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Catalytic and Non-catalytic Supercritical Water Gasification of Microalgae and Glycerol

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In this study, we present the gasification of microalgae (*Chlorella vulgaris*) and glycerol in supercritical water (SCW) using batch (quartz capillaries) and continuous flow reactors. Preliminary tests of algae gasification were done with quartz capillaries at varying operating conditions such as temperature (400–700 °C), reaction time (1–15 min), and the addition of catalysts. The dry gas composition of uncatalyzed gasification of algae in SCW mainly comprised of CO₂, CO, CH₄, H₂, and some C₂–C₃ compounds. Higher temperatures, low algae concentrations, and longer residence times favored the algae gasification efficiency (GE). The addition of catalysts to the capillaries resulted in higher yields of hydrogen and lower CO yields via enhanced water–gas shift activity. The addition of catalysts accelerated the gasification efficiency up to a maximum of 84% at 600 °C and 2 min reaction time with nickel-based catalysts. Complete gasification is achieved at higher temperatures (700 °C) and with excess amounts of (Ru/TiO₂) catalyst. To elucidate part of the difficulties related to the SCWG of algae, reforming of a model compound (here glycerol) in SCW was carried out in a continuous flow reactor in the presence of additives like amino acids (L-alanine, glycine, and L-proline) and alkali salt (K₂CO₃) and combinations thereof. The amino acids L-alanine and glycine have a minor effect on the gasification process of glycerol, and a significant reduction of the gasification efficiency was observed in the presence of L-proline. Coke formation and colorization of the reactor effluent were more noticeable with glycerol–amino acid mixtures. In the absence of amino acids, the glycerol solution gasified without any coke formation and colorization of the reactor effluent. Again this effect was more pronounced in the presence of L-proline. The addition of K₂CO₃ enhanced the glycerol gasification efficiency and increased the hydrogen yields promoting the water–gas shift reaction.

1. Introduction

The rising population combined with the increased use of fossil fuels has led to the depletion of their sources at alarming levels, and this has prompted exploration of alternate renewable and sustainable energy sources like wind, solar, and biomass. As a consequence, there is a growing interest in harnessing the chemical energy from biomass which is more sustainable, is CO₂ neutral, and can be converted in to high heating value fuels: either liquid or gaseous.

Microalgae are a plausible biomass energy source, as they are the fastest growing, sunlight-driven cell factories that can convert atmospheric CO₂ into potential biofuels and chemicals.^{1–5} The growth rates of algae can be as much as ten times higher than for terrestrial plants, thereby minimizing the “land-claim” for fuel production and avoiding direct competition with food/feed production for arable land. Algae cells (with or without triglycerides included) are produced as “wet biomass” for which conversion technologies like pyrolysis and “dry” gasification compare unfavorably due to the high water content and the consequent high-energy requirement to dry the biomass. Using water as a reaction medium for wet biomass conversion would eliminate the need for the drying process.

Supercritical water gasification (SCWG) is a probable technology for the conversion of wet biomass streams having a low overall heating value to produce high heating value product gases. At temperatures and pressures above the critical point ($T \geq 374$ °C, $P \geq 220$ bar), water undergoes significant changes in its physical properties with a drastic decrease in dielectric

constant, density, ionic product, viscosity, and thermal conductivity.^{6–26} At such conditions, water behaves like an adjustable environmentally benign solvent with good transport properties but also with a strong ability to break down hydrocarbons and carbohydrates, resulting in the production of pressurized gases mainly rich in H₂, CO, CO₂, and CH₄. The selectivity of the gas production toward H₂, syngas (H₂ + CO), or CH₄ can to some extent be steered by tuning the process conditions and by the use of catalysts.^{7,8,11,24,28}

The heat effects in SCWG related to water evaporation are marginal when compared with ambient conditions.^{9–11,17,29} The use of an efficient counter-current heat exchanger between the feed streams and the reactor effluent can result in high thermal efficiencies, allowing us to process low energetic aqueous (waste-) streams.^{9,10,21,23,24,29} The efficiency of this feed-product heat exchange is, however, crucial for the success of this process concept.

Generally, the feedstock for this type of process should either be homogeneous liquid or pumpable slurry. A majority of the studies in the past have used synthetically made effluents (by dissolving biomass model compounds in water) to evaluate their gasification behavior in SCW.^{8,11–14,20,22,24–27} The extent of carbon conversion and the product gas distribution achieved under these conditions may or may not be reproduced with real biomass, as these often contain variable amounts of compounds which can have a significant influence on the gasification. For example, alkaline salts are known to intensify the gas yields, whereas, e.g., proteins are reported to be difficult to gasify.^{19,20,26} Several state-of-the-art review articles^{10,18,21,23} were recently published, giving a clear insight into the issues involved in sub- and supercritical water gasification of biomass.

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An associated advantage of using this process in an “algae biorefinery” is the option to integrate energy production with CO₂ capture and to reuse minerals retained in the process water by recycling them to the algae growth reactors/ponds (“closed nutrient loop”).^{1–5,28} At present the algae growth reactors are, however, considered to be too expensive,⁵ but the economics may be improved upon integrating the use of industrial waste effluents as feedstock for growth reactors (e.g., flue gas from power plants as a source of CO₂ or utilizing wastewater streams as a source of nutrients for algae production), by extracting the value added chemicals (e.g., proteins, amino acids, oil/lipids) as a source of food and feed ingredients and by upgrading the extracted algae oil for biodiesel production. Effluent streams from the latter separation step, but also the complete algae broth, can be gasified using SCWG to produce combustible gases. The product gas containing H₂, obtained from the SCWG, could be used for the hydrogenation of lipids extracted from the algae.

To date, very few studies with only a very limited number of experimental runs (less than 15) have been reported on the SCW gasification of algae. Antal⁶ was the first, who studied the gasification of macroalgae solutions (*Gracilaria*) of three different concentrations (0.1, 0.3, and 2.5 wt %) in SCW at 550 °C and 345 bar. He observed large variations in the product gas yields as well as in the carbon gasification efficiencies for the triplicates carried out, and the nine test runs reported should be regarded as scouting experiments. Minowa and Sawayama²⁸ have proposed a new method of cultivation of microalgae in the recovered solution obtained from the low-temperature (near-critical) catalytic gasification of algae. They performed three experimental runs with *Chlorella vulgaris* at low temperature (350 °C) and in the presence of nickel catalyst and obtained a methane-rich gas with carbon conversion ranging between 35 and 70%. Haiduc et al.³ performed six tests of hydrothermal gasification of *Phaeodactylum tricornutum* at low temperatures (360–420 °C) aiming toward methane production in the presence and absence of ruthenium catalyst. For the uncatalyzed gasification, the carbon conversion is in the range of 4–8%, while it was 34–74% with the catalyst and long reaction times (over 1 h was required). Recently, Stucki et al.⁴ reported 13 experimental runs of microalgae (*Spirulina platensis*) gasification in supercritical water at 400 °C in a small unstirred batch reactor system (30 mL) and in the presence of Ru/C and Ru/ZrO₂ catalysts. Complete conversion of algae to a methane-rich gas was achieved at low concentrations (2.5 wt %) for 6 h reaction time and in the presence of a high catalyst to dry algae ratio of 8.

