, xylose, cellulose, sugarcane bagasse	All cases, except sugarcane bagasse	All cases	All cases	[82–86]
Sodium Hydroxide (NaOH)	Chlorella vulgaris, Spirulina platensis, Saccharina latissimi, Fructose, sugarcane bagasse	Fructose only	All	all	[17,83,86]
Potassium Carbonate (K_2CO_3)	Nannochloropsis gaditana, Acutodesmus obliquus, sawdust, straw, sewage sludge, lignin, glycine, glucose, catechol, xylose, sugarcane bagasse, cauliflower residue, acorn, tomato residue, extracted acorn, hazelnut shell, glycerol	All but glycine, sugarcane bagasse	All but glycine	All but glycine	[4,22,41,82,84,86–88]
Sodium Carbonate (Na_2CO_3)	Nannochloropsis gaditana, leucine, glutamic acid, glycine	All but glutamic acid, glycine	All but glutamic acid, glycine	All but glutamic acid, glycine	[22]
Trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$)	Cauliflower residue, acorn, tomato residue, extracted acorn, hazelnut shell	All cases	All cases	All cases	[41]
Sodium Bicarbonate($NaHCO_3$)	Sugarcane bagasse	All cases	All cases	All cases	[86]
Potassium Bicarbonate ($KHCO_3$)	Sugarcane bagasse	All cases	All cases	All cases	[86]
Iron Chloride ($FeCl_3$)	Humic acid	All cases	All cases	All cases	[89]

when compared with a similar concentration of pure protein or amino acid. Therefore, alkali metal salts should still have a significant effect.

Alkali metal salts also impact upon the liquid phase reactions; the addition of either K_2CO_3 and KOH produced a lower furan but higher phenol content in the liquid product when gasifying glucose [82,91], as shown in Fig. 6. This could be through rapid conversion of furans into smaller molecules and phenol, or direct conversion of glucose to phenol rather than via 5-HMF (5-(hydroxymethyl)furfural) and other furans. However, phenols are undesirable, and hence this is a disadvantage of these catalysts.

For the different alkali metal salts, while all increase the hydrogen yield, the extent to which this takes place, varies. Except for glycine [22], potassium salts outperformed sodium salts on gasifying a particular feedstock. KOH gave a higher hydrogen yield than NaOH when gasifying fructose [83] and sugarcane bagasse [86], while K_2CO_3 produced a higher hydrogen yield than Na_2CO_3 on sugarcane bagasse [86] and most significantly *Nannochloropsis gaditana* [22]. Additionally, it is often found that in terms of hydrogen yield, they follow the order of hydroxides > carbonates > bicarbonates [86,92]. This would indicate, given the role of formates in the WGS reaction, that potassium salts (especially KOH) more readily produces formates. However, there could be many other factors involved, requiring further work to fully understand it.

The above makes salts ideal catalysts to maximise hydrogen production from SCWG. However, other factors must be considered. Alkali catalysts also catalyse phenol production [92] which, as discussed in section 2, is highly undesirable. They can also increase the corrosion in the system [91], which may mitigate against the reduction in corrosion achieved through lower temperatures. This can also alter the product distribution (as mentioned in 3.2.3). Both increased phenol content and corrosion can limit the ability to recycle the inorganic portions of the biomass to be used in microalgae growth, increasing costs and wastes (see section 4.1). Moreover, the low solubility of salts in supercritical water can lead to precipitation, plugging of the reactor and are much more difficult to recover than heterogeneous catalysts [80]. This results in reduced operability and homogenous increased
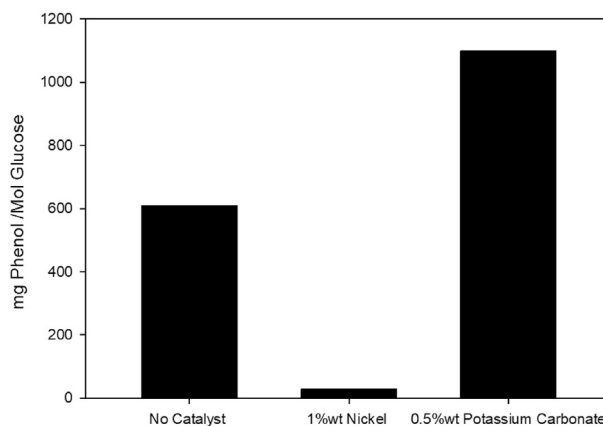
Fig. 6 — Phenol content in the effluent of the supercritical water gasification of glucose. Adapted from [91].

cost due to increased downtime from blockages and frequent supply of a new catalyst for each run. Therefore, to mitigate such disadvantages diligent reactor design is required for catalytic reactions. The use of alloys with a high nickel content or sacrificial liners can help minimise the impacts of corrosion [76] and the use of downflow reactors or hydro cyclone reactors can reduce solid deposition [93,94].

In addition to this, $FeCl_3$ has also been studied for the SCWG of humic acid, as a model compound for the humic compounds sewage sludge [89]. This was found to be more effective at increasing the hydrogen yield and total gas yield of alkali or transition metal catalysts (K_2CO_3, nickel, $ZnCl_2$). Furthermore, a machine learning aided study of literature for SCWG of wet waste feedstocks by Li et al. [95] found that $FeCl_3$ was more effective than other transition metals. Despite this, far less literature is available on these catalysts and further work is needed to study these effects on other feedstocks such as microalgae before a more conclusive picture can be drawn.

3.2.2. Heterogeneous catalysts
3.2.2.1. *Nickel catalysts*. Heterogeneous catalysts form another phase to the reaction media, often a solid in a packed bed or suspended in media. Transition metal catalysts, often supported on another material, are commonly used as heterogeneous catalysts in SCWG. Due to their low cost, nickel catalysts are most commonly used, in pure form or supported on different compounds. nickel catalysts are effective at increasing C$-$C bond cleavage, which results in a higher conversion and thus higher hydrogen yields in most cases. The catalysts used on algae and other biomass feedstocks is summarised in Table 4.

An increased conversion was seen universally for nickel catalysts, when compared with similar reactions without a catalyst. However, the impact on the composition of the gas produced was less consistent than that of the homogeneous catalysts. Sinag et al. [91] stated that the interaction between hydrogen and nickel makes it a good hydrogenation catalyst which would enhance methanation. The hydrogen dissociates on the nickel surface and combines with the carbon to form methane, as shown in equations (9)$-$(11).

$$H_2 \leftrightarrow 2(H)_m \tag{9}$$

$$2(H)_m + C \rightarrow (CH_2)_m \rightarrow (CH_4)_m \tag{10}$$

$$(CH_4)_m \rightarrow CH_4 \tag{11}$$

Where m denotes the entity adsorbed onto the metal. This strong hydrogenation activity also has a significant impact on the composition of the liquid effluent. Far less phenol was present in the gasification of glucose with a Raney nickel catalyst than without [91], as shown in Fig. 6. Given the refractory nature and tendency of phenol to polymerise, reduction in phenol content is likely to be a major contributor to the increased gasification efficiency in the presence of nickel catalysts. On the other hand, the hydrogenation effect would result in a higher methane content and lower hydrogen. Some of the literature reinforces this assertion. Azadi et al. [99] found while gasifying glucose, cellulose and xylan, that increasing the nickel dispersion increased the methane formed and reduced hydrogen selectivity, indicating that nickel does catalyse the methanation reaction. Similar effects were also seen with nickel on activated carbon

Catalyst	Biomass or Model Compound	Increase in CGE?	Increase in Hydrogen Yield?	Increase in Hydrogen content in gas?	Sources
Nickel on Alumina (Al_2O_3), pure and modified with lanthanum or cerium	*Chlorella vulgaris, Scenedesmus quadricauda, Spirulina platensis, Nannochloropsis oculata,* glucose, fermentation stillage, cellulose, xylan, lignin, bark	All cases	All cases except *Scenedesmus quadricauda, Spirulina platensis*	All cases	[17,18,96$-$100]
Nickel oxide on silica (SiO_2)	*Chlorella* sp.	All cases	All cases	All cases	[101]
Nickel on silica-alumina	Oleic Acid	All cases	All cases	All cases	[35]
Nickel on zirconia (ZrO_2)	Switchgrass Biocrude	Not stated	Not stated	Not stated	[102]
Nickel on zeolite	*Chlorella pyrenoidosa*	All cases	All cases	All cases	[24]
Nickel on activated carbon	Xylose, Valine	All Cases	All cases	True when stated	[54,84]
Nickel on graphene oxide	*Chlorella* sp.	All cases	All cases	All cases	[103]
Nickel on hydrotalcite	Glucose, cellulose, xylan, lignin, bark	All cases	All cases	All cases	[99]
Raney Nickel	*Chlorella vulgaris, Scenedesmus quadricauda* Fermentation Stillage, sugarcane bagasse, glucose, fructose, cellulose, xylan, lignin, bark	All cases	All cases	All cases	[18,86,98,99]
Raney Nickel with molybdenum	Sewage sludge	All cases	All cases	All cases	[88]
Nickel wire	*Chlorella vulgaris*	All cases	All cases	All cases	[4]
Inconel powder	*Chlorella vulgaris*	All cases	All cases	All cases	[4]
Ni$-$5132P	Cellulose, lignin, sawdust, rice straw	All cases	All cases	All cases	[104]
Nickel and iron on alumina	*Enteromorpha intestinalis*	All cases	All cases	All cases	[105]

Table 4 $-$ Nickel catalysts used in the supercritical water gasification of biomass feedstocks.

gasifying xylose [84] and when Raney nickel was used to gasify sugarcane bagasse [86]. However, while using nickel on lanthanum-modified alumina when gasifying glucose [96], on yttrium-modified activated carbon when gasfiying valine [54], on zeolite when gasifying *Chlorella pyrendiosa* [24] and on graphene oxide when gasifying *Chlorella* sp [103], the methane content decreased, favouring more hydrogen and CO_2. This indicates that in these cases methanation was suppressed and the water gas shift reaction was favoured, Sinag et al. [91] who claimed nickel increased methanation.

