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A parametric study on supercritical water gasification of Laminaria hyperborea: a carbohydrate-rich macroalga

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The potential of supercritical water gasification (SCWG) of macroalgae for hydrogen and methane production has been investigated in view of the growing interest in a future macroalgae biorefinery concept. The compositions of syngas from the catalytic SCWG of Laminaria hyperborea under varying parameters including catalyst loading, feed concentration, hold time and temperature have been investigated. Their effects on gas yields, gasification efficiency and energy recovery are presented. Results show that the carbon gasification efficiencies increased with reaction temperature, reaction hold time and catalyst loading but decreased with increasing feed concentrations. In addition, the selectivity towards hydrogen and/or methane production from the SCWG tests could be controlled by the combination of catalysts and varying reaction conditions. For instance, Ru/Al_2O_3 gave highest carbon conversion and highest methane yield of up to 11 mol/kg, while NaOH produced highest hydrogen yield of nearly 30 mol/kg under certain gasification conditions.

Key words: hydrothermal gasification, macroalgae, syngas, algae biorefinery

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1.0 Introduction

Biomass-derived fuels have received increasing attention as one of the solutions to reducing global warming and in tackling anthropogenic climate change. Technologies in utilising biomass for power generation and transportation fuel are now well established but there are concerns regarding environmental and socio-economic consequences. These arise from increased land use for growing biomass for fuel which leads to competition with arable land for food crops. As such, biofuels production is shifting to non-food sources – lignocellulosic biomass – but these still require large arable areas as well as sufficient quantities of water and fertilisers to grow.

The utilisation of macroalgae as a raw material for energy production compared to terrestrial biomass is appealing due to a number of factors. Macroalgae has a faster growing rate due to no water limitations (Gellenbeck and Chapman, 1983) and a lesser effect on temperature variation. It also has a higher photosynthetic efficiency of 6-8% (FAO, 1997) compared to 1.8-2.2% for terrestrial biomass and a higher productivity than that of terrestrial crops. Cultivated macroalgae (e.g. brown seaweed) demonstrate a productivity 6.5 times the maximum projected yield for sugarcane on an aerial basis (Gao and Mckinley, 1994). However, the feasibility of production of macroalgae for energy production, in a scale similar to terrestrial biomass has thrown up some uncertainties relating to where and how it will be produced and the economics of its production and subsequent conversion to fuels (Elliott, 2008).

Despite macroalgae being extensively grown and used as food in Asiatic countries, as well as a source of chemicals, the fuel from algae concept does not face the same challenges compared to first and second generation biofuels in terms of food production and requirement of large areas of land, water and fertilisers.

The carbohydrates in macroalgae have potential for producing biofuels and while conversion has focused on biogas production by anaerobic digestion (Matsui and Koike, 2010), recent work has focused on utilising the laminarin and mannitol for bioethanol production by fermentation (Borines et al., 2013; Yeon et al., 2011). Thermochemical conversion routes like direct combustion, pyrolysis, gasification and liquefaction have received less attention due to the high moisture and ash content of macroalgae. Studies have indicated the high fouling potential of the ash in macroalgae which if combusted could lead to component failure unless macroalgae is introduced in a carefully controlled fuel blend so as to control the ash chemistry (Ross et al., 2009, 2008). In addition, relatively dry feedstocks are required for thermochemical conversion and the energy penalty of drying can make the process uneconomical. As such, hydrothermal processing routes are more suited for direct conversion of macroalgae – a feedstock containing up to 90% water.

Hydrothermal processing is a flexible process in terms of products. Algal biomass has been converted into a solid (char) through hydrothermal carbonisation (HTC) at temperatures less than 200 °C (Heilmann et al., 2010) and into a bio-oil at temperatures between 200-375 °C through hydrothermal liquefaction (HTL) (Brown et al., 2010; Duan and Savage, 2011). Hydrogen and synthetic natural gas are produced from temperatures exceeding 375 °C through hydrothermal gasification (HTG) with the products either directly combusted or further upgraded to hydrocarbons.

Hydrothermal gasification of macroalgae is of particular interest due to a number of advantages the process offers. Not only is the process tolerant to the ash content of macroalgae, the alkali salts have a catalytic effect resulting in higher hydrogen yields and better gasification efficiencies (Sınağ et al., 2003). However, inorganic salts are insoluble in supercritical water and thus can precipitate during the SCWG process. This can cause reactor plugging, fouling and even corrosion. There have been several attempts to solve this challenge in recent years and it appears salt separation prior to SCWG is mostly favoured. This has resulted in a number of reactor designs based on supercritical water oxidation (SCWO) technology including the Modar reactor (Huang et al. 1992), transpiring wall (Wellig et al., 2005) and cooled wall (Cocero and Martinez, 2004) reactors. Zohrer et al. (2014) recently reported their KONTI-2 test rig which comprised of a biomass sample preheater, a salt precipitator and a catalytic SCWG reactor for the hydrothermal processing of fermentation residues. They found that high levels of desalination was achievable but with an adverse effect of tar/char formation in the salt precipitator, resulting in poor liquefaction of the biomass.

In addition, a carbohydrate-rich biomass has been shown to be desirable feedstock for HTG and most macroalgae are particularly carbohydrate-rich. HTG also serves as a clean-up process for algal energy conversion, since it is easier to obtain clean syngas products, free from metals and other heteroatoms compared to char from HTC and bio-oil from HTL. If supercritical water is used as the gasifying medium (water above 374 °C and 22 MPa), the process is referred to as supercritical water gasification (SCWG) and results in almost complete gasification of the feedstock with high hydrogen and carbon dioxide yields and low char and tar formation. SCWG is still in its early development stage and scale up issues are yet to be addressed in terms of overcoming reactor plugging/corrosion and process economics. However, the technology has demonstrated its economic competitiveness with other hydrogen production methods; Spritzer & Hong (2003) estimate the cost of hydrogen production from SCWG of biomass to be about US$3/GJ. In addition, biomass thermochemical processes produce hydrogen gas coupled with other gas constituents – mainly carbon dioxide – and therefore separation and purification of hydrogen gas is required. SCWG of biomass has the advantage of producing a product gas at high pressure, reducing further compression costs, and carbon dioxide can be easily separated because it is much more soluble in water at high pressure compared to hydrogen. In terms of an algal biorefinery – a concept discussed by recent studies (Chakraborty et al., 2012; Alba et al., 2012) – the captured carbon dioxide can be used for microalgal cultivation and the hydrogen for upgrading the algal oil. In addition, the clean/sterile process water from SCWG which is rich in nutrients can be recycled along with the carbon dioxide for microalgal cultivation (Cherad et al., 2013).