The aim of this work is to check the feasibility of microalgae gasification in SCW at high temperatures (above 550 °C) using quartz capillary microreactors. This high-throughput screening technique for the conversion of biomass and model compounds at near- and supercritical conditions of water has been extensively used within our research group^{8,11,12,16,17,24} to study the effect of different process conditions like temperature, reaction time, concentration, and screening of different catalysts to determine the product gas distribution and the gasification efficiency.

Algae form a complex feedstock, consisting of proteins, fats, carbohydrates, amino acids, lipids, and minerals. The gasification of glycerol is used as a model system to study the influence of cogasification of amino acids and alkali-salts on the gasification process. Glycerol is also relevant for algae gasification as it forms the backbone of lipids (present up to 40 wt % in algae), and more general, glycerol is coproduced in the transesterification process for biodiesel making. Additionally, glycerol

Table 1. Characteristics of the Catalysts

catalyst	composition	BET (m ² /g)	particle size (μm)
Ru/TiO ₂ [Ru]	Ru (2%)	49	125
NiMo/Al ₂ O ₃ [NiMo]	Ni (4%); Mo (21%)	182	125
PtPd/Al ₂ O ₃ [PtPd]	Pd (0.68%); Pt (0.63%)	372	125
CoMo/Al ₂ O ₃ [CoMo]	Co (5%); Mo (20%)	220	125
inconel powder	—	—	125
Ni wire	—	—	—

Table 2. Analysis of Microalgae *Chlorella vulgaris*

Properties	
moisture content (wt %)	92.7
dry solid content (wt %)	7.3
Chemical Composition (wt %) ^{a,b}	
crude protein	50
crude fat	13
crude fiber	15
ash	7
carbohydrates	15
Elemental Composition of Organic (wt %)	
C	45.8
H	7.9
N	7.5
O ^c	38.7
Mineral Content (g/kg) ^{a,b}	
Ca	43
P	12.9
Na	1.1
K	7.1
Mg	6.1
Total Amino Acids (mg/kg) ^a	246.2

^a As given by supplier. ^b On a dry solid basis. ^c Calculated by difference.

appears to be a suitable model compound as it decomposes in SCW without coke formation.^{7,11,24,25}

2. Experimental Section

2.1. Materials. Microalgae (*Chlorella vulgaris*) slurry was received from Ingrepro, The Netherlands. Nickel wire (thickness -0.25 mm) was obtained from Sigma Aldrich. Commercial catalysts Ru/TiO₂ (2 wt %), NiMo, CoMo, PtPd, AND Ni wire were used as provided, and their details are given in Table 1. The amino acids L-alanine, glycine, and L-proline were obtained from Sigma Aldrich. The composition of algae as provided by the supplier and those analyzed by us is given in Table 2.

2.2. Quartz Capillaries. More details of preparation methods in quartz capillaries can be found in the literature.^{8,11–14} In short, quartz capillaries (ID, 0.2 cm; OD, 0.4 cm; L, 15 cm; V, ~0.5 cm³) sealed at one end were loaded with algae slurry that corresponds to a water density of 0.07–0.08 g/cm (±240 bar) at a respective temperature that is studied, flushed with argon, and flame-sealed at the other end and heated in a fluidized sand bed that is set to the desired experimental temperature. The heating time in the fluidized sand bed was ~30 s, and the reaction time that is reported here includes the heating time. Gas analysis was done after rapid quenching of the capillaries in a water bath and by crushing it in a steel chamber (50 cm³). The gases evolved are analyzed immediately using gas chromatography attached to the crushing chamber. For catalytic experiments, a known amount of powdered catalyst was added to the capillary along with the biomass and is reacted in a fluidized sand bed after sealing and with no shaking. For the screening experiments with different catalyst, the ratio of catalyst to sample was maintained at an arbitrary ~0.7 g/g, and for

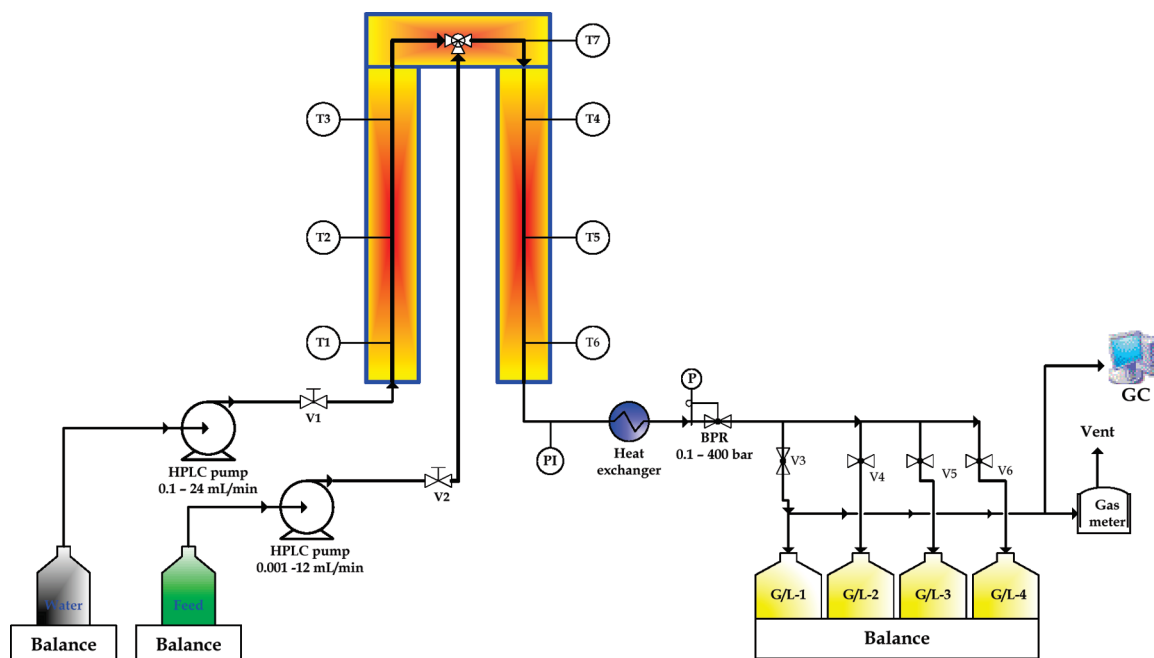


Figure 1. Schematic diagram of the continuous flow apparatus for SCWG of biomass.

excess catalyst it was ~ 2 g/g. For experiments with nickel wire, a 9 cm long nickel wire is inserted into the capillary along with the algae solution. For each single data point/experimental condition, four to six capillaries were used, and the average value is reported.