In other works, it was commonly observed that the addition of a nickel catalyst increased both hydrogen and methane. This was the case upon gasifying glucose when Raney Nickel, nickel on cerium-modified alumina and nickel-aluminium-magnesium catalysts, were employed [91,97,106]. It was also true for nickel and molybdenum on alumina, Inconel powder and nickel wire gasifying *Chlorella vulgaris* [4], as well as nickel oxide on silica, gasifying *Chlorella* sp [101]. Moreover, when gasifying cellulose, Ni—5132P catalyst increased the hydrogen in product gas/hydrogen in organic feed (hydrogen gasification efficiency (HGE)) above 100%, showing that the water played a significant role, while also increasing methane [104].

One factor for this is that at milder temperatures decarboxylation dominates, making CO_2 the main product, with little hydrogen or methane [15,107,108]. The catalyst allows other reactions to progress at these conditions leading to further degradation of the biomass and therefore an increase in both hydrogen and methane contents. However, this cannot explain every case and thus suggests that nickel catalysts increase methane forming reactions (such as methanation or cracking of hydrocarbons) and hydrogen producing reactions (such as steam reforming and WGS) reactions, even though, in some cases one dominates, so it can appear to catalyse one or the other. It is difficult to be certain of the reason for why one can dominate in different situations, as a wide range of feeds, supports and operating conditions were used all of which, can significantly impact the gas composition. If this can be used advantageously, nickel catalysts offer a low-cost way of increasing the hydrogen yield and selectivity in SCWG of algal biomass.

3.2.2.2. Ruthenium catalysts. Ruthenium catalysts have also been extensively used to successfully increase conversion and hydrogen yields, with a variety of supports and on a wide range of feeds, including various species of microalgae, as summarised in Table 5. As with nickel, the literature summarised in the table shows the proficiency of ruthenium catalysts at accelerating the C—C bond cleavage. Chakinala et al. [4] compared ruthenium to nickel catalysts and found that nickel was more proficient at increasing CGE. However, they all contained varying amounts of metal, so this was not standardised, making it difficult to draw conclusions. Nguyen et al. [98] did compensate for the quantity of metal, claiming that ruthenium catalysts were superior to nickel at converting fermentation stillage. This is a much more appropriate comparison, especially as they considered industrially available catalysts with the same supports. While this may differ for microalgae, this indicates the ruthenium being the superior catalyst when considering performance. However, the much higher cost of ruthenium (approximately 970 times that of nickel in April 2023 [109]) means nickel may still be more economically viable. The rate of deactivation must also be considered when comparing the catalysts, as discussed in section 3.2.2.4.

Table 5 — Ruthenium catalysts used in the supercritical water gasification of biomass feedstocks.

Catalyst	Biomass or Model Compound	Increase in CGE?	Increase in Hydrogen Yield?	Increase in Hydrogen Content in Gas?	Sources
Ru on alumina (Al_2O_3)	*Chlorella vulgaris, Enteromorpha intestinalis, L. digitata, L. hyperborea, Saccharina latissimi and A. esculenta,* glucose, cellulose, fructose, xylan, pulp, alkali lignin, bark, fermentation stillage, xylose, oleic acid	All cases	All cases	All cases	[23,35,84,98,99,105,110,111]
Ru on zirconia (ZrO_2)	*Spirulina platensis*	All cases	All cases	no	[112]
Ru on charcoal	*Chlorella vulgaris, Phaeodactylum tricornutumpr*	True when stated (*Ch Vulgaris*)	True when stated (*Ch Vulgaris*)	True when stated (*Ch Vulgaris*)	[110,113]
Ru on activated carbon	*Chlorella vulgaris, Chlorella pyrenoidosa, Spirulina platensis, Nannochloropsis species, Schizochytrium limacinum,* glucose, cellulose, fructose, xylan, pulp, alkali lignin, bark, xylose	All cases	All cases except lignin	All cases except *Spirulina platensis*	[56,84,98,99,110,112,114]
Ru and Rh (Rhodium) on activated carbon	*Chlorella pyrenoidosa*	All cases	All cases	All cases	[15]
Ru on titanium oxide (TiO_2)	*Chlorella vulgaris,* switchgrass biocrude	All cases	All cases	All cases	[4,102]

As with nickel catalysts, ruthenium appear to enhance both the WGS and methanation reactions. Ruthenium supported on activated carbon increased hydrogen selectivity when gasifying xylose or *Chlorella pyrendiosa* [15,84], as did ruthenium on graphene oxide, gasifying *Chlorella* sp [103]. However, Azadi et al. [99] found that ruthenium supported on either carbon or alumina, reduced hydrogen selectivity favouring methanation and produced larger amounts of methane. An increase in both hydrogen and methane content was also observed with ruthenium supported on charcoal, alumina and carbon [23,35,110]. This means that, as with nickel, ruthenium can catalyse WGS and methanation reactions. The one example where only methanation was observed, was at a low temperature (380 °C) [99], which suggests that at lower temperatures the catalyst favours methanation. However, as with the nickel catalysts, many other factors make it more difficult to be certain and further investigation is needed.

To achieve a higher gas yield and reduced char formation, ruthenium catalysts have a significant impact on the reaction pathways that form both the intermediates and final products. In the gasification of glucose, alumina supported ruthenium catalysts were found to inhibit the formation of furans, precursors to the formation of phenols, a refractory intermediate which leads to char formation (as shown in Fig. 1). Moreover, the high hydrogenation and C—C bond scission activity promoted the degradation of phenols, which did not occur without the presence of this ruthenium catalyst [23]. However, when gasifying oleic acid, ruthenium on alumina facilitated the diels-alder addition, increasing the phenol content when compared to no catalyst or a nickel catalyst [35]. Hence, for high lipid algae strains, ruthenium catalyst may be less effective.

3.2.2.3. Other transition metals.
Other transition metals have also been tested for the SCWG of biomass. Cobalt-molybdenum and platinum-palladium were both used successfully to increase CGE and hydrogen yield when gasifying *Chlorella vulgaris* [4]. Copper, cobalt, chromium, and manganese were all used successfully when supported on graphene oxide [103]. However, in these cases, they had a smaller impact on hydrogen yield than the equivalent nickel or ruthenium catalyst. Copper nanoparticles were also found to be effective at increasing hydrogen yield from methanol gasification [115]. It would be interesting to investigate if nickel or ruthenium are more effective than copper when in nanoparticle form, given that they are more effective when as part of a supported catalyst, but that has not been tested to date.

In some studies, the higher activity of nickel and ruthenium is less apparent. Cobalt outperformed nickel and ruthenium in terms of CGE when gasifying switchgrass biocrude. However, it did not progress the WGS reactions, leading to large amounts of CO being present in that case and a lower hydrogen yield [102] so would not be suitable for hydrogen production without further alterations. Manganese oxide was more effective than nickel oxide at gasifying *Chlorella* sp, although this can be attributed to the lower activity of nickel oxide compared with nickel metal [101]. Therefore, while other transition metals are effective, the higher activity towards hydrogen production of nickel and ruthenium, means they are still the preferred metals for use in heterogeneous catalysts.

