SUPERCRITICAL WATER GASIFICATION OF ALGAE

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The candidate confirms that the work submitted is his own, except where work which has formed part of jointly-authored publications has been included. The contribution of the candidate and the authors to this work has been explicitly indicated below. The candidate confirms that appropriate credit has been given within the thesis where reference has been made to the work of others.

The details of chapters 4, 5 and 6 of the thesis are based on the following published papers respectively:

1. Cherad, R., Onwudili, J.A., Williams, P.T., Ross, A.B., 2014. A parametric study on supercritical water gasification of *Laminaria hyperborea*: a carbohydrate-rich macroalga. *Bioresource Technology*, 169, 573–80. doi:10.1016/j.biortech.2014.07.046
2. Cherad, R., Onwudili, J.A., Ekpo, U., Williams, P.T., Lea-Langton, A.R., 2013. Macroalgae Supercritical Water Gasification Combined with Nutrient Recycling for Microalgae Cultivation. *Environmental Progress and Sustainable Energy*, 32, 902–909. doi:10.1002/ep
3. Cherad, R., Onwudili, J.A., Biller, P., Williams, P.T., Ross, A.B., 2016. Hydrogen production from the catalytic supercritical water gasification of process water generated from hydrothermal liquefaction of microalgae. *Fuel*, 166, 24–28. doi:10.1016/j.fuel.2015.10.088

Details of contributions from the candidate and co-authors are listed below:

1. The candidate performed all the experiments, analysis and write up. Ms. Ekpo performed the growth trials. Dr. Onwudili supported in the experimental and analytical techniques and proof reading. Dr. Ross and Professor Williams contributed with comments, guidance and proof reading.
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ABSTRACT

Diversification of our energy supplies – especially in the transport and electricity generation sectors – is required to meet decarbonisation targets. Algae have been identified as suitable alternative feedstocks for third generation biofuels due to their fast growth rates and non-competitiveness with land for food crops. Hydrothermal processing of algae is an appropriate conversion route as it allows the processing of wet feedstock thus removing the energy penalty of drying.

In this study, supercritical water gasification was used for (i) the hydrothermal processing of macroalgae for the production of gaseous fuel – mainly hydrogen and methane – and (ii) the upgrading of the process water from hydrothermal liquefaction of microalgae for hydrogen production for biocrude hydrotreating.

The supercritical water gasification (SCWG) of the four macroalgae species investigated (*Saccharina latissima*, *Laminaria digitata*, *Laminaria hyperborea*, and *Alaria esculenta*) produced a gas that mainly consisted of hydrogen, methane and carbon dioxide. Non-catalytic SCWG resulted in hydrogen yields of 3.3 - 4.2 mol $kg^{-1}_{macroalgae}$ and methane yields of 1.6 - 3.3 mol $kg^{-1}_{macroalgae}$. Catalytic SCWG (using ruthenium) resulted in hydrogen yields of 7.8 - 10.2 mol $kg^{-1}_{macroalgae}$ and methane yields of 4.7 - 6.4 mol $kg^{-1}_{macroalgae}$.

The yield of hydrogen was approximately three times higher when using sodium hydroxide as catalyst (16.3 mol H_2 $kg^{-1}_{macroalgae}$) compared to non-catalysed SCWG of *L. hyperborea* (5.18 mol H_2 $kg^{-1}_{macroalgae}$). The energy recovery (an expression of how much chemical energy of the feedstock is recovered in the desired product

following hydrothermal processing) was 83% when sodium hydroxide was used as a catalyst, compared to 52% for the non-catalytic SCWG of *L. hyperborea*.

The yield of methane was approximately 2.5 times higher (9.0 mol CH_4 $kg^{-1}_{macroalgae}$) when using ruthenium catalyst compared to the non-catalysed experiment (3.36 mol CH_4 $kg^{-1}_{macroalgae}$) and the energy recovery increased by 22% to 74%.

The selectivity of methane or hydrogen production during the SCWG of macroalgae can be controlled using ruthenium or sodium hydroxide respectively. Longer hold 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 concentrations of sodium hydroxide, lower algal feed concentration and shorter hold times (30 min). Increasing reaction times (>30 min) with a base catalyst (sodium hydroxide) decreased the hydrogen yield. Overall energy recovery was highest at the lowest feed concentrations; 90.5% using ruthenium and 111% using sodium hydroxide.

The process waters from the hydrothermal liquefaction (HTL) of microalgae (*Chlorella*, *Pseudochoricystis*, and *Spirulina*) were gasified under supercritical water conditions to maximise hydrogen production. Hydrogen yields ranged from 0.18 - 0.29 g H_2 $g^{-1}_{biocrude}$ from SCWG of the process water of HTL along with near complete gasification of the organics (~98%). Compared to the hydrogen requirements for hydrotreating algal biocrude (~0.05 g H_2 $g^{-1}_{biocrude}$), excess hydrogen can be produced from upgrading the process water through SCWG. The results indicate that process waters following SCWG are still rich in nutrients that can be recycled for algal cultivation.