2.3. Continuous Flow Tubular Reactor. A schematic diagram of the continuous flow tubular reactor used for the glycerol gasification is shown in Figure 1. The experimental setup consists of two high-performance liquid chromatography (HPLC) pumps from Lab Alliance that can deliver pressures of up to 400 bar. One pump was used to feed the water to supercritical conditions, and it can deliver flow rates up to 0.1–24 mL/min. The second pump is used to pump the feedstock into supercritical water at the mixing junction at a flow rate of 0.01–12 mL/min. All experiments were conducted using the injection mode of operation, in which the glycerol solution is fed into SCW in the mixing chamber. The reactor tubing (ID, 0.2 cm; OD, 0.6 cm) is made of Inconel 600 having a composition of Ni ($\sim 72\%$), Cr ($\sim 15\%$), and Fe ($\sim 8\%$) and is placed inside temperature-controlled electrical heaters. The tube length in total is 143 cm, and the reactor tube length after the mixing junction is 71.5 cm. Three electrical ovens were used for heating purposes, and these can be individually controlled and monitored (Eurotherm). As it was difficult to fix the thermocouples (type K) inside the reactor tube, they were placed outside the reactor wall, and the outside temperature profile is logged using PICO software. The system pressure was controlled by a back pressure regulator (TESCOM), and the exit gas mixture from the reactor was cooled using a water-cooled double pipe heat exchanger. The gas–liquid mixture was separated using a phase separator, and the exit gas flow rate was measured using a wet gas meter (G1.6 Gallus 2000). The product gas composition was determined with an online sampling gas chromatograph (Varian 450-GC). The liquid phase product collected in the gas–liquid separator was then analyzed for the carbon content using the CHNS-O elemental analyzer (EA 1108, Fisons Instruments). Before and after each experiment the reactor was cleaned by pumping water alone to supercritical conditions for about 2 h to flush any remaining solids present in the reactor.

2.4. Analysis. The dry matter content of the algae slurry received was determined by drying at 80°C in an oven, and it was found to be ~ 7.3 wt %. The ultimate analysis of the dry and wet algae slurry was carried out using an Elemental Analyzer (EA 1108, CHNS-O, Fisons instruments).

Product gases from capillaries were analyzed using a gas chromatograph (GC) (Varian, CP-4900) after crushing them in the steel chamber which is connected to the GC. Continuous analysis of the gaseous products with the continuous setup was analyzed using a refinery GC (Varian, 450 - GC).

2.5. Terms and Definitions. In discussing the results, the following definitions are used.

The yield (Y_i) of product gas is defined as given below

$$Y_i = \frac{N_i}{N_{\text{feed}}}$$

The gasification efficiency (GE) (or) carbon–gas conversion is defined as the degree of conversion of carbon in the feed to permanent gases

$$\text{gasification efficiency, GE (\%)} \text{ or } (X) = \frac{\sum_i N_{c,i}}{N_{c,\text{feed}}} \times 100$$

The residence time (τ) in the continuous flow tubular reactor is calculated as follows

$$\tau = \left[\frac{V^* \rho_{T,P}}{\phi^* \rho_{STP}} \right]$$

where V is the volume of the reactor; $\rho_{T,P}$ is the density of water reaction temperature and pressure; ρ_{STP} is the water density at ambient conditions; and ϕ is the total volumetric flow rate (STP).

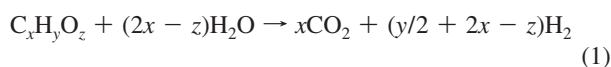
2.6. Chemical Equilibrium. Chemical equilibrium calculations were obtained using an in-house developed Matlab program that calculates according to the Gibbs minimization method,³⁰ and the fugacity coefficients were calculated with the modified Soave–Redlich–Kwong equation of state.³² The parameters for the modified Soave–Redlich–Kwong equation

of state were obtained from Bertuccio and Soave.^{31,33} Thermodynamic properties were obtained from the NIST-JANAF source. The equilibrium program calculates the yield (mol gas/mol feed) of permanent gases (H₂, CO, CO₂, and CH₄); the yields of C₂–C₃ compounds are neglected in this program as their values are considered to be very small; and it is only valid for glycerol experiments reported in this study.

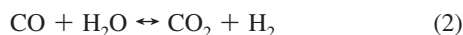
3. Experimental Results

The results of SCWG of microalgae in quartz capillaries and glycerol gasification in SCW using a continuous flow tubular reactor are discussed in the subsequent sections. The decomposition of organics in SCW into H₂, CO, CO₂, and CH₄ can be considered to proceed through the following set of reactions:

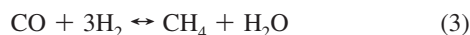
1. Steam reforming



2. Water gas shift reaction



3. Methanation reaction



The list of possible reactions is not complete; many other side reactions can and will occur, like cracking, chain rearrangements, condensation, and polymerization reactions. The underlying reaction mechanisms are not fully resolved, but there is consensus about ionic reactions being dominant in the subcritical region and free radical reactions prevailing in the supercritical region.^{18–22,25,26,29} The more complex the (biomass) feedstock, the more complex is the chemistry involved. The focus of this work on the gasification of a complex feedstock like algae is therefore not to resolve the reaction networks but to identify the feasibility of the (complete) formation of gaseous products and to get a first impression of the reaction rate. Coke and tar formation is here seen as loss of gasification efficiency.