3.2.2.4. Catalyst deactivation.
A major issue with heterogeneous catalysts is deactivation. The activity of the catalyst reduces over time, thus requiring it to be replaced or regenerated to regain the original activity. This is undesirable as it adds cost and complexity to the process, so should be limited as much as possible. Poisoning of a catalyst through the adsorption of a chemical species in the feed, is a common cause. This is often caused by sulphur, which is present in many organic feeds, including microalgae. Peng et al. [114] and Bagnoud-Velásquez et al. [113] found significant sulphur poisoning when gasifying microalgal biomass (*Chlorella vulgaris* and *Phaeodactylum tricornutum* respectively), using a carbon supported ruthenium catalyst. The latter authors found that adsorption had dropped to zero after the reaction, so the activity had been completely lost by the poisoning. The effect of poisoning is shown in Fig. 7 by the rapid drop in CGE observed a short period after switching from a low sulphur feed of glycerol to a higher sulphur microalgae feed [113]. Sulphur was also found to poison copper nanoparticles and nickel catalysts gasifying other feedstocks [99,115]. Techniques to overcome this such as adsorbents before the catalyst [114] or regeneration of the catalysts through oxidation [116] can be used. However, these add downtime and cost to the process, so must be considered when proposing heterogeneous catalysts, especially ruthenium, as an option.

Another common deactivation mechanism is coking, where solid char is deposited on the catalyst, blocks the active sites and hence reduces the activity. Significant coking was found when gasifying *Chlorella pyrendiosa* with zirconia supported nickel catalysts, with the acidic nature of the catalyst being a significant driver [24]. Coking was also experienced with nickel on γ-alumina supports when gasifying glucose [97]. Given the abundance of acid sites (proton donating sites) on γ-alumina [117], this was likely to also be a factor and therefore, supports containing large amounts of acid sites should be
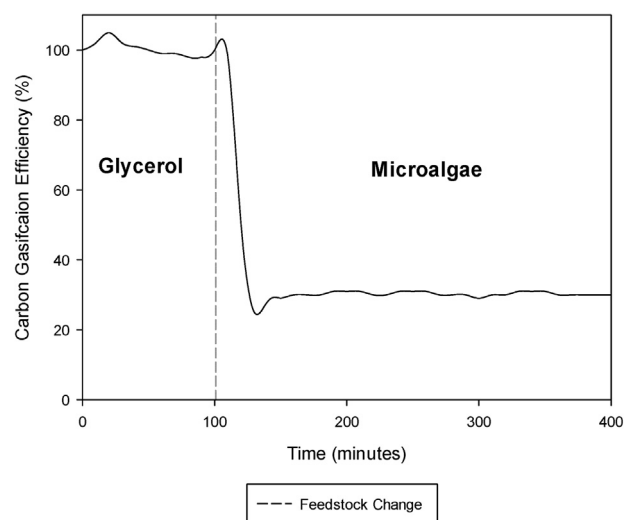

Fig. 7 — Change in carbon gasification efficiency in time on stream of the continuous supercritical water gasification of glycerol and Phaeodactylum tricornutum using an activated carbon supported ruthenium catalyst. glycerol is gasified from time 0—100 min, Phaeodactylum tricornutum thereafter. Adapted from Ref. [113].

avoided to prevent excessive coke build up. Feedstocks such as switchgrass biocrude and lignin both promoted issues with coking, but they are much more susceptible to carbon deposition on the catalyst during SCWG than microalgae so are less relevant in the latter context [99,102].

Irreversible changes to the catalyst can also occur because of the extreme conditions in SCWG. Ruthenium on charcoal catalysts showed a significantly reduced CGE after 3 runs. This was due to metal leaching into the reaction media, reducing the total metal available from the catalyst [110]. This effect is also detrimental the recovery of inorganic nutrients (as mentioned in section 4.1). Alternatively, Raney nickel, nickel on alumina and nickel on zirconia, all showed an increase in nickel crystal size [24,98]. This reduces the active surface area of the metal, lowering the activity. The effect was outlined by Xie et al. [24] where the hydrogen yield fell with each run of a nickel on a zirconia support when gasifying *Chlorella pyrenoidosa*, even when the coke was removed. Nickel has also been shown to react with the alumina support, reducing its surface area and activity [96,100]. These are all examples of the catalysts being unstable at supercritical conditions, with nickel catalysts being particularly problematic. This would mean replacing the catalyst more frequently, without being able to easily regenerate them. While this is a significant barrier, the lower cost of nickel catalysts may make them still more economically viable than the ruthenium alternatives.

3.2.2.5. Effect of the support. As well as the active metal, the support can play a major role in the gasification reaction.

Many materials used in support can be used as catalysts for SCWG. Activated carbon has been used to successfully increase the CGE on sugarcane bagasse [86], valine [54] and glucose [118] with the source of the activated carbon significantly affecting its performance. Similarly, zirconia was found to increase the conversion of glucose and cellulose, while also increasing the WGS reaction [119]. Titanium dioxide also increased hydrogen yield, if combined with calcium oxide [38]. While these catalysts were less effective than the alkali metal salts and transition metal catalysts mentioned previously, they show how support material can contribute to the overall performance of a catalyst.

This is evident in the significant variation in CGE between different forms of alumina and carbon supported ruthenium catalysts gasifying *Chlorella vulgaris* where γ-alumina and charcoal outperformed α-alumina and activated carbon, converting approximately 20% more carbon to gas. Moreover, the CH_4/CO_2 ratio in the products, significantly varied, indicating differing methanation performances. This shows that, despite changing with different conversions, the CH_4/CO_2 ratio is always higher for γ-alumina than charcoal supported catalysts, indicating the enhancement of methanation with γ-alumina supported catalyst [110], as shown in Fig. 8. Additionally, lanthanum-modified alumina supports were found to adsorb CO_2, which impacted the gas composition in glucose gasification [96]. This shows that the support is a factor in the disparity between ruthenium catalysts in terms of gas composition (as observed in section 3.2.2.2). Xie et al. [24] provided further evidence to the support impact, showing that
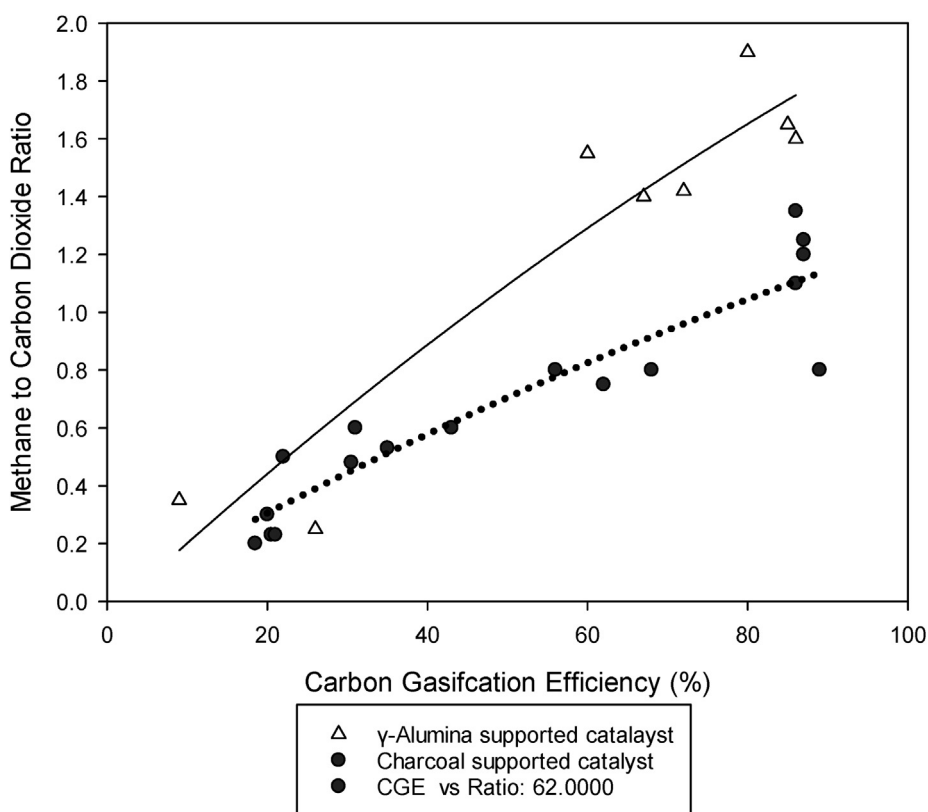

Fig. 8 — **Methane-carbon dioxide ratio at different total carbon gasification efficiencies during the supercritical water gasification of chlorella vulgaris using ruthenium catalysts with different supports. Adapted from [110].**

the zeolites with more strong acid sites had a higher CGE and HGE when supporting nickel in the gasification of *Chlorella pyrendiosa,* despite the same quantity of metal.