The work on hydrothermal gasification of macroalgae is limited. Schumacher et al. (2011) investigated the supercritical water gasification of macroalgae at 500 °C and produced 12g and 13g of H_2/kg seaweed from L. digitata and A. esculenta respectively. More recently, Onwudili et al. (2013) investigated the catalytic SCWG of S. latissima producing 30g of H_2/kg seaweed in the presence of sodium hydroxide as a catalyst and noting a doubling of methane yield in the presence of nickel catalyst to 112g CH_4/kg seaweed. In addition, previous work yielded 20.4g H_2 and 102g CH_4/kg seaweed from the SCWG of S. latissima using ruthenium catalyst whilst highlighting the effect of sulphur on catalyst activity – a point also raised by Guan et al. (2012) in demonstrating the deactivation of Ru/C catalyst during the SCWG of the microalga Nannocholoropsis.

The focus of this work is to study the effects of various parameters on the supercritical water gasification of a macroalga: Laminaria hyperborea. Sodium hydroxide and alumina-supported ruthenium and nickel catalysts were chosen as catalysts due to their known effect in catalysing biomass gasification (Azadi et al., 2012; Onwudili and

Williams, 2013; 2009). The effect of different catalysts, catalyst loading, feed concentration, hold time and temperature were investigated to understand their effect on gas yields, gasification efficiency and energy recovery.

2.0. Experimental

2.1. Materials

L. hyperborea was harvested off the Scottish coast of Easdale and freeze dried. The dry material was ground and sieved to a particle size of <90 μm. The ground sample has a moisture content of 8.52% and an ash content of 20.84%. The C, H, N, S and O contents (ultimate analysis) of the macroalgae are as follows, with O determined by difference: 35.21, 4.57, 1.35, 0.64 and 37.39%. The algae sample has a higher heating value of 13.42 MJ/kg. Three different loadings of ruthenium-alpha alumina (Ru/Al_2O_3) catalyst and supplied by Catal Limited, a UK-based SME, and used as received. The three nominal loadings of ruthenium impregnated on 2-4mm diameter alumina spheres were 5, 10 and 20%. The catalyst has a specific surface area of 21 m^2 g^{-1} and an average metal particle size of 1.7nm.

2.2. Experimental procedure

Supercritical water gasification experiments were performed in a batch unstirred Inconel reactor obtained from Parr, USA. The reactor has been described previously (Onwudili and Williams, 2010) and the relationship between temperature, pressure and water loading has been studied (Onwudili and Williams, 2009). Briefly, the reactor has a 75 ml volume capacity and is rated to 600 ℃ and 35MPa. The reactor was heated by a 1.5kW ceramic knuckle heater and the reactor temperature was monitored by J-type thermocouple held in a thermowell at the bottom of the reactor. The operating pressure was measured with a pressure gauge mounted on the reactor head. Each experiment involved loading the reactor with a paste made from the dry macroalgae and an amount of deionised water required for the feed concentration under investigation. When required, the ruthenium catalyst was suspended at the top of the reactor on a stainless steel mesh gauze. The reactor was purged with nitrogen and heated at an average rate of 30 °C/min to the required temperature and held for the designated reaction time. At the end of each test, the reactor was rapidly cooled using compressed air and the final pressure noted once the reactor reached room temperature.

The product gas was sampled for offline gas chromatography analysis by taking two to four 30 ml gas samples to allow for reproducible gas analysis from each experiment. Three separate experiments were repeated several times with results showing a standard deviation of < 5% from gas analysis. In addition, several results have been published using the same batch reactor with good reproducibility (Onwudili and Williams, 2009). The aqueous fraction was transferred from the reactor using deionised water and filtered to determine the solid residue fraction. A fraction of the filtrate was dried to determine the water soluble products (WSP). The reactor was rinsed with dichloromethane (DCM) to extract any remaining tar products.

2.3. Analysis of products

2.3.1. Gas analysis

Hydrocarbon gases including methane and C_2–C_4 gases were analysed using a gas chromatograph fitted with a flame ionisation detector (Varian C-3380 GC/FID). The column was 2 m long by 2 mm diameter and packed with 80–100 mesh Hysesp.

Hydrogen, nitrogen, oxygen, carbon monoxide and carbon dioxide were analysed by separate gas chromatographs fitted with thermal conductivity detectors (GC/TCD). A 2m long by 2mm diameter, 60–80 mesh packed molecular sieve column was used to separate hydrogen, oxygen, nitrogen and carbon monoxide. A packed Hysesp column of similar dimensions was used for carbon dioxide analysis. Results were obtained in volume percent, converted to moles using the general gas equation, from which the mass of which gas product was obtained.

2.3.2. Process water analyses

The aqueous fraction was diluted to a known volume and analysed for total organic carbon content by a TOC analyser (HACH IL 550 TOC-TN). The inorganic carbon content (IC) was also noted as this represents the dissolved carbon dioxide in the water.

2.3.3. Carbon gasification efficiency and energy recovery

The carbon gasification efficiency is defined as the percentage conversion of the carbon in the feed into permanent gases and aqueous inorganic carbon in the process water. The carbon content of the gases is calculated from the yields of the carbon containing gases. The energy recovery is calculated with the following equation:

$$Energy\ recovery = \frac{HHV\ of\ combustible\ gas\ product * mass\ of\ combustible\ gas\ product}{HHV\ of\ feed * mass\ of\ feed}\ x100\%$$

2.3.4. Catalyst

Spent catalyst was dried at 105 °C for 1 hour then re-weighed to determine any loss in mass. On average, the mass loss between fresh and spent catalyst was less than 0.1% indicating its hydrothermal stability.

3.0. Results and discussion

3.1. Catalytic SCWG of macroalgae: L. hyperborea

A study of the effect of various catalysts on the supercritical water gasification (SCWG) of L. hyperborea was investigated at a reaction temperature of 500 °C, hold time of 30 minutes and an algal feed concentration of 6.66%. Figure 1 shows the gas yields from the use of ruthenium, nickel and sodium hydroxide catalysts compared to a non-catalysed experiment and Table 1 shows the mass balances, carbon gasification efficiency and energy recovery.

The mass balance for each experiment was >97%. Hydrogen, methane and carbon dioxide were the main three constituents of the gas product from non-catalysed SCWG of L. hyperborea. Small amounts of carbon monoxide and $C_2 – C_4$ hydrocarbons were also produced. Higher hydrogen and methane yields were observed using ruthenium and sodium hydroxide catalysts. There was no significant effect on gas yields using nickel catalysts compared to the non-catalysed experiment.