3.1. Effect of Temperature on Microalgae Gasification Using Quartz Capillaries. To ascertain the influence of the gasification temperature on product gas composition and gasification efficiency of noncatalytic SCWG of microalgae (7.3 wt %), a series of gasification experiments were conducted at different temperatures of 400, 470, 500, 550, 600, and 700 °C. For the reaction time of 2 min, the results are presented in Figure 2. As expected, temperature has a significant influence on the product gas composition, total gas yield, and the gasification efficiency (GE). The GE increased as a function of temperature from 14% to 82% with increasing temperature from 400 to 700 °C, respectively (Figure 2b). At lower temperatures, decarboxylation reactions^{15,20} are more dominant (similar trends have been observed in, e.g., fast pyrolysis and torrefaction), and as a result, CO₂ is the main product obtained at 400 °C (Figure 2a). At higher temperatures (~600 °C and above), SCW becomes a more powerful oxidant, and free radical reactions prevail.^{15,18–20,25,26} Accompanied by an increased gas phase reactivity for the water gas shift reaction and methanation, this finally results in the formation of a mixture of gases containing H₂, CO₂, CO, CH₄, and some C₂–C₃ compounds. Visual observations of the capillaries after the reaction indicated coke formation as the reactor walls are coated to a more or lesser extent by black solid products. The color of reactor walls was less intensive (gray color) at higher temperatures (above 600 °C) indicating a

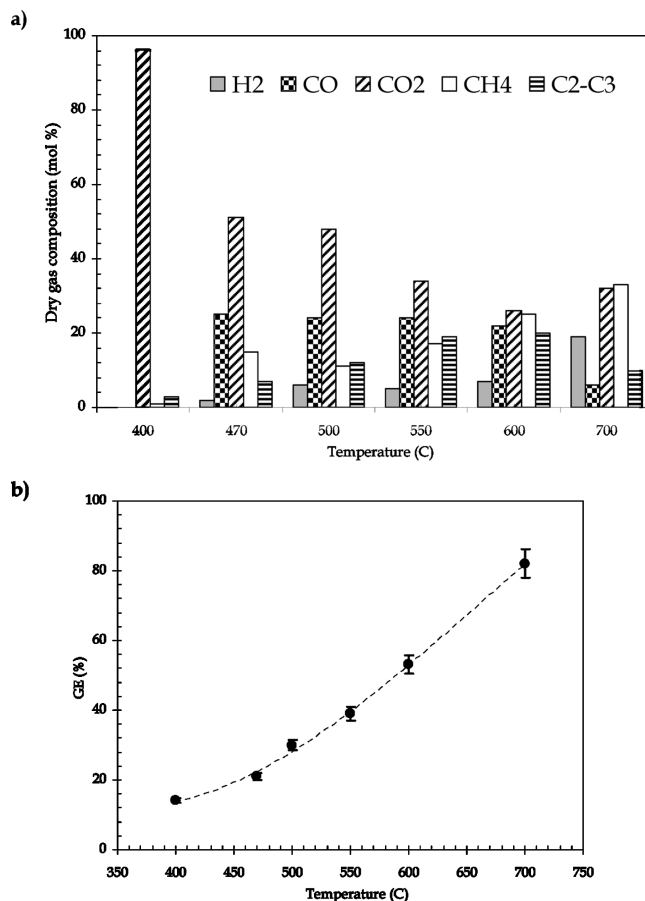


Figure 2. Effect of temperature on dry gas composition (a) and gasification efficiency (b) of algae gasification in quartz capillaries. [Experimental conditions: reaction time, 2 min; algae, 7.3 wt %; pressure, ± 240 bar].

reduced coke formation. Similar observations of less coating of the reactor walls has been reported for glycine gasification at 500 °C in the presence of a nickel catalyst when compared with uncatalyzed gasification.²⁷

3.2. Effect of Reaction Time on Microalgae Gasification Using Quartz Capillaries. Throughout the reaction time range studied (1–15 min), the distribution of gas yield and GE for the uncatalyzed SCWG of algae at 580 °C in quartz capillaries is as shown in Figure 3. After 5 min of reaction time, the carbon conversion reached the maximum value (73%), and further increasing the reaction time had no influence on the carbon conversion but the product gas distribution was changed. The H₂ and CH₄ content in the gas phase increased with reaction time at the expense of CO and C₂–C₃ fractions which can be attributed to the reforming of C₂–C₃ components to methane and hydrogen production via the water–gas shift reaction. The CO₂ content was found to be independent of the reaction time within the range studied. Similar findings of no further increase in the carbon conversion after a certain reaction time for glucose gasification at 600 °C were reported earlier.^{8,11} The limited (maximum) gasification efficiency thus seems to be caused by either a fraction of the biomass being resistant against SCWG conditions or by an irreversible “kinetically determined” selectivity toward coke/tar formation, which on its turn can not be gasified under the conditions studied. The latter is the most probable, as nonfirst-order behavior is also observed for glucose.¹⁷ Amino acids, and possibly proteins as they are formed from amino acids, are suspected to cause difficulties in gasification.^{7,19,20,26,27} The large fraction of proteins in the algae studied (around 30 wt %) may have caused the incomplete

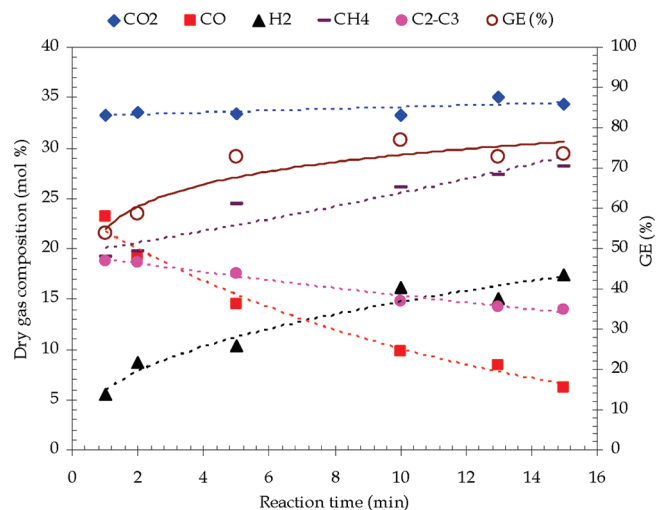


Figure 3. Effect of reaction time on gas composition and gasification efficiency for SCWG of algae. [Experimental conditions: algae, 7.3 wt %; temperature, 580 °C; pressure, ± 240 bar].