The support material can significantly impact upon the favourability of different reaction pathways, a major contributing factor for the impact on overall gasification performance observed. When gasifying the amino acid valine in the presence of activated carbon as catalyst or support for nickel, no nitrogenous organic compounds were observed. This indicates that the decarboxylation route is suppressed, favouring deamination to form ammonia and organic acids. As these acids are more easily gasified than nitrogenous compounds such as amine, the CGE increased in the presence of activated carbon [54]. This could mitigate the negative effects of protein content on gasification (see section 3.1.1), thus activated carbon catalysts are desirable for high protein feedstocks such as many species of microalgae. Moreover, this would allow algae to be grown in the exponential phase, where the protein content is higher [47], with a reduced detrimental effect on the hydrogen yield and therefore a reduced land requirement.

The supports can also play an important role in the deactivation of the catalyst. The nature of the catalysts such as number of acid sites (see section 3.2.2.4) or the interaction between the metal and support, can significantly affect deactivation. Modifications can be attempted to minimise this. Modifying alumina supports with lanthanum reduced the interaction with nickel, hence reducing deactivation through sintering, which allows more active metal to be available for longer, increasing the activity [96,100]. Similarly, modifying activated carbon with platinum or palladium reduced crystallisation of nickel, which reduces the active surface area and therefore deactivates the catalyst [54]. Modifying alumina with cerium oxide also limited deactivation by reducing the coke deposition and lowering the temperature needed to remove the easily removable coke, allowing easier recycling of the catalyst [97]. However, these modifications will increase the costs of the catalyst. It is important, when choosing a catalyst support, to balance the need for increased hydrogen yield and reduced deactivation, with the cost of the catalyst.

3.2.3. Catalytic wall effects

Nickel based alloys, including Inconel, are often used in SCWG, due to their high resistance to corrosion, high strength at elevated temperatures and resistance to hydrogen embrittlement [76]. Chakinala et al. [4] observed that Inconel powder or nickel wire at elevated temperatures had a significant positive impact on both the CGE and the yield when gasifying the microalga *Chlorella vulgaris*. Therefore, it is likely that the reactor wall will have an impact on the reaction, which must be considered. While, to the authors' knowledge, no work has been carried out to investigate this effect on microalgal gasification, other relevant work studying the effects of the wall material has been carried out.

Yu et al. [120] observed a higher hydrogen yield in an Inconel tubular reactor than in an identical Hastelloy reactor, for the SCWG of acetic acid or glucose. When the Hastelloy reactor was corroded with potassium chloride, the hydrogen yields increased. However, it is better to compare the new (uncorroded) reactors as it is hard to differentiate whether this is due to an increased surface area, or the salts being released which also catalyse the reaction. Castello et al. [121] compared stainless steel and Inconel 625 batch reactors for the gasification of glucose and beech sawdust. They found that the Inconel reactor produced a higher gas yield, with a higher methane and lower hydrogen yield, indicating enhanced C–C bond scission and methanation, when compared with the stainless-steel reactor. Additionally, they found that beech sawdust was less affected than glucose, due to the natural salts within the biomass dominating the wall catalytic effect. Microalgae, like sawdust, contain natural salts, so the impact of the reactor walls is expected to be less significant. However, the results described above identify that the wall can have an effect, which should be considered if comparing results from different reactors.

3.3. Temperature

Temperature is a major operating condition, which has the most significant impact on the reactions in SCWG [95], strongly affecting the biomass conversion and product distribution in the gas. The overall reaction to form hydrogen and CO_2 from biomass (equation (2b)) is endothermic (346 kJ mol^{-1} for glucose), while the overall reaction to form methane (equation (2a) followed by 4a) is exothermic (-148 kJ mol^{-1} for glucose) [105,122]. According to Le Chatelier's principle, higher temperatures favour the formation of hydrogen and suppress methane [123]. Thermodynamic models of microalgae and other biomass also agree with this, stating that at equilibrium, a higher temperature increases hydrogen concentration and reduces methane concentration [77,124–126]. The models also predict that the solid carbon produced is also reduced at higher temperatures [124], which increases CGE and reduces negative effects of plugging or catalyst deactivation.

The models listed above only include the equilibrium conditions and do not consider the kinetics. Guan et al. [16] modelled the kinetics of SCWG based on experimental data where *Nannochloropsis* sp. was gasified at temperatures ranging from 450 to 550 °C (723–823K). This showed that increasing the temperature increases the CGE and the total energy in the product gases. Increasing temperature always increases the reaction rate and leads to shorter reaction times. However, this study showed that the higher conversion was seen obtained at longer reaction times too. This was attributed to temperature having a larger effect on the rate of formation of intermediates less resistant to gasification, reducing the biomass converted into the recalcitrant intermediates such as phenols, which are difficult to gasify, and are more likely to polymerise into chars, reducing the overall conversion. These models show that, in theory, a higher temperature is preferred to maximise the hydrogen yield from microalgal SCWG.

In real systems, Chakinala et al. [4] (see Fig. 9), Duan et al. [15] and Zhang et al. [108] all observed that without a catalyst, increasing the temperature significantly increased conversion. Increasing the temperature from 400 to 700 °C (673–973K) increased the CGE of *Chlorella vulgaris* from 14 to 82% [4], increasing from 380 to 600 °C (653–873K) increased the CGE of *Chlorella pyrenoidosa* from 31.59 to 68.02% [15] and increased the total gas yield from 4 to 13 mol/kg on a mix of
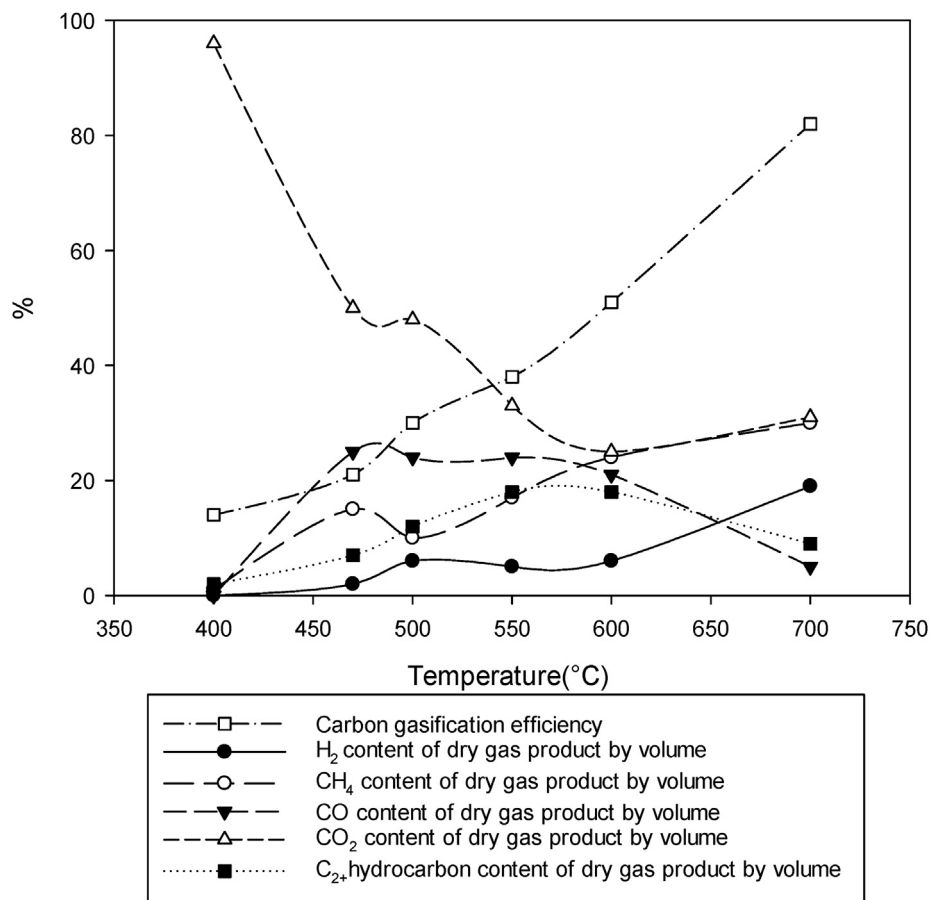
Fig. 9 — Dry gas composition and gasification efficiency for the non-catalytic supercritical water gasification of Chlorella vulgaris in a batch reactor at 240 bar, 7.3 wt%, 2 min reaction time. Adapted from [4].

cyanobacteria [108]. However, at low temperatures (653 or 673K), all authors observed almost entirely CO_2. This indicates that decarboxylation reactions prevailed, showing that the kinetics of the other main reactions, such as steam reforming, WGS or other intermediate reactions were significantly slower. As a result, in all three, higher temperatures, despite increasing the hydrogen content, this also significantly increased the methane content of the gas. This shows how kinetics can explain the large deviations from equilibrium values. Duan et al. [15] suggested the increased pressure at higher temperatures favoured methanation. While this could be factor in that case, especially with a longer reaction time, the other two cases were performed at constant pressure, so a kinetic explanation is more likely (see Fig. 9).