The yield of hydrogen was approximately three times higher when using sodium hydroxide (16.27 mol H_2/kg algae) compared to non-catalysed SCWG of L. hyperborea (5.18 mol H_2/kg algae). This can be attributed to the role sodium hydroxide plays in capturing the CO_2, decomposing the feedstock into relevant intermediates, ultimately catalysing the water gas shift reaction (Onwudili and Williams, 2009). The relatively high mass of water soluble products when using sodium hydroxide is due to the removal of carbon dioxide as sodium carbonate which is soluble in water.

The product gas using sodium hydroxide mainly consists of hydrogen and methane with small amounts of $C_2 – C_4$ hydrocarbons resulting in a higher energy recovery of 82.9% compared to 52.4% for the non-catalysed experiment (Table 1). The yield of methane was approximately 2.5 times higher when using ruthenium catalyst compared to the non-catalysed experiment. Similar results have been reported from the use of ruthenium in catalysing the hydrothermal gasification of biomass (Elliott, 2008).

The gas yields, gasification efficiencies and energy recoveries from the catalysed SCWG of L. hyperborea using sodium hydroxide and ruthenium is explored by examining the effect of parameters such as catalyst loading, feed concentration, hold time, and temperature.

3.2. Effect of catalyst loading

The effect of ruthenium loading and sodium hydroxide concentration was studied at conditions of 500 °C, 30 min hold time and a feed concentration of 6.66%. The weight of Ru/Al_2O_3 catalyst was fixed at 1g. Figure 2 shows the trend of gas yields, gasification efficiencies and energy recoveries of increasing concentration of catalysts compared to non-catalysed experiments. Increasing the ruthenium loading from 5% to 20% caused a slight increase in hydrogen yields but had no effect on methane yields. The mass of carbon in the gas product increased with higher loading of ruthenium resulting in higher carbon gasification efficiencies but this was due to the increase in CO_2 yield. The energy recovery using 20% Ru/Al_2O_3 was 91% due to the higher yield of H_2 compared to lower ruthenium loadings. An increase in sodium hydroxide concentration from 0.5M to 3M resulted in a near doubling of hydrogen yield and a threefold decrease in the amount of C_2 – C_4 hydrocarbons present in the product gas. As such, the energy recoveries show no variation as the concentration of base catalyst is increased.

3.3. Effect of feed concentration

The solid concentration in the feedstock has an important effect on the gasification efficiency in supercritical water with experimental data (Mettanant et al., 2009;

Schmieder et al., 2000) indicating a decline in gasification efficiency when the feed concentration exceeds 2% (Basu, 2010). However, very low feed concentrations require high pumping costs and effluent disposal/recovery thus impeding commercialisation of supercritical water gasification technology. Figure 3 shows the effect of feed concentration on the SCWG of L. hyperborea at 500 °C, 30 min hold time using 20% Ru/Al_2O_3 and 1.5M NaOH catalysts. Methane yields from the ruthenium catalysed experiments showed no significant difference with varying feed concentrations of 3.33, 6.66 and 13.3%. However, hydrogen yield decreased by 50% on average when the feed concentration was doubled. The energy recovery using ruthenium was 90.5% at a feed concentration of 3.33%. Increasing the feed concentration to 6.66% and 13.3% resulted in a decrease in energy recovery to 78.7 and 67.4% respectively. The product gas obtained using a feed concentration of 3.33% and 1.5M NaOH as catalyst contained 29.2 mol H_2/kg L. hyperborea and 6.21 mol CH_4/kg L. hyperborea resulting in an energy recovery of 111.3%. The overage in energy recovery is due to the participation of the water medium as a reactant for hydrogen gas production. Increasing the feed concentration to 6.66 and 13.3% resulted in a larger decrease in energy recovery to 82.9 and 50.4% respectively.

3.4 Effect of hold time

The effect of varying hold times (0, 30, 60 and 120 minutes) on the SCWG of L. hyperborea was studied at 500 °C and a feed concentration of 6.66%. Figure 4 shows the results from non-catalysed experiments and experiments using 5% Ru/Al_2O_3 and 1.5M NaOH. Generally, longer hold times allow for better yields and this is reflected in the increase in hydrogen and methane yields for the non-catalysed experiments as the hold time increased. No significant increase in hydrogen and methane yields were observed as the hold time was doubled from 30 min to 60 min using ruthenium catalyst. Doubling the hold time to 120 min resulted in a 30% increase in hydrogen and methane yields to 10.4 and 11.2 mol /kg L. hyperborea respectively. The highest hydrogen yield obtained using sodium hydroxide was 16.27 mol /kg L. hyperborea at a hold time of 30 min. As the reaction time increases beyond 30 min, the hydrogen yield decreases and the methane yield increases slightly suggesting consumption of hydrogen in the methanation reaction to produce methane and water.

3.5 Effect of temperature

Temperature has a significant effect on the gas yields from biomass gasification. The enthalpy change for H_2 formation is endothermic while that of CH_4 formation is slightly exothermic and as such, the formation of H_2 is favoured over that of CH_4 at higher temperatures (Lu et al., 2007). The yields of hydrogen and carbon dioxide increase as the temperature increases due to the promotion of free-radical reactions which promote gas formation (Buhler et al., 2002). Figure 5 shows the effect of increasing temperature (400, 450, 500 and 550 °C) on the SCWG of L. hyperborea at a feed concentration of 6.66% using 20% Ru/Al_2O_3 catalyst and a total reaction time of 32 minutes. An increase in temperature to 550 °C causes a doubling in the yield of H_2 compared to 400 °C. Due to the presence of ruthenium catalyst which promotes the methanation reaction, the CH_4 yield remains relatively high (~8.0 mol /kg L. hyperborea) compared to non-catalysed SCWG.

Improvements in gasification efficiencies or yields high calorific value gases by raising reaction temperatures do not always translate to net gains in energy. Hence, it is important to evaluate the energy balance in terms of energy requirements for the SCWG process at 400 and 550 ℃ against the net gain in energy recovered towards contributing to a simple techno-economic assessment of the process. To do this, the energy required to heat the macroalgae up to the reaction temperature (E_{SG} or Energy Input) was calculated by using the following equation (Xu et al., 2011).

$$E_{SG} = w_{H_2O} \times (\mathit{\Delta H}_{H_2O}^{T_1} - \mathit{\Delta H}_{H_2O}^{T_0}) + w_{cell\times} C_{ps}(T_2 - T_0)$$

where w_{H_2O} is the mass of water fed (0.015 kg), T_1 is the reaction temperature (K), T_0 is the ambient temperature (K), $\mathit{\Delta H}_{H_2O}^{T}$ is the enthalpy of water at a certain temperature (NIST, 2008), w_{cell} is the DW of the macroalgae (0.001 kg), C_{ps} is the average specific heat of the macroalgae (assumed to be 1.34 kJ kg^{-1} K^{-1}, based on literature survey), T_2 is the temperature when the reaction will start (assumed to be 200 ℃).