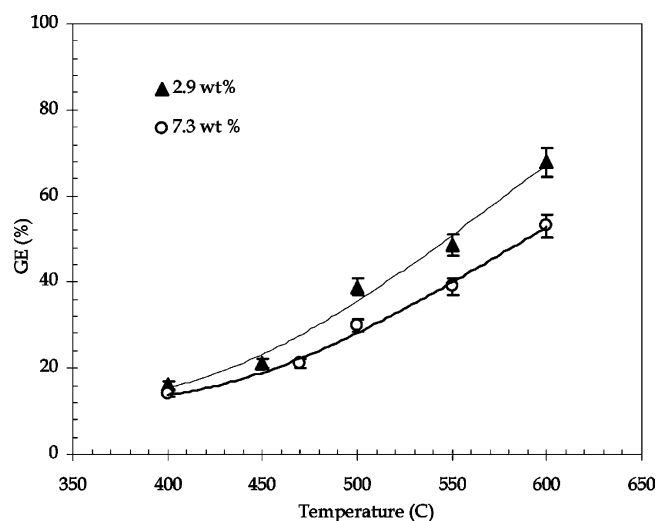


Figure 4. Influence of algae concentration (2.9 and 7.3 wt %) on gasification efficiency at different temperatures. [Experimental conditions: reaction time, 2 min; pressure, ± 240 bar].

gasification, and hence, the effect of adding (some) amino acids on SCWG was investigated (see section 3.5). To confirm this, additional tests with L-alanine and L-proline (5 wt %) as model compounds in the quartz capillaries at 600 °C and 2 min reaction time were done, and for this (uncatalyzed) system indeed hardly any carbon to gas conversion was noticed (results not presented).

3.3. Effect of Algae Concentration on Microalgae Gasification Using Quartz Capillaries. Generally, the initial concentration of a reactant is an important parameter for many reaction systems. For SCWG, it is often found to have a significant influence on the gasification rate and, moreover, on the extent of gasification in supercritical water.^{8,11,22,29} Knežević et al.¹⁷ have recently shown that the reaction rate for glucose conversion in hot compressed water is found to be first order with respect to gas formation, while it was variable order ($n > 1$) for char formation. The influence of two different algae concentrations (2.9 and 7.3 wt %) on the gasification efficiency at different temperatures after two minutes of reaction time is shown in Figure 4. It is obvious that higher carbon to gas conversion is achieved at the lower algae concentration (2.9 wt %). For the systems studied, maximum conversions are obtained at 600 °C, and it was 68% and 53% with algae concentrations

of 2.9 wt % and 7.3 wt %, respectively. From a few scouting experiments with even more diluted algae solutions, the conversions seems to increase even further (up to complete conversion) with increasing dilution. However, the reproducibility of these experiments with quartz microcapillaries proved to be poor due to the small amounts of products formed, and hence, no values are reported here.

The product gas composition showed similar composition and change in composition with increasing the temperature for both the 7.3 wt % and the 2.9 wt % algae concentration series. High CO yields were obtained with 2.9 wt % algae concentrations at all temperatures when compared with 7.3 wt % concentration. In addition to H₂, CO, CO₂, and CH₄, there is always some C₂ (C₂H₄, C₂H₆) and C₃ (C₃H₆, C₃H₈) compounds produced at all temperatures and concentrations, independent of the initial algae concentration (data not shown).

3.4. Effect of Catalysts on Microalgae Gasification Using Quartz Capillaries. Although higher temperatures and longer residence times are favorable for higher gas production, from a process point of view it is more economical to work at lower temperatures and shorter residence times. The need for catalysts arises to achieve higher gasification efficiencies and equilibrium gas yields. An effective catalyst for the production of H₂ in SCWG of biomass should facilitate the scissioning of C–C and C–H bonds and, preferably, favor the water–gas shift reaction.³⁸ Different catalysts were screened for the SCWG of algae in the quartz capillaries at 600 °C and two minutes of reaction time. The dry gas compositions obtained and the carbon-based GE are shown in Figures 5a and 5b and are compared with uncatalyzed gasification of algae. It is clear from the figures that the total gas yields and compositions can be significantly different with different catalysts (for a given reaction time). Complete gasification was not achieved for these conditions, and significantly longer reaction times, lower algae concentration, and/or higher gasification temperatures are required to achieve this.

The catalytic wall effect of metal reactors on gasification behavior and its tendency to promote water–gas shift activity in hot compressed water has been clearly established.^{8,11,12} To try to mimic the reactions in metal reactors while using quartz capillary reactors, we used Inconel powder and nickel wire acting as pseudo catalysts. High gas yield, GE of 84%, and CH₄ yield (12 mol/kg algae) were obtained in the presence of Inconel powder acting as a pseudo catalyst, even when compared to other actual catalysts. From the results, it is obvious that metal reactor walls exhibit a significant catalytic effect and enhance the water–gas shift activity and possibly the methanation reaction (as evidenced by the high methane content, see Figure 5a).

The activity of catalysts with respect to the gasification efficiency of algae in SCW at 600 °C decreases in the order of Inconel > Ni > Ru > PtPd > CoMo > NiMo. Higher H₂ yields (10 mol/kg algae) were obtained with the Ru/TiO₂ catalyst, and the activity of catalysts for high H₂ yields is in the order of Ru > NiMo > Inconel > Ni > PtPd > CoMo. Complete gasification was achieved with hydrogen-rich product gas with Ru/TiO₂ at 700 °C and 2 min reaction time. Complete algae GE was also obtained at 600 °C and 2 min reaction time with an excessive amount of Ru/TiO₂ catalyst (cat./sample: 2 g/g). Complete gasification with excessive amounts of catalyst and incomplete conversion in the earlier runs both at 600 °C can be attributed to poor contacting of the catalyst and reaction medium, catalyst poisoning, and also sintering at these conditions. A proper mixing of the catalyst and the biomass can however slightly improve the GE. The same will be the case of