The effect of temperature on conversion with a catalyst followed a similar trend. Duan et al. [15] observed a similar increase of the CGE with temperature, with or without a ruthenium and rhodium catalyst. The exception was that the conversion was higher for a given temperature than the non-catalytic equivalent, as shown in Fig. 10. The increase in gasification efficiency at higher temperatures, both with and without a catalyst, was also observed in other biomass feedstocks [127]. However, the effect on gas composition on catalytic SCWG of real biomass can vary.

Elsayed et al. [87] found that, when gasifying *Acutodesmus obliquus* with a K_2CO_3 catalyst, increasing the temperature between 600 and 700 °C (873 and 973K) increased the hydrogen content of the gas and reduced the methane. This is similar to that predicted in the mathematical models, indicating it was close to equilibrium. This was not the case reported by Duan et al. [15] when increasing the temperature between 380 and 600 °C (653−873K) in the gasification of *Chlorella pyrenoidosa*, with Ru/C and Rh/C catalysts. These authors observed that increasing the temperature increased methane and short alkanes at the expense of CO_2, with almost constant hydrogen content and yield. This indicates that increasing the temperature favoured more cracking reactions and methanation, with any hydrogen created in the process being converted to methane. These examples used different catalysts, temperatures, and feedstocks, which can potentially impact upon the effect of temperature. Therefore, it is hard to predict the impact of an increased temperature on the gas product composition and further work should be completed to investigate the interaction between these parameters.

Nonetheless, the yield of hydrogen almost always increases with temperature, to the higher conversion achieved and higher equilibrium concentration. Therefore, higher temperatures are usually preferred. However, this requires more energy to heat up the reactor contents, which cannot be fully recovered [77] and requires more expensive materials to withstand the temperatures [76], so it is important to consider the whole system when selecting a reaction temperature.
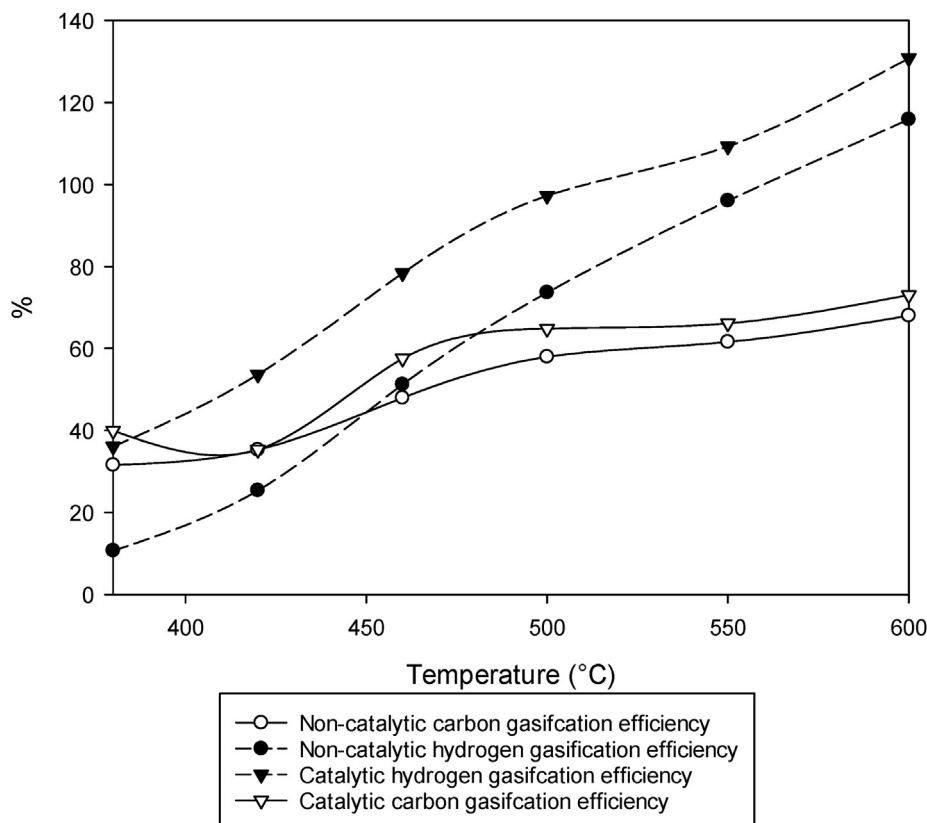
Fig. 10 — Impact of temperature on the carbon and hydrogen gasification efficiencies for the supercritical water gasification of Chlorella pyrenoidosa. Reaction time 1h, 10 wt%, Ru/C + Rh/C catalysts. Adapted from [15].

Catalysts and feedstock selection can be used to help minimise the required temperature to achieve high yields, increasing the overall efficiency.

3.4. Biomass concentration

Water plays an important role in many of the main reactions involved in SCWG. Le Chatelier's principle means that if the concentration of water is high, the equilibrium will shift to remove it. This would increase hydrolysis, WGS and steam reforming, where water is a reactant, while reducing the methanation reaction, where water is a product [128]. This favours an increased conversion, high content of hydrogen in the feed and thus a high hydrogen yield. This explains the reduction in hydrogen and the increase in methane content observed in thermodynamic models of the gasification of microalgae and other biomass feedstocks at higher biomass concentrations [124—126]. Moreover, Guan et al. [16] found that first order kinetics were insufficient to show the effect of

biomass concentration on hydrogen production. This shows that biomass concentration also has a strong role in kinetics too.

In real systems, Elsayed et al. [87], Samiee-Zafarghandi et al. [101] and Guan et al. [129] found that increasing the biomass concentration significantly reduced the concentration of hydrogen and increased the concentration of methane in the product gas during the SCWG of microalgae. This was a unanimous finding, for different algae strains, temperatures, catalysts, and range of biomass concentration (outlined in Table 6). Moreover, the former two authors observed a significant decrease in CGE. Guan et al. [129] observed that, while the hydrogen yields significantly fell with concentration, the carbon compounds had consistent yields, so CGE changed minimally. In this case a major production of carbon gas (CO, CO_2 and CH_4) may be from direct conversion of biomass in processes like decarboxylation [16], so the loss of CO_2 from reduced steam reforming is compensated by increases production from these sources. Higher biomass concentrations

Table 6 — Microalgae experiments in which a decrease in hydrogen content was observed with an increase in biomass concentration in the feed.

Feedstock	Catalyst	Temperature (K)	Biomass Concentration (wt%)	Hydrogen Yield at M in wt% (mmol/g)	Hydrogen Yield at M ax wt% (mmol/g)	Source
Acutodesmus obliquus	K_2CO_3	963	2.5—20	299.33	63.3	[87]
Chlorella sp.	None	628—653	1—8	1.2	0.714	[101]
Nannochloropsis sp.	Ru/C	683	2—13.5	11.6	2.8	[129]

can also lead to an increase of undesirable compounds such as phenol [19].

These observations verify the models by demonstrating that a lower biomass concentration increases hydrogen yield, which would be preferable for hydrogen production. However, as with temperature, this increases the energy lost, due to the larger quantities of water requiring heating to supercritical temperatures and pumped through the system [77]. The heat is often provided from the product gas, so reduces the overall yield. Furthermore, the concentration of microalgal slurry can be highly energy intensive, so a lower concentration reduces the energy required to produce the feedstock [130]. Therefore, the whole system should be considered when choosing the ideal feedstock concentration.

3.5.   Residence or reaction time

Longer reaction times naturally allow the reactions to proceed further. Since the hydrolysis step is fast [16], longer reaction time allows further conversion of the intermediates to final products and therefore it is expected that gasification efficiency is increased. This was the case described by Miller et al. [131] when continuously gasifying *Spirulina* and by Samiee-Zafarghandi et al. [101] when gasifying *Chlorella* sp. in a batch reactor. However, the case is not quite that simple as some chemicals formed (such as amino acids or phenols, which are both found to occur in SCWG of algae) are very difficult to gasify and/or favour polymerisation to tar and chars than gas [4,16]. Hence, under the milder conditions they may not gasify in a reasonable time frame. This was evidenced by the asymptotic curve that never reaches 100% when longer reaction times were used [110], as shown in Fig. 11. This was the case with and without the ruthenium catalyst, although the catalyst promoted a higher maximum yield and achieved this more rapidly (30 min instead of 90). This shows that the catalyst accelerates the reactions allowing the "easier" reactions occur more rapidly and some of the more difficult reactions to progress in a more reasonable time.

Even after the gasification efficiency has plateaued, a further increase in reaction time can alter the gas composition. Once the faster reactions that affect gasification efficiency (steam reforming and decarboxylation) have reached a maximum, the slower gas reactions (WGS and methanation) progress with time, until the gas has reached equilibrium. This is illustrated in Fig. 12, where the CO content reduces over time with hydrogen and methane contents increasing correspondingly [4], in this case CO_2 remains constant as the extra created in WGS is consumed in methanation reactions. Similarly, an increase in the residence time increased both hydrogen and methane content at the expense of CO in non-catalytic continuous SCWG of *Chlorella* sp. and *Chlorella vulgaris* [59,101].