The energy of the product gas (E_{PG}), which can represent the Energy Output from the SCWG was simply estimated from the sum of the mass of each component (M_n) multiplied by its calorific value (CV_n).

$$E_{PG} = \sum (M_1 * CV_1, M_2 * CV_2, \ \ .... \ \ M_n * CV_n)$$

Table 2 below shows the ESG and the EPG obtained from the SCWG at the two different temperatures. Clearly, there was a 37% increase in the energy requirement to conduct the SCWG at 550 C compared to the process at 400 C. However, the increase in Energy Output of more than 82% was obtained by raising the reaction temperature to 550 °C from 400 °C. This represented a 1.3 times net energy gain, indicating that, on the basis of energy balance alone, it was beneficial to carry out the SCWG at the higher temperature. However, other considerations, particularly regarding the mechanical requirements of the reactor, are also of immense importance in a complete process.

3.6. Challenges of scaling-up SCWG results from batch to continuous reactors

Extending these results from a batch reactor to a continuous reactor is often not straight forward due to a number of reasons, including differences in reactor heat-up time and reaction residence times as well as allowable feedstock concentrations. When using a solid catalyst, the scalability of batch reactor results to design a continuous process must be studied carefully as the catalyst is premixed with the feedstock in these batch experiments. On the contrary, in continuous operations, the catalysts are held in a fixed bed over which the feed solution is passed. In addition, in a batch reactor the feed/catalyst mixture is heated from ambient temperature to reaction temperature, in which case reactions could occur during the heat-up period. This is mirrored in a continuous process where the feed is preheated to improve efficiency and increase reaction rates. Tar and coke can be formed from the early reactions of biomass in the preheater of a continuous reactor, similar to what might happen during heat-up in a batch reactor and therefore assessing the coke formation potential of L. hyperborea is important. However, the gasification conditions proposed in this study (>500 °C) minimise the amount of tar and coke in the final products. Further work on the scalability of batch reactor results using solid catalysts at sub-critical conditions would be needed for the design of a continuous sub-critical gasification process for macroalgae. Furthermore, continuous processes have the flexibility of heat recovery. For instance, the heat content of the aqueous effluent can easily be recovered and used in the preheater, whereas in a batch reactor this not often possible.

Often times, higher concentrations of an insoluble solid feedstock can be gasified in a batch reactor as opposed to a continuous one due to reactor plugging issues in the latter. In a comparative study of the SCWG Of glycerol in the presence of water-soluble alkaline catalysts, Wu et al., (2011) found that residence time in the reactors was the main cause of the discrepancies between the results from batch and continuous reactors. For example, the gas yield/liquid feed ratio for the same residence time of 60 min was 24 for a continuous reactor but was 55 for a batch reactor. Although, this might indicate better performance from the batch reactor, such results are largely due to differences in the quantity of liquid feed. Compared to a continuous system, liquid feed treated in a batch reactor is often smaller.

Furthermore, high ash-content feedstocks such as macroalgae are a problem for both types of SCWG reactors due to insolubility of inorganic salts in supercritical water. Inorganic salts tend to precipitate under supercritical water conditions and this can plug reactors or cause fouling and corrosion. Essentially, a salt precipitator can be fitted prior to either a batch or a continuous SCWG reactor (Huang et al. 1992; Cocero and Martinez; 2001; Wellig et al., 2005; Zohrer et al., 2014)

4.0 Conclusions

The use of ruthenium or NaOH in the SCWG of L. hyperborea can control the selectivity of methane or hydrogen production, respectively. Longer residence times and increased reaction temperature favoured methane production when using ruthenium. An increase in catalyst loading had no significant effect on the methane yield. Higher hydrogen yields were obtained through using higher concentration of NaOH, lower algal feed concentration and shorter residence times (~30 min). Increasing reaction times (> 30min) with NaOH a base catalyst decreases the hydrogen yield. Overall energy recovery was highest at the lowest feed concentrations; 90.5% using ruthenium and 111.3% using NaOH.

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Bibliography

[1] Azadi, P., Khan, S., Strobel, F., Azadi, F., Farnood, R., 2012. Hydrogen production from cellulose, lignin, bark and model carbohydrates in supercritical water using nickel and ruthenium catalysts. Appl. Catal. B Environ. 117-118, 330–338. doi:10.1016/j.apcatb.2012.01.035

[2] Basu, P., 2010. Biomass Gasification and Pyrolysis: practical design and theory. Elsevier, The Boulevard, Langford Lane, Kidlington, Oxford.

[3] Borines, M.G., de Leon, R.L., Cuello, J.L., 2013. Bioethanol production from the macroalgae Sargassum spp. Bioresour. Technol. 138, 22–9. doi:10.1016/j.biortech.2013.03.108

[4] Brown, T.M., Savage, P.E., Duan, P., 2010. Hydrothermal Liquefaction and Gasification of Nannochloropsis sp. Energy & Fuels 24, 3639–3646. doi:10.1021/ef100203u

[5] Buhler, W., Dinjus, E., Ederer, H.J., Kruse, A., Mas, C., 2002. Ionic reactions and pyrolysis of glycerol as competing reaction pathways in near- and supercritical water. J. Supercrit. Fluids 22, 37–53.

[6] Chakraborty, M., Miao, C., McDonald, A., Chen, S., 2012. Concomitant extraction of bio-oil and value added polysaccharides from Chlorella sorokiniana using a unique sequential hydrothermal extraction technology. Fuel 95, 63–70. doi:10.1016/j.fuel.2011.10.055

[7] Cherad, R., Onwudili, J.A., Ekpo, U., Williams, P.T., Lea-langton, A.R., Camaro-Valero, M., Ross, A.B., 2013. Macroalgae Supercritical Water Gasification Combined with Nutrient Recycling for Microalgae Cultivation. Environ. Prog. Sustain. Energy 32, 902–909. doi:10.1002/ep

[8] Cocero, M. J., and Martinez, J. L., 2004. Cool wall reactor for supercritical water oxidation: Modelling and operation results. J. Supercrit. Fluids 31, 41 – 55**.** doi: 10.1016/j.supflu.2003.09.023

[9] Duan, P., Savage, P.E., 2011. Hydrothermal Liquefaction of a Microalga with Heterogeneous Catalysts. Ind. Eng. Chem. Res. 50, 52–61. doi:10.1021/ie100758s

[10] Elliott, D.C., 2008. Catalytic hydrothermal gasification of biomass. Biofuels bioprod. bioref. 254–265. doi:10.1002/bbb

[11] FAO, 1997. Renewable biological systems for alternative sustainable energy production. Food and Agriculture Organization of the United Nations (FAO), Agricultural Services Bulletin – 128.