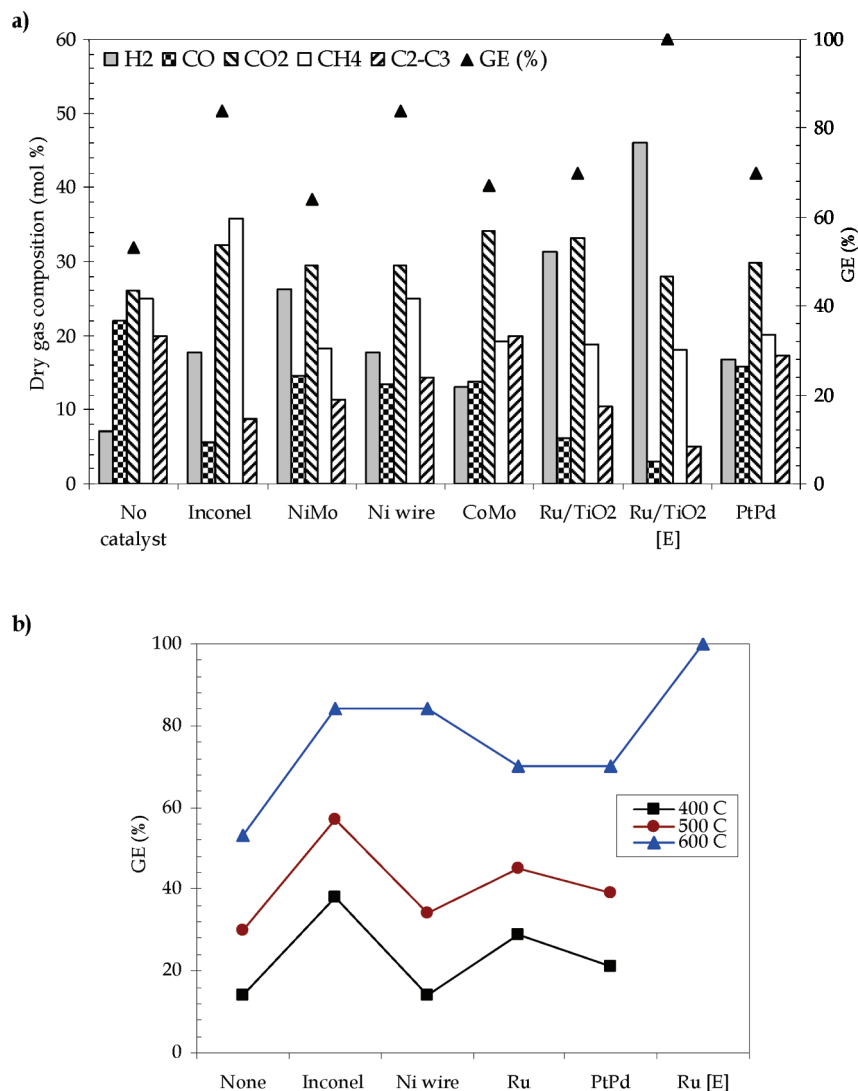


Figure 5. Influence of different catalysts on (a) product gas distribution and GE of microalgae at 600 °C and (b) GE at different temperatures. [Experimental conditions: concentration, 7.3 wt %; reaction time, 2 min; pressure, \pm 240 bar; catalyst/sample, 0.7 g/g for Ru/TiO₂, [E] it was 2 g/g, [E] is excess].

poor contact with the catalyst, and the reaction mixture can also imply for reactions done in the metal batch reactors if no proper shaking or mixing has been done that has been reported so far in the literature. However, the contact limitation of the catalyst and the reaction media is not pertinent for the experiments reported with nickel wire.

3.5. Glycerol Gasification in a Continuous Flow Tubular Reactor. In this section, we present the results of glycerol gasification in the continuous flow reactor shown in Figure 1 with the aim to look at the influence of the presence of different additives like amino acids (here: L-alanine, glycine, and L-proline) and alkali salt (here: K₂CO₃) on the product gas composition and carbon conversion to gaseous products. The continuous setup was validated by five test runs with 10 wt % glycerol gasification in SCW at 600 °C, 250 bar, and 5 s residence time carried out on different dates for about an hour. The results showed good reproducibility and repeatability attaining complete carbon closure both from liquid and gas phase analysis, and the gasification efficiencies obtained were 63, 64, 66, 66, and 66%. For glycerol experiments, the effluent was colorless, and no evidence of coke formation also from the balance was noticed.

3.5.1. Influence of Process Conditions (Temperature and Residence Time). Figure 6 shows the comparison of gas yields and gasification efficiencies obtained experimentally and with

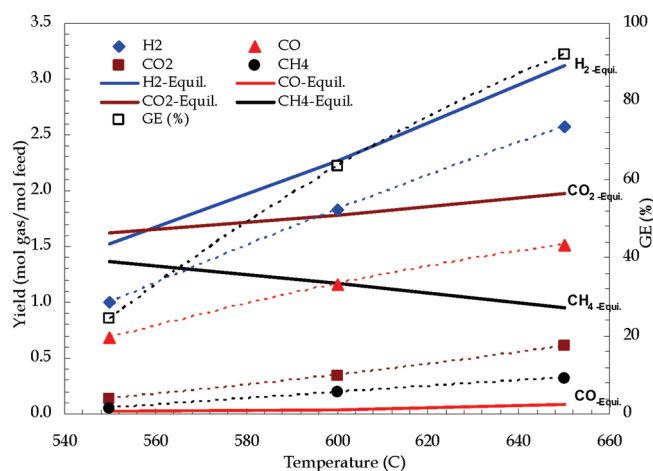


Figure 6. Comparison of the equilibrium gas yields with the experimental values at different temperatures for glycerol gasification. [Experimental conditions: concentration, 10 wt %; residence time, 5 s; pressure, 250 bar].

the predicted equilibrium values at different temperatures of glycerol gasification (10 wt %) in SCW. From thermodynamics perspective, complete gasification is attained at all temperatures, and the product gas of glycerol gasification in SCW mainly

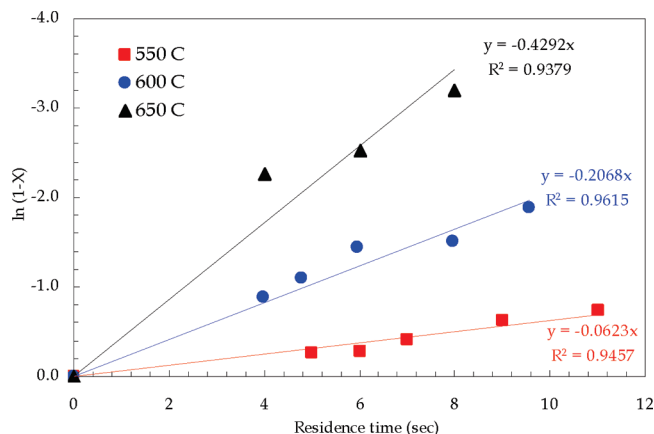


Figure 7. Normalized decomposition profile for 10 wt % glycerol conversion at 250 bar and three different temperatures.

consisted of H_2 , CO_2 , and CH_4 with smaller amounts of CO (less than 1 vol %). The predicted yields of H_2 increase, and the CH_4 yield declines as temperature increases. A marginal increase in CO_2 and CO yield is expected at higher temperatures. The calculated CO yield was relatively very small (0.0795 mol/mol feed at 650 °C) for 10 wt % glycerol gasification.