In catalytic gasification, similar effects occur but at a faster rate. Zhu et al. [23] gasified glucose with and without a ruthenium catalyst for reaction time ranges of 30−1800s and the effect on gas composition is shown in Fig. 13. Without a catalyst, at short reaction times CO_2 dominated, with CO increasing (steam reforming) up to 600s where the CO content reduced, producing more hydrogen and methane. With a catalyst, the WGS and methanation reactions progressed more rapidly, being more significant at shorter times but the hydrogen and methane content also increased with time. However, there was little change after 300s indicating the system had reached equilibrium. As the reaction time increases, the gas composition will progress towards the equilibrium values. As the position of equilibrium is dictated by reaction conditions, the effect of higher residence times on composition of the gas will be dependent on these. This was shown by Samiee-Zafarghandi et al. [101], who found the increase in hydrogen yield with longer residence times was more significant at higher temperatures (where the equilibrium hydrogen fraction in the gas is higher [124]).

3.6.   Other factors

3.6.1.   Pressure
La Chatelier's principle implies that lower pressures favour reactions with more moles of products than reactants. This would suit the steam reforming and WGS reactions while suppressing methanation at low pressures, leading to a higher hydrogen concentration. This is observed in thermodynamic models of SCWG of microalgae and other biomass [124,125]. Although the effect was small, relative to that of temperature, this was investigated in some literature. Duan et al. [15] observed an increase in hydrogen content at lower water density (higher biomass concentration but lower pressure). As noted in section 3.4, a lower biomass concentration increases hydrogen, so the pressure effect must have promoted the higher hydrogen.

In contrast, work on other feedstocks has found that increasing pressure marginally increased hydrogen and reduced methane [132]; there was an optimum pressure above or below which the hydrogen yield was reduced [133]; or pressure had little impact [134]. This is caused by the change in reaction kinetics due to the increased water density. This can increase collisions and solvent cage effects, which increase reaction rates and reactions involving water (such as WGS). However, it also increases the dielectric constant that reduces the free-radical reactions [10], key reactions in SCWG. Hence positive and negative impacts can come from increased pressure. These impacts are seen where kinetics play more of a key role, with harder to gasify feedstocks, when there is no catalyst or short residence times. Although, the impact is far less significant than that of the temperature, biomass concentration and feedstock composition [135]. It is also important to consider that increased pressure increases the pumping energy required [136] and the required strength of the reactor material [76].Therefore, in many cases, particularly with a catalyst, lower pressures (still above the critical point) are preferred. However, in some cases the pressure may be significant and effect of pressure should be considered.

3.6.2.   Heating rate
The heating rate is an important factor in SCWG as it dictates the time the feed spends in the subcritical region. In this region, different intermediates are favoured, that may have a negative impact on the overall gasification performance. For example, a slower heating rate using glucose increases the formation of furfurals and phenol, which are difficult to gasify and are more likely to polymerise to form unwanted tar and
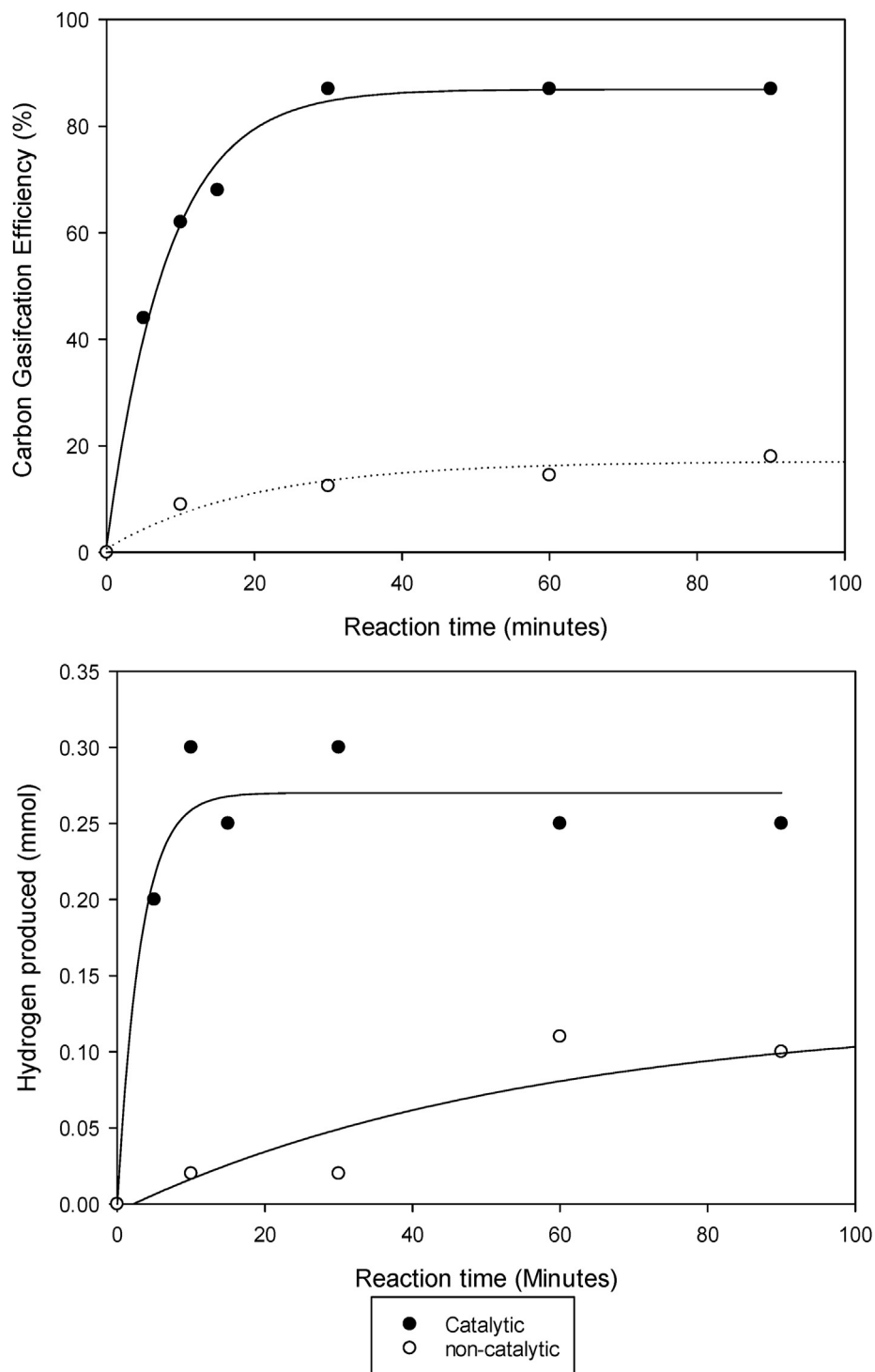
Fig. 11 — **Carbon gasification efficiency at different reaction times for the batch supercritical water gasification of Chlorella vulgaris, with and without a charcoal supported ruthenium catalyst. 4.8%wt biomass, 385 °C and 0.83g of catalyst (if used). Adapted from [110].**

chars. This reduces the gas and hydrogen yields [91]. As glucose is a major component in many carbohydrates in microalgae, this effect should also occur in this case. Caputo et al. [22] observed that preheating the feed reduced gasification efficiency and increased solid residue, when gasifying *Nannochloropsis gaditana*. This has the same effect as a slower heating rate, thus showing the effect found on glucose should