[12] Gao, K., Mckinley, K.R., 1994. Use of macroalgae for marine biomass production and CO_2 remediation : a review. J. Appl. Phycol. 6, 45–60.

[13] Garcia Alba, L., Torri, C., Samorì, C., Van der Spek, J., Fabbri, D., Kersten, S.R. and Brilman, D.W.F. (Wim), 2012. Hydrothermal Treatment (HTT) of Microalgae: Evaluation of the Process As Conversion Method in an Algae Biorefinery Concept. Energy & Fuels 26, 642–657. doi:10.1021/ef201415s

[14] Gellenbeck, K., Chapman, D., 1983. Seaweed uses: the outlook for mariculture. Endeavour 7, 31–37.

[15] Guan, Q., Wei, C., Savage, P.E., 2012. Hydrothermal Gasification of Nannochloropsis sp. with Ru / C. Energy & Fuels 26, 4575-4582. doi:10.1021/ef3007992

[16] Heilmann, S.M., Davis, H.T., Jader, L.R., Lefebvre, P.A., Sadowsky, M.J., Schendel, F.J., von Keitz, M.G., Valentas, K.J., 2010. Hydrothermal

carbonization of microalgae. Biomass and Bioenergy 34, 875–882. doi:10.1016/j.biombioe.2010.01.032

[17] Huang, C., Barner, H. E., Killilea, W. R., Hong, G. T., 1992. Method for supercritical water oxidation . International Patent WO 92/21621

[18] Lu, Y., Guo, L., Zhang, X., Yan, Q., 2007. Thermodynamic modeling and analysis of biomass gasification for hydrogen production in supercritical water. Chem. Eng. J. 131, 233–244. doi:10.1016/j.cej.2006.11.016

[19] Matsui, T., Koike, Y., 2010. Methane fermentation of a mixture of seaweed and milk at a pilot-scale plant. J. Biosci. Bioeng. 110, 558–63. doi:10.1016/j.jbiosc.2010.06.011

[20] Mettanant, V., Basu, P., Butler, J., 2009. Agglomeration of biomass fired fluidized bed gasifier and combustor. Can. J. Chem. Eng. 87, 656–684. doi:10.1002/cjce.20211

[21] Onwudili, J.A., Lea-Langton, A.R., Ross, A.B., Williams, P.T., 2013. Catalytic hydrothermal gasification of algae for hydrogen production: composition of reaction products and potential for nutrient recycling. Bioresour. Technol. 127, 72–80. doi:10.1016/j.biortech.2012.10.020

[22] Onwudili, J.A., Williams, P.T., 2009. Role of sodium hydroxide in the production of hydrogen gas from the hydrothermal gasification of biomass. Int. J. Hydrogen Energy 34, 5645–5656. doi:10.1016/j.ijhydene.2009.05.082

[23] Onwudili, J.A., Williams, P.T., 2010. Hydrothermal reactions of sodium formate and sodium acetate as model intermediate products of the sodium hydroxide-promoted hydrothermal gasification of biomass. Green Chem. 12, 2214–2224. doi:10.1039/c0gc00547a

[24] Onwudili, J.A., Williams, P.T., 2013. Hydrogen and methane selectivity during alkaline supercritical water gasification of biomass with ruthenium-alumina catalyst. Appl. Catal. B Environ. 132-133, 70–79.

[25] Ross, A.B., Anastasakis, K., Kubacki, M., Jones, J.M., 2009. Investigation of the pyrolysis behaviour of brown algae before and after pre-treatment using PY-GC/MS and TGA. J. Anal. Appl. Pyrolysis 85, 3–10. doi:10.1016/j.jaap.2008.11.004

[26] Ross, A.B., Jones, J., Kubacki, M., Bridgeman, T., 2008. Classification of macroalgae as fuel and its thermochemical behaviour. Bioresour. Technol. 99, 6494–504. doi:10.1016/j.biortech.2007.11.036

[27] Schmieder, H., Abeln, J., Boukis, N., Dinjus, E., Kruse, a., Kluth, M., Petrich, G., Sadri, E., Schacht, M., 2000. Hydrothermal gasification of biomass and organic wastes. J. Supercrit. Fluids 17, 145–153. doi:10.1016/S0896-8446(99)00051-0

[28] Schumacher, M., Sınağ, A., Yanık, J., Kruse, A., 2011. Hydrothermal conversion of seaweeds in a batch autoclave. J. Supercrit. Fluids 58, 131–135. doi:10.1016/j.supflu.2011.04.009

[29] Sınağ, A., Kruse, A., Schwarzkopf, V., 2003. Key Compounds of the Hydropyrolysis of Glucose in Supercritical Water in the Presence of K_2CO_3. Ind. Eng. Chem. Res. 42, 3516–3521. doi:10.1021/ie030079r

[30] Spritzer, M., Hong, G., 2003. Supercritical water partial oxidation; Hydrogen, Fuel Cells, and Infrastructure Technologies: FY 2003 Progress Report. Proceedings of the 2002 U.S. DOE Hydrogen Program Review.

[31] Xu, L., Brilman, D. W.F., Withag, J. A.M., Brem, G., Kersten, S., 2011. Assessment of a dry and a wet route for the production of biofuels from microalgae: Energy balance analysis. Bioresource Technology 102 5113–5122. doi:10.1016/j.biortech.2011.01.066

[32] Wellig, B., Lieball, K., Rohr, P.R., 2005. Operating characteristics of a transpiring-wall SCWO reactor with a hydrothermal flame as internal heat source. J. Supercrit. Fluids 34, 35–50. doi:10.1016/j.supflu.2004.07.003

[33] Wu, Q., Bulza, S., Corcoveanu, C., Weiss-Hortala, E., Barna, R., Loppinet-Serani, A., Aymonier, C. 2011. Supercritical water conversion of glycerol: Comparative parametric study between batch and continuous reactors, Proceedings of 13th European Meeting on Supercritical Fluids. Accessed Online <July 6, 2014> http://www.isasf.net/fileadmin/files/Docs/DenHaag/HtmlDir/Papers/CO42.pdf

[34] Yeon, J.-H., Lee, S.-E., Choi, W., Kang, D., Lee, H.-Y., Jung, K., 2011. Repeated batch operation of surface-aerated fermentor for bioethanol production from the hydrolysate of seaweed Sargassum sagamianum. J. Ind. Microbiol. Biotechnol. 21, 323–331.

[35] Zöhrer, H., De Boni E., Vogel, F., 2014. Hydrothermal processing of fermentation residues in a continuous multistage rig: Operational challenges for liquefaction, salt separation, and catalytic gasification. Biomass and Bioenergy, 65, 51 - 633

Figure 1 Gas yields from the SCWG of L hyperborea at 500 °C, 30 min hold time, 6.66% feed concentration, with and without catalysts.