It is evident from Figure 6 that the experimentally measured values are not in line with the equilibrium values. The equilibrium yields predicted for H_2 , CH_4 , and CO_2 were higher than the experimentally measured values. The CO yield obtained experimentally exceeds the equilibrium values, indicating that glycerol decomposition probably proceeds predominantly via the formation of CO and H_2 . The experimentally obtained gasification efficiencies increased almost linearly as a function of temperature, and it was 24%, 63%, and 92% at temperatures 550, 600, and 650 °C, respectively. With a raise in temperature from 550 to 650 °C, the total gas yield increased from 1.88 to 5.16 mol gas/mol feed, and the product gas was mainly rich in H_2 and CO with less CO_2 and CH_4 yields over the temperature range studied. Additionally, a slight increase in the molar fraction of C_2 – C_3 compounds (0.73–2.82 vol %) was noticed with increasing the temperature from 550 to 650 °C (results not in graph).

The decomposition profile for glycerol conversion over a range of residence time (4–11 s) at different temperatures (550, 600, and 650 °C) is shown in Figure 7. The carbon conversion increases linearly with increasing residence time over the temperature range that is studied. An apparent pseudo first-order kinetics for glycerol decomposition in SCW is fitted based on the gasification efficiency, and the activation energy (E_a) was found to be 111 kJ/mol which is in close agreement with the value reported in the literature.²⁵ Maximum gasification efficiencies of 52%, 85%, and 96% are achieved at 550, 600, and 650 °C and at longer residence times (11, 10, and 8 s), respectively.

3.5.2. Influence of Amino Acids and Alkali Salts. A few studies^{19,20,26,27} have pointed out the possible influence of proteins and amino acids on SCW gasification. Di Leo et al.²⁷ examined the gasification of phenol and glycine (an amino acid) as model compounds for plants and protein biomass, respectively, in SCW and reported solids deposition on the quartz reactor wall for glycine at 500 °C in the presence and absence of nickel wire as a catalyst. They found that glycine was more resistant to gasification than phenol, and the addition of a nickel wire catalyst assisted glycine gasification and reduced char formation, as evidenced by less char coating on the reactor wall. Kruse et al. studied the influence of proteins on hydrothermal

gasification and liquefaction of real biomass feed stock (zoo mass)¹⁹ and with model compounds (glucose).²⁰ They noticed a reduction in the glucose gasification efficiency in the presence of proteins/amino acids.

A set of experiments with glycerol gasification in SCW has been performed in the presence of three different amino acids (glycine, L-alanine, and L-proline) and an alkali salt (K_2CO_3). Table 3 illustrates the influence of additives on the gas composition, gas yields, and gasification efficiency under different conditions studied.

At 600 °C, no significant change in the product gas distribution of glycerol (10 wt %) gasification in SCW was observed in the presence of amino acids. It is noteworthy to mention that at 600 °C enhanced GE was observed with the addition of 0.5 wt % glycine and with the addition of 0.5 wt % L-alanine, when compared with no additives. However, the GE and total gas yield decreased significantly in the presence of L-proline (again 0.5 wt %). The reported GE values refer to the complete C-gasification efficiency of the total mixture, hence including the C introduced via the amino acids and/or alkali salts (total C out via gas phase over total C in via glycerol and amino acids). On the other hand, at 550 °C no or a minor effect on the GE was observed in the presence of glycine and L-alanine, and again, no change in product gas distribution was noted.

A more clear effect of the presence of amino acids was observed with respect to coke formation. As indicated above, no coke formation was observed during SCWG with glycerol alone. However, when cleaning the reactor after each experiment with glycerol and amino acid mixtures, the formation of some black solid particles (coke) was noticed. Unfortunately, we were not able to quantify the coke that is formed after these experiments. Coke formation was most pronounced when using the glycerol–proline mixture. This suggests a lower reactivity of glycine and alanine when compared to L-proline.

The coke observed is either directly produced from the amino acids added or from reaction products of the amino acids (or their decomposition intermediates/products) with glycerol (or its decomposition intermediates/products). In the literature, indeed an indication was found for a relatively high reactivity of L-proline, especially toward glucose.³⁴

In the glycerol SCWG experiments without additives, the reactor effluent was colorless, but in the presence of amino acids the effluent color changed with respect to the type of amino acid used. The effluent color in the case of the glycine addition was light yellow, while with L-alanine it turned dark yellow in color. According to the literature,^{34–37} this can indicate the formation of Maillard intermediates during the reaction. Surprisingly, the effluent color with L-proline was completely different to what is found with the other amino acids as it was chocolate brown in color and contained oily material. No oily matter was found in the effluent with either glycine or L-alanine. It is noteworthy to mention that also in the case of the addition of K_2CO_3 to the glycine–glycerol mixture at 500 °C an oily like substance in the effluent was noticed.

Several researchers^{8,11,19,20,26} have already reported the significant influence of alkali salts on biomass gasification, leading to higher gas yields by improving the water–gas shift activity. The behavior of alkali salts in combination with amino acids on glycerol gasification was studied by adding K_2CO_3 and glycine (Table 3). The addition of K_2CO_3 induced an (essentially) complete conversion of glycerine and intensified the H_2 yield by promoting the water–gas shift. Remarkably, the addition of glycine (0.5 wt %) along with K_2CO_3 (0.5 wt %) reduced the GE of glycerol at 600 °C again below completion

Table 3. Influence of the Additives on 10 wt % Glycerol Gasification at 5 s Residence Time

condition	none	glycine (0.5 wt %)	alanine (0.5 wt %)	proline (0.5 wt %)	none	glycine (0.5 wt %)	alanine (0.5 wt %)	K ₂ CO ₃ (0.5 wt %)	K ₂ CO ₃ (0.5 wt %) + glycine (0.5 wt %)
T, [°C]	600	600	600	600	550	550	550	600	600
P, [bar]	250	250	250	250	250	250	250	250	250
GE %	66 ± 1.4	69	73	57	24	24	22	100	89
Dry Gas Composition (mol %)									
H ₂	50 ± 4	51	51	50	54	54	54	55	53
CO	32 ± 3	32	32	31	30	29	31	1	1
CO ₂	9 ± 1	10	9	11	11	14	12	30	28
CH ₄	5 ± 1	5	5	5	2	2	2	5	6
^a C ₂ –C ₃	3 ± 2	2	3	4	2	2	2	9	13
Yield (mol gas/mol Glycerol)									
H ₂	1.84 ± 0.32	2.09	2.22	1.59	0.77	0.82	0.74	2.69	2.61
CO	1.18 ± 0.14	1.32	1.42	0.98	0.43	0.44	0.42	0.04	0.03
CO ₂	0.32 ± 0.04	0.39	0.39	0.34	0.16	0.21	0.16	1.48	1.40
CH ₄	0.19 ± 0.03	0.20	0.24	0.15	0.03	0.03	0.03	0.25	0.28
^a C ₂ –C ₃	0.12 ± 0.07	0.10	0.11	0.14	0.03	0.03	0.02	0.44	0.63
dissolved carbon in effluent (wt %)	1.2	1.3	1.3	2.4	2.3	2.6	3.1	—	0.3
effluent color	colorless	light yellow	dark yellow	brownish color	colorless	light yellow	dark yellow	colorless	lightyellow