also be applicable for microalgae. Therefore, heating rate should be maximised in SCWG of microalgae. Using a hot water stream that rapidly mixes with a cold microalgal feed, providing extremely fast mixing is a potential method to achieve this [93]. However, it will be more difficult to regain the heat from the product stream and will require a higher feed concentration. A whole system approach is needed to assess
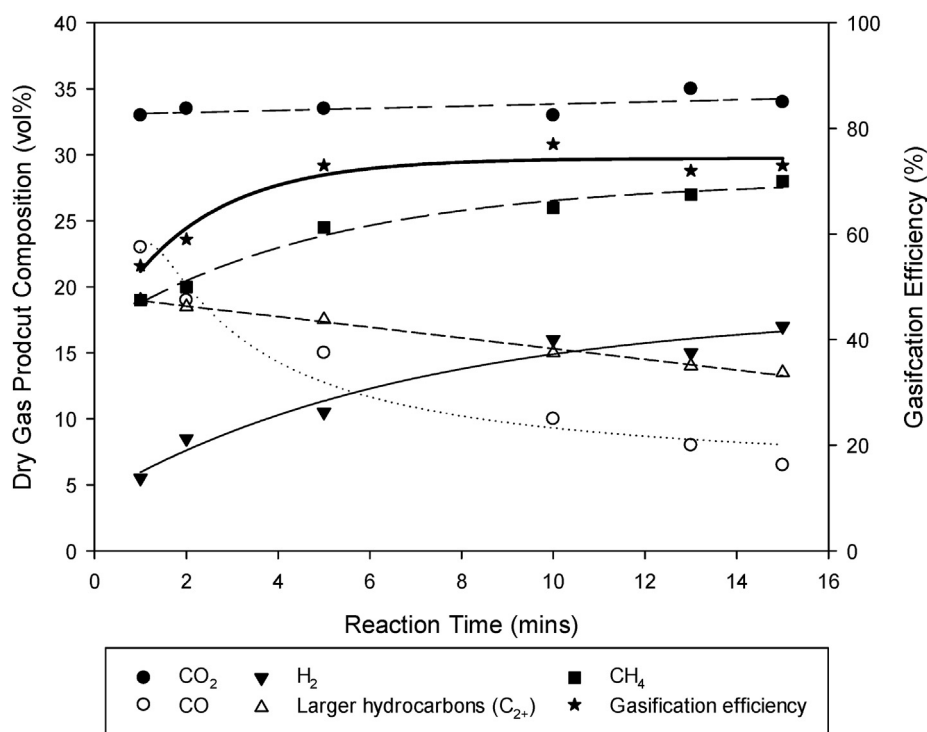
Fig. 12 — Change in gas composition and gasification efficiency over time, for supercritical water gasification of Chlorella vulgaris without a catalyst. Temperature: 580 °C, Concentration 7.3%wt, pressure 24 MPa. Adapted from [4].

whether the added benefits of this approach outweigh the increased energy requirement from heating and pumping the feed.

4. Supercritical water gasification systems

4.1. Nutrient recycling

To grow large amounts of algae requires nutrients such as nitrogen and phosphorus, as well as inorganic carbon (usually CO_2) for growth. These (particularly CO_2) contribute significantly to the cost of the algae production, which is a major cost in the whole of the process, and a barrier to the development of microalgal SCWG systems [78,137]. Furthermore, many of the fertilisers used today to provide these nutrients are energy intensive to produce [138] or are already limited in supply. Thus, large scale algal production could put further strain on the fertilizer supply, threatening food supplies in an expanding world population [139]. Therefore, it is important to limit nutrient use as much as possible. SCWG is advantageous as it can completely mineralise the inorganic parts of the algae, allowing it to be recycled more easily [17]. Moreover, the gas product does not contain toxic pollutants such as hydrogen sulphide. Thus, minimal processing is required to recycle the CO_2. Achieving the maximum CO2 recovery is vital for minimising costs, as it remains the highest operating cost in the algal growth even at 90% recovery [78]. This would allow a large reduction in nutrients required, without affecting the algae growth.

Elsayed et al. [87] and Patzelt et al. [140] found that a very high percentage (85–100%) of the nitrogen in *Acutodesmus obliquus* was recovered in the aqueous phase after SCWG, mostly in the form of ammonium ions. Phosphorus and the trace metals were largely precipitated out in the reactor due to their low solubility in supercritical water. Therefore, it is important that regular purging of the reactor with subcritical water is required to recover these salts is included, otherwise the nutrients would be lost, and the reactor would be plugged. When the purge was included, over 85% recovery was achieved for phosphorus, nitrogen, potassium, calcium, magnesium, sulphur, sodium, with a recovery close to 100% in many cases [87]. Despite high nutrient recovery, several toxic organic compounds such as phenols would be present in the aqueous phase, so algal growth was not achieved if the untreated aqueous phase is used as the growth media [87,140]. Dilution as treatment method worked in both cases [140] and for growing Chlorella vulgaris in the aqueous phase of following the SCWG of the macroalga *Saccharina latissimi,* but that remained impractical as it would overfill the growth vessel. Activated carbon and ultraviolet (UV) treatment were both successfully used to reduce the toxic compounds and achieve growth, but UV also destroyed some of the nitrogen [87,140]. Elsayed et al. [87] found that the aqueous phase treated with activated carbon outperformed the original media used for growth, as shown in Fig. 14. Moreover, in other tests involving phenol, activated carbon filters were easily regenerated using a mixture of ethanol and sodium hydroxide [141]. Hence, the use of activated carbons offers a promising solution to remove toxic compounds and allow for nutrient recycling.

The SCWG reactions themselves are also important to achieving successful nutrient recycling and limiting the steps required after the reaction. Gokkaya et al. [84], observed that
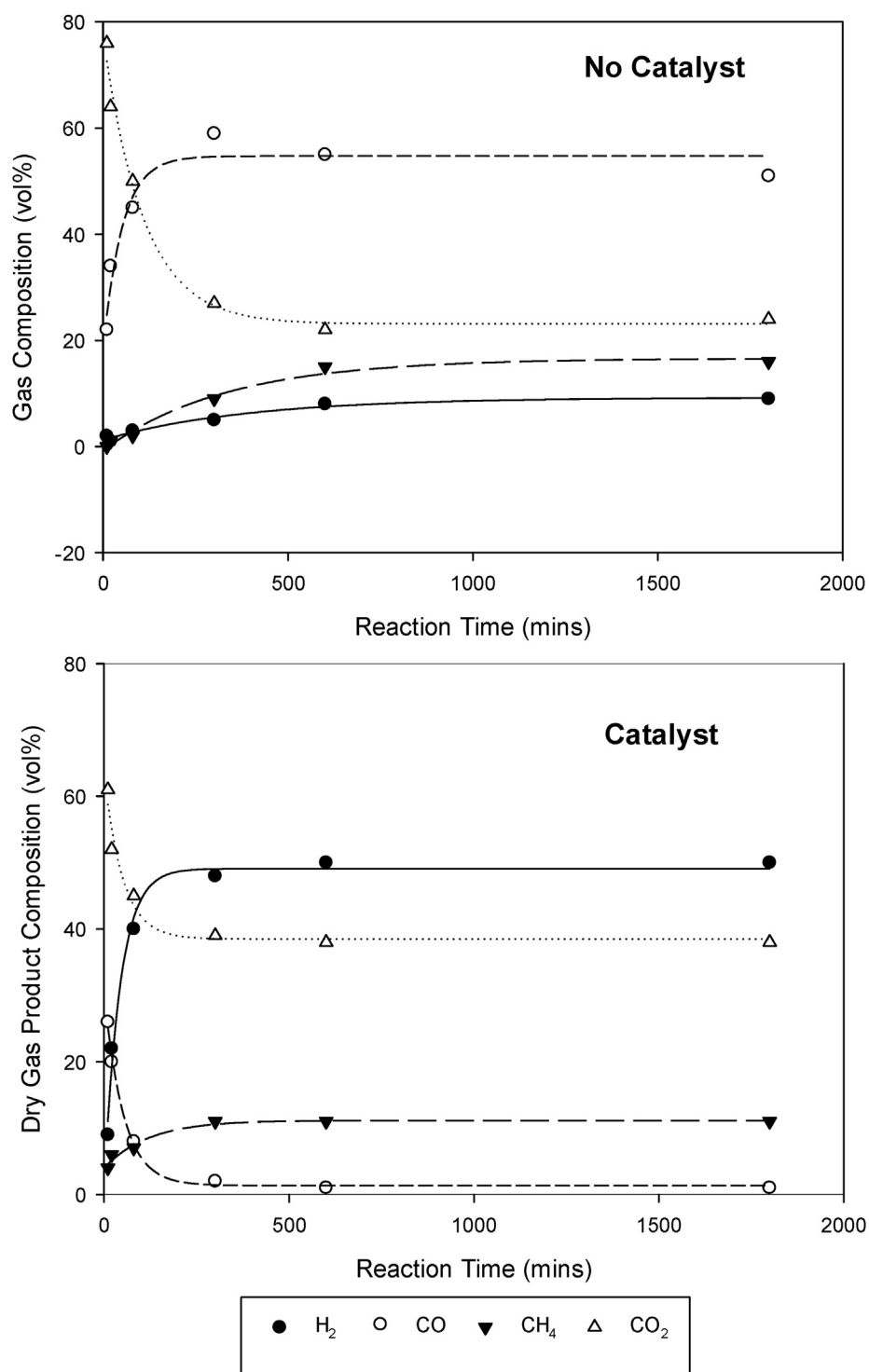
Fig. 13 – Gas composition over time for the supercritical water gasification of glucose with either no catalyst or a ruthenium on alumina catalyst. Temperature 500 °C, Concentration 5%wt Adapted From Ref. [23].