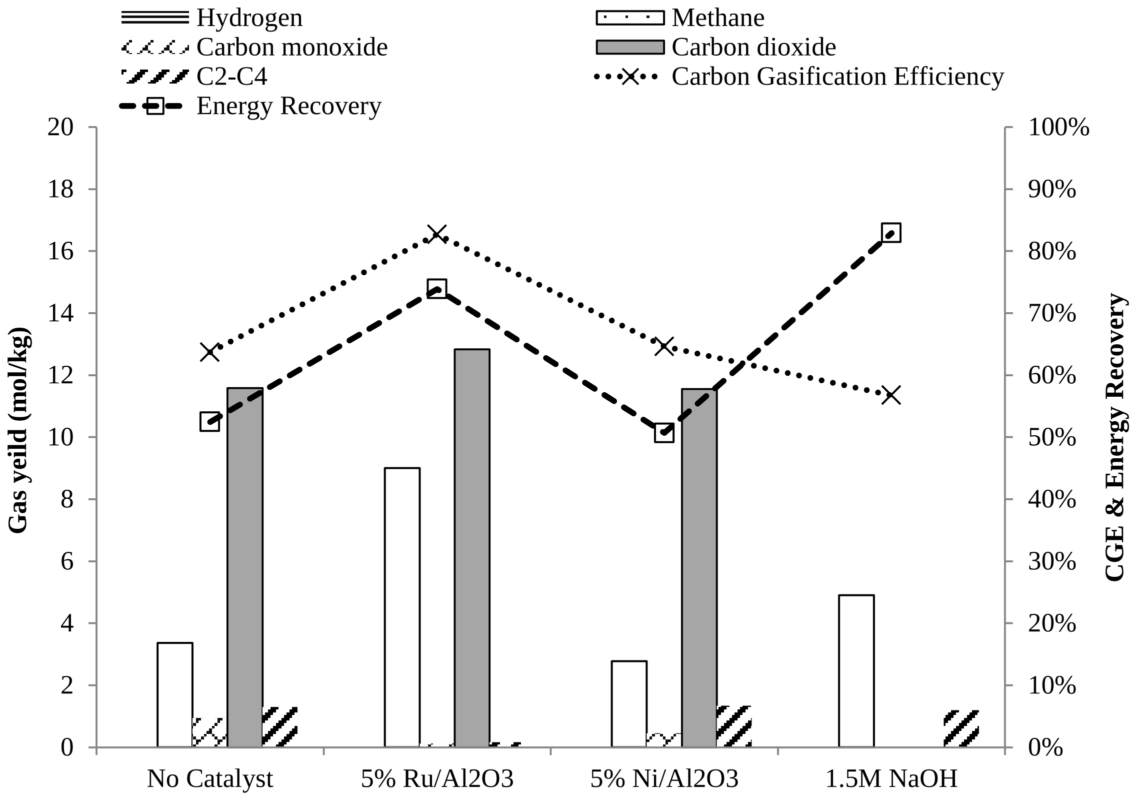

Figure 2 **Effect of catalyst loading on SCWG of L. hyperborea at 500 °C, 30 min hold time, 6.66% feed concentration. (a) Ru/Al_2O_3 (b) NaOH**

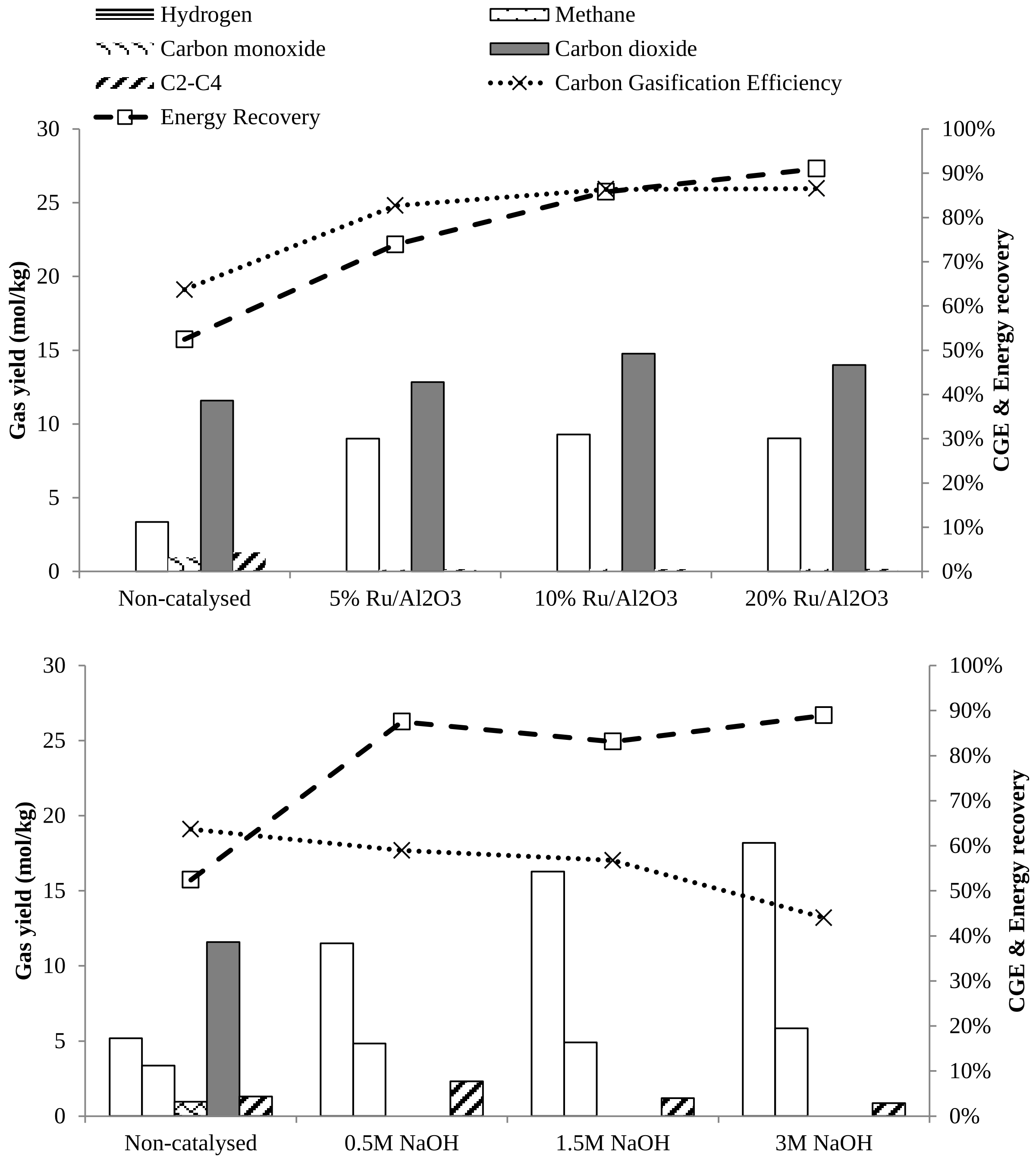

Figure 3 **Effect of feed concentration on SCWG of L. hyperborea at 500 °C, 30 min hold time with catalysts: (a) 20% Ru/Al_2O_3 (b) 1.5M NaOH**