^a C₂–C₃ gases include C₂H₄, C₂H₆, C₃H₆, and C₃H₈.**Table 4. Comparison of Algae Results in SCW with Other Reported Studies Using Quartz Capillaries**

references	this work	potic ¹⁰	Kersten et al. ⁷	Resende et al. ¹²	Resende et al. ¹³	Sricharoenchaiikul ²⁸
feedstock	algae	wood	glucose	lignin	cellulose	blackliquor
reaction time [min]	2	1	1	45	5	1
pressure [bar]	240	300	300	310	310	300
temperature [°C]	600	600	600	600	600	650
concentration [wt %]	7.3	10	10	9	9	10
Dry Gas Composition (mol %)						
H ₂	7	1	12	11	15	10
CO	22	20	60	16	24	10
CH ₄	25	12	13	35	18	14
CO ₂	26	59	9	37	43	8
C ₂ –C ₃	20	8	6	—	—	36
GE (%)	53	47	69	19	35	66

when compared to the situation without amino acid. Alternatively, one could state that adding K₂CO₃ to the glycerol–glycine system increased the GE, although not (yet) to completion.

4. Discussion

Protein biomass (like algae) generally contains a significant portion of proteins, which are made of amino acids that act as building blocks. The various amino acids present in the proteins have different chemical structures and hence different reactivity, but they all can undergo similar decarboxylation to produce carbonic acid and amines and deamination reactions to produce ammonia and organic acids.^{7,34–36}

An incomplete carbon conversion of algae could potentially be ascribed due to the presence of these proteins/amino acids, as they have been reported to be quite recalcitrant during gasification and also due to the presence of carbohydrates.^{10,18–21,27,34–36}

In the experiments with the continuous flow reactor, having a catalytically active Inconel wall, the gasification of glycerol was, however, not affected, if not enhanced, by the presence of L-alanine and glycine. This seems, at first glance, in contradiction with results presented by Kruse et al.²⁰ who noticed a reduction in the glucose gasification efficiency in the presence of proteins/amino acids. They suggested a mechanism in which the formation of relatively stable free radical anions (or nitrogen-containing aromatics) generated via the Maillard reaction of proteins and carbohydrates results in a radical scavenging effect.

As free radical chain reactions are considered highly relevant for gas formation, this then results in a reduction of the gasification efficiency. Probably Maillard-type reactions seem less prevalent in the case of glycerol gasification in the presence of glycine and L-alanine but more dominant with the L-proline.

The apparent reducing effect of L-proline on the gasification efficiency is therefore not likely due to this type of reaction, but more probably related to a direct radical scavenging effect, for which in recent years evidence was found.^{34,37} Proline is also known to accumulate in plant tissues during abiotic oxidative stresses, most likely for its radical scavenging properties. In line with the findings reported in this study, Kaul et al.³⁷ have also indicated that, in contrast to the radical scavenging effect of proline, glycine does not interact with free radicals.

Our findings of enhanced coke formation are confirmed by the few experiences reported in the literature. Kruse et al.²⁰ observed not only an increase in coke formation but also extensive nickel leaching due to corrosion in the presence of amino acids. Antal et al.⁷ have also reported extensive corrosion and leaching of reactor walls during the tests with real biomass (potato waste) gasification in SCW.

Table 4 illustrates the comparison of gasification behavior of algae with other model compounds and real biomass. Lignocellulosic biomass (as pine-wood) is mainly comprised of cellulose, hemicellulose, and lignin and minor amounts of other ingredients as minerals. Protein biomass, such as algae,

consists of proteins, carbohydrates, fats, and other minerals. The composition of the biomass dictates the gasification behavior and the product gas distribution. From Table 4, it is obvious that for the lignocellulosic biomass the lignin is the most difficult fraction to convert. Algae seem to be a promising feedstock for the conversion in SCW, not only considering the exceptional growth rates but also due to the fact that they seem to be more readily converted via SCWG.

5. Conclusions

The gasification of microalgae (protein biomass) in supercritical water was tested in quartz capillaries. For the uncatalyzed conversion, it was found that, similar to earlier studies with lignocellulosic biomass, the gasification efficiency of algae (here: *Chlorella vulgaris*) increases with higher temperature and lower concentrations.

For the uncatalyzed gasification, the maximum algae gasification efficiency was found to be 75% at 600 °C for reaction times of 4 min and higher. This maximum selectivity seems to be “kinetically determined” and can be increased by increasing temperature, decreasing concentration, and the application of catalysts. Experiments with an excessive amount of Ru/TiO₂ catalyst show that complete gasification can be obtained. As evidenced by the Inconel powder experiments, Ni-containing metal walls will exhibit catalytic activity for the gasification.

The role of some amino acids (building blocks of proteins) and alkali salts present in the algae has been investigated by adding three different amino acids and potassium carbonate, separately and in combination, to a 10 wt % glycerol solution and testing for the SCWG behavior. Whereas L-alanine and glycine are inert or even slightly enhance gasification, especially L-proline suppresses the gasification efficiency possibly by free radical scavenging. The presence of amino acids led in all cases to significant coke formation and colorization of the reactor effluent, possibly due to reaction products from Maillard-type reactions. Potassium carbonate enhances the glycerol gasification and promotes H₂ formation via the water–gas shift reaction.

Algal biomass can be more easily gasified in supercritical water, and further evaluation of optimum process conditions and catalyst development is however required to achieve complete gasification at technically and economically more favorable reaction conditions.

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Appendix

Nomenclature and Abbreviations

Y_i = Gas yield, mol/mol

$\rho_{T,P}$ = Density of water at reactor conditions, g/cm³

ρ_{STP} = Density of water at STP, g/cm³

$N_{c,feed}$ = Number of moles of carbon in feed, mol

$N_{c,i}$ = Number of moles of carbon in product gas (i) produced, mol

N_{feed} = Number of moles of feed, mol

ϕ = Total flow rate, mL/min

τ = Residence time, s

GE = Gasification efficiency (or) carbon conversion, %

X = Carbon conversion, %

P = Pressure, bar

T = Temperature, °C

V = Reactor volume, cm³

E_a = Activation energy, KJ/mol

SCW = Supercritical water

SCWG = Supercritical water gasification

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