ruthenium catalysts reduced the phenol content and alkali catalysts increased it in the gasification of xylose. While the reverse has been observed in some microalgae examples [17,110], this shows that the choice of catalyst can significantly affect the recyclability of the aqueous phase and should be considered in the choice of a catalyst. Further work should focus on the effect of the catalysts on the recyclability of the aqueous phase. Furthermore, metals such as nickel and aluminium, often used in catalysts and the wall material, are known to limit microalgal growth [17,113,142]. Both were found in large quantities when both nickel on alumina and NaOH were used due to reaction between the catalysts [17]. It is therefore important to ensure supported metal catalysts are stable in the reaction environment and corrosion is
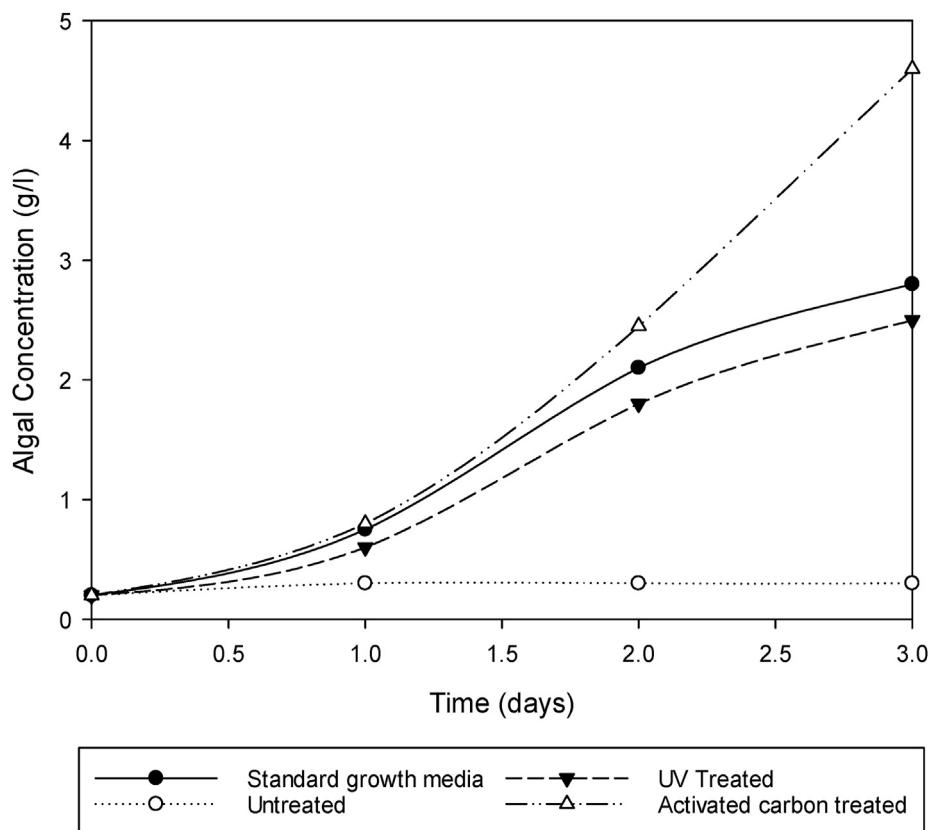
Fig. 14 — Microalgae growth in the residual water following the supercritical water gasification of *Acutodesmus obliquus*, comparison of the different treatment methods. Adapted from [87]:

minimised, to keep the metal content in the aqueous phase to a minimum.

4.2. Integrated systems

The SCWG reactor will not stand alone and must be placed within a whole system that includes algal growth, purification of the gas stream and storage of produced gases. It is possible to recover energy from parts of the process and therefore increase the efficiency of system. A general system of this is shown in Fig. 15. Nurdiawati et al. [78] proposed a system that included chemical looping for purification, hydrogenation of

liquid organic carriers (in this case toluene) for hydrogen storage and gas turbines to recover excess pressure as electricity. Chemical looping is particularly advantageous as it has a high process efficiency and produces highly concentrated CO_2 and hydrogen from the mix of gases produced in SCWG [143]. This allows the hydrogen to be used in any application without further purification and the CO_2 to be easily recycled or stored. Also, system allows the heat from chemical looping regained, as well as maximising energy recovery of the SCWG system. The result predicted total efficiencies of over 50% in some cases, exceeding that of the more mature technology of dry gasification although, this may differ in real life
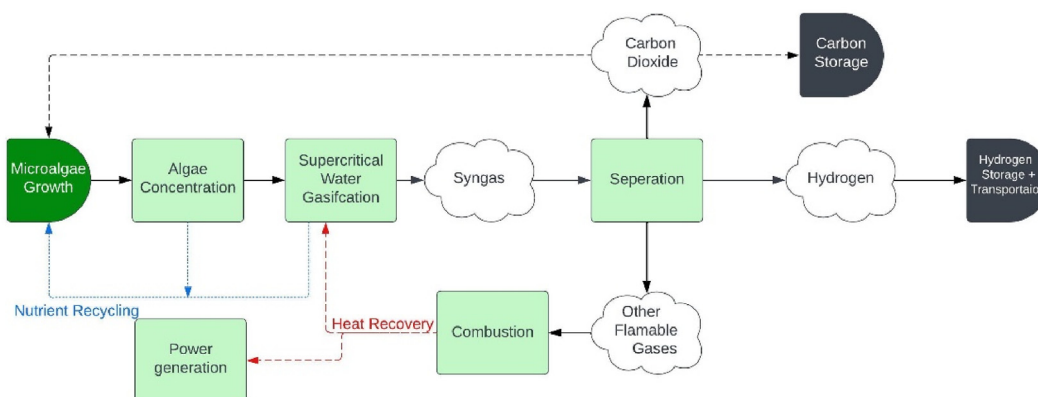

Fig. 15 — Potential supercritical water gasification of microalgae system to produce hydrogen and capture carbon dioxide.

applications. In other cases, with suitable climates, concentrated solar heating can be used to heat the reaction and reduce losses [144,145].

Systems as such are vital to maximising efficiency and reducing costs in the process, with models being important for seeing the impacts of operating conditions on the whole model. Nurdiawati et al. [78] found that the optimum reaction temperature depended on the biomass concentration into the reactor; a higher temperature was preferred at a higher biomass concentration and conversely lower temperature at lower biomass concentrations. However, this does not include the difference in energy requirement for concentrating the algae. This must be incorporated to obtain the ideal operating conditions. Aziz [136] proposed a similar system except with a membrane separation in place of chemical looping and a fluidised bed reactor. In this model, pressure and fluidisation velocity were investigated. Both were found to reduce energy efficiency when they were increased, due to higher pumping energy. However, this model did not consider kinetics which can be influenced by the pressure and levels of turbulence from the higher velocities. Thus, a real system may differ from this. Combination with a direct use of the hydrogen, such as ammonia production [146], can also help maximise efficiencies.

5. Conclusion

Supercritical water gasification of microalgal biomass offers an alternative source of green hydrogen that does not rely on the electrical grid and can potentially be carbon negative. It also brings several other advantages, when compared to other biomass conversion processes, such as reduced char formation, no drying requirement, possibility of energy recovery and reuse, and the potential for recycling the inorganic nutrients and CO_2 required for algal growth. These are important to minimise costs and strain on the fertilizer supply so should be considered in the system. This includes choosing an appropriate catalyst and the use of post reaction treatment such as activated carbon filters.

The composition of the algae, catalyst selection and operating conditions all impact upon the gasification performance. A higher carbohydrate content is usually favourable for a high hydrogen yield, a high protein content usually reduces the gas produced and lipids are easily gasified but tend to produce methane. However, this is not always the case, due to the large range of compounds within those categories and other factors such as algal cell wall thickness. Alkali metal salts can be used as a homogeneous catalyst to increase the hydrogen yield and selectivity but can be difficult to recover and increase corrosion. Supported nickel and ruthenium catalyst can increase hydrogen yield but often increase the methane produced at the expense of hydrogen. They also are prone to deactivation and careful selection of the support is needed to minimise this. Adjustments to the catalysts and or the reactor systems are required to maximise their positive impact.

A high temperature and low biomass concentration in the reactor both favour a higher biomass conversion, hydrogen yield and hydrogen selectivity. However, in real systems these require a greater energy input in heating and pumping of the water, which reduces the overall efficiency of the process.

Moreover, the feed should be heated rapidly to maximise efficiency and minimise char. A longer residence time can also increase conversion and yield but only up to a point where further increases have little effect. Despite a low pressure often being preferred, in some cases the increased kinetics from higher pressure may be the better option. These factors are all important to consider for the design of a supercritical water gasification system, to produce hydrogen from microalgae. Further work should investigate how the catalysts, biomass composition and the overall system can be optimised to maximise efficiency and reduce the cost of hydrogen produced in this way.

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.

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