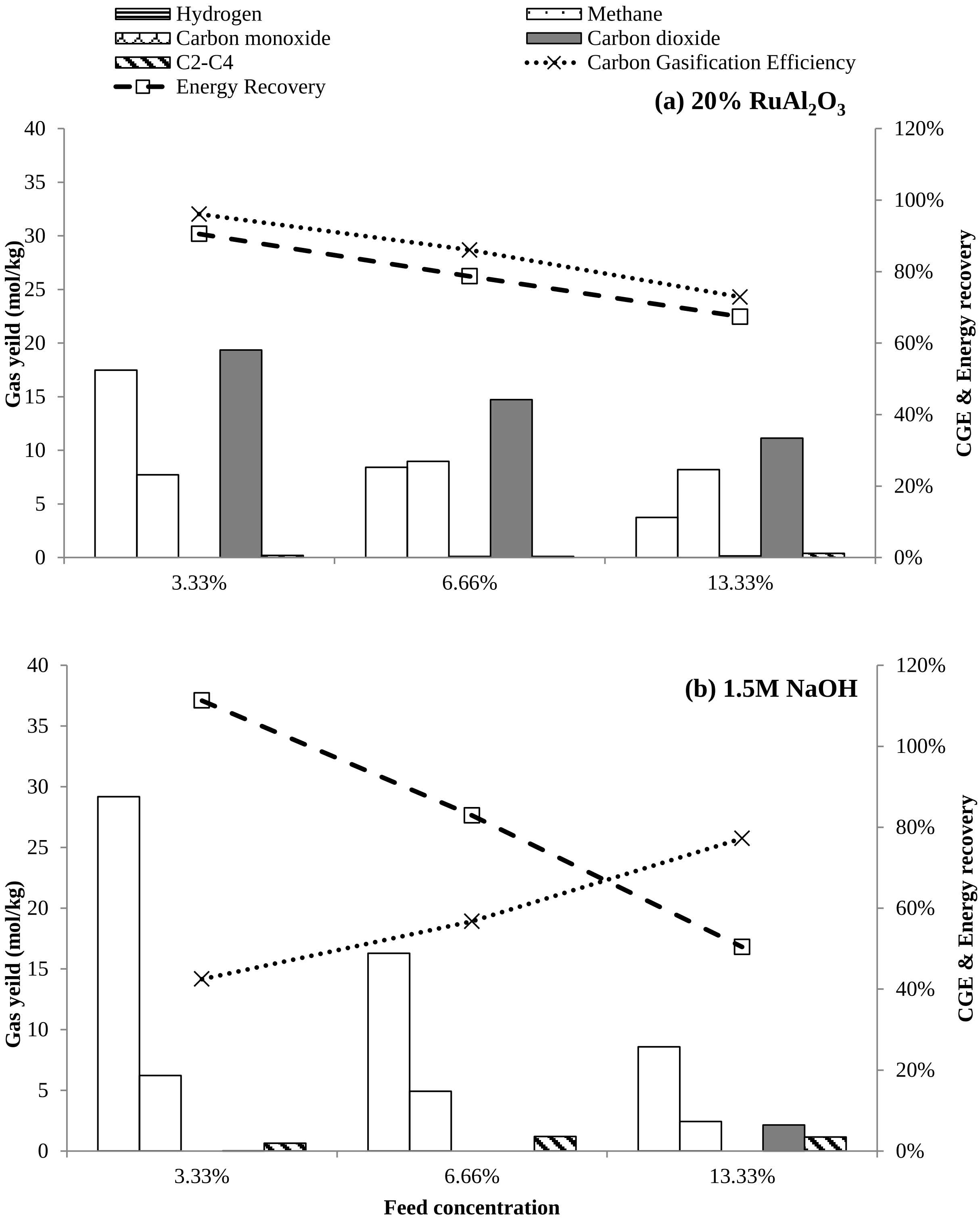

Figure 4 Effect of hold time on SCWG of L. hyperborea at 500 °C, 6.66% feed concentration (a) non-catalysed (b) 20% Ru/Al_2O_3 (c) 1.5M NaOH

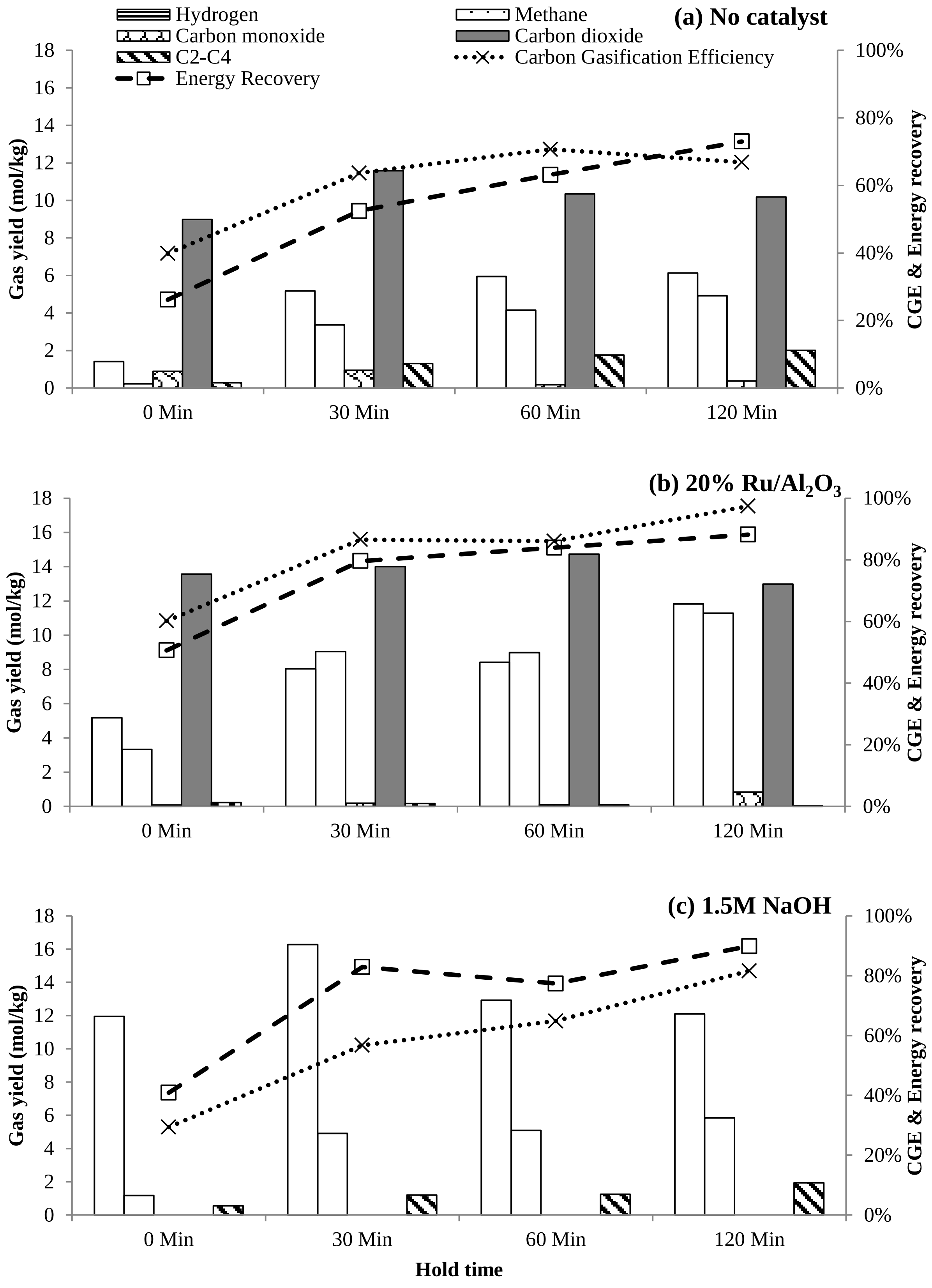

Figure 5 **Effect of temperature on SCWG of L. hyperborea. 30 min hold time 6.66% feed concentration with 20% Ru/Al_2O_3 as a catalyst**

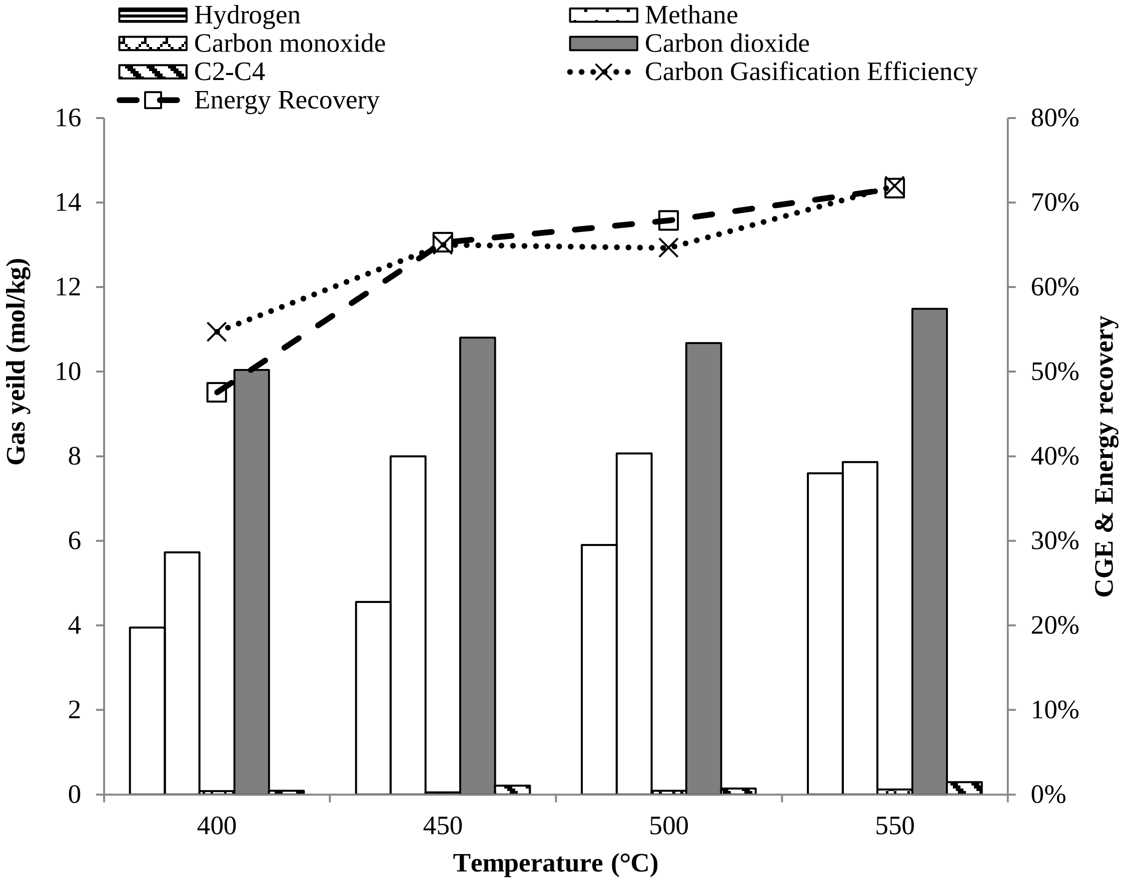

Table 1: Typical mass balances, carbon gasification efficiencies (CGE) and energy recovery from the SCWG of L hyperborea at 500 °C, 30 min hold time, 6.66% feed concentration, with and without catalysts.

	Catalyst loading	Gas (g)	Residue (g)	WSP* (g)	Balance (%)
No Catalyst	-	0.65	0.08	0.25	98.4
Ru/Al_2O_3	5%	0.73	0.05	0.19	97.1
Ni/Al_2O_3	5%	0.63	0.04	0.31	98.3
NaOH	1.5M	0.15	0.07	1.67	99.4

*WSP = Water soluble products

Table 2: Simple energy balance for SCWG of L. hyperborea at 400 °C and 550 °C

	Reaction Temperature (°C)		ΔE (kJ)
Energy Parameters	**400**	**550**	
$\Delta H(H_2O)$ (kJ/kg)	2816.8	3291.9	-
Energy Input (kJ)	5.90	8.10	2.20
Energy Output (kJ)	6.14	11.2	5.06

ΔE = Difference between Energy Input/Output at 550 ℃ and 400 ℃

Highlights

- L. hyperborea was gasified to produce substantial yields of hydrogen and methane
- Gas yields and CGE increased with temperature, catalyst loading and reaction hold time
- Ru/Al_2O_3 catalyst produced highest yields of methane and with CGE up to 98%
- Sodium hydroxide produced highest yields of hydrogen up to 30 mol/kg