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NOMENCLATURE

AHTL	Algal Hydrothermal Liquefaction
BET	Brunauer–Emmett–Teller Theory
BBM	Bold's Basal Media
C_{ps}	Specific Heat Capacity
CGE	Carbon Gasification Efficiency
CHG	Catalytic Hydrothermal Gasification
CP	Critical Point
CSTR	Continuously Stirred Tank Reactor
CV	Calorific Value
EDXS	Energy-Dispersive X-ray Spectroscopy
EI	Energy Input
EO	Energy Output
E_{PG}	Energy Output (Product Gas)
E_{SG}	Energy Input
FID	Flame Ionisation Detector
GC	Gas Chromatography
MS	Mass Spectrometry
GE	Gasification Efficiency
GtC	Gigaton Carbon
HGE	Hydrogen Gasification Efficiency
HHV	Higher Heating Value
HT	Hydrothermal
HTC	Hydrothermal Carbonisation
HTG	Hydrothermal Gasification
HTL	Hydrothermal Liquefaction

IC	Inorganic Carbon
ICP	Inductively Coupled Plasma Spectrometer
LHSV	Liquid Hourly Space Velocity
MJ	Mega joule
MPa	Mega Pascal
Mw	Molecular Weight
MW	Mega-watt
NOx	Nitrogen Oxides
ppb	parts per billion
ppm	parts per million
RF	Response Factor
SCWG	Supercritical Water Gasification
SCWO	Supercritical Water Oxidation
SEM	Scanning Electron Microscope
SOx	Sulphur Oxides
TC	Total Carbon
TCD	Thermal Conductivity Detector
TOC	Total Organic Carbon
TP	Triple Point
TWh	Tera-watt hours
WSP	Water Soluble Products

OUTLINE OF THE THESIS

Chapter 1 provides an insight into the role biofuels will play in tackling climate change and meeting renewable targets and obligations. The role of biofuels as a mitigation technology in the energy sector is placed in context. The development of renewable energy in the UK between 2009 and 2013 is discussed with a focus on the electricity generation sector and the transport sector. The significance of biofuels in renewable transport energy is discussed which highlights the relevance of the work covered in this thesis. The sources of biomass for bioenergy are reviewed by providing insight into the development of first, second and third generation biofuels. The sources and conversion routes of first and second generation biofuels are introduced along with their limitations and inherent drawbacks. The advantages of algae as a source of biofuels (third generation biofuels) are presented and the processing of algae for fuel is discussed. The objectives of this thesis are presented at the end of Chapter 1.

Chapter 2 introduces macroalgae and microalgae by discussing their classification, cultivation and structures. A hydrothermal system for the processing of algae is presented and a detailed review on research into the hydrothermal liquefaction and gasification of both microalgae and macroalgae is also presented. Finally, supercritical water gasification (SCWG) technology is introduced and reviewed in terms of its application in producing biofuels from biomass.

Chapter 3 provides a description of the methodology used in the experiments in this thesis – allowing others to replicate the experiments. A description of the samples

used, instruments and equipment is provided. A description of results analysis (gas composition, HHV, gasification efficiency, energy recovery, etc.) is also provided.

Chapter 4 presents results from the SCWG of four macroalgae species: *Saccharina latissima*, *Laminaria digitata*, *Laminaria hyperborea* and *Alaria esculenta*. The species were chosen due to their wide distribution and abundance along British and European coasts. The influence of macroalgal composition due to seasonal variation is also assessed. The effect of ruthenium catalyst (a known catalyst in hydrothermal gasification of biomass) on macroalgal SCWG was studied, including catalyst activity due to sulphur poisoning. The recovered process water was used in cultivation trials of a microalga, *Chlorella vulgaris*, and compared to cultivation in standard growth media. The results from the work carried out in this chapter have been published in the journal 'Environmental Progress and Sustainable Energy' (Cherad et al., 2013).

Chapter 5 discusses the potential of supercritical water gasification (SCWG) of a macroalga, *Laminaria hyperborea*, for hydrogen and methane production. Ruthenium, nickel and sodium hydroxide were used as catalysts during SCWG. The gas yield, gasification efficiency and energy recovery from the catalytic and non-catalytic SCWG of the macroalga were investigated under varying parameters including catalyst loading, feed concentration, hold time and temperature. Selectivity towards hydrogen and/or methane production from macroalgal SCWG was assessed as to whether it can be controlled by the combination of catalysts and varying reaction conditions. Results from this chapter were published in the journal 'Bioresource Technology' (Cherad et al., 2014).

Chapter 6 investigates the integration of hydrothermal liquefaction (HTL) and SCWG for enhanced energy recovery and potential biocrude upgrading. Three microalgae species were investigated due to their varying biochemical content: *Chlorella vulgaris, Pseudochoricystis ellipsoidea* and *Spirulina platensis.* The process water from microalgal HTL was upgraded using SCWG to maximise hydrogen production. The amount of hydrogen produced was compared to the amounts needed for complete hydrotreating of the biocrude. The nutrient content of the process water post SCWG was analysed to determine suitability of nutrient recovery for algal growth. Results from this chapter were published in the journal 'Fuel' (Cherad et al., 2016).

The main findings from each chapter are discussed in a conclusion section at the end of each chapter with an overall summary of conclusions from all the experimental work presented in **Chapter 7**. The limitations of the research as well as the potential for further work are discussed in **Chapter 8**.

1 Introduction

Insecure energy supply, rising energy prices, increased emissions and an ever increasing energy demand all dominate the energy and environment discourse. According to BP (BP Statistical energy review, 2014), at the end of 2013, the total proven reserves of oil and natural gas in the world were estimated at 1.69 trillion barrels and 185 trillion cubic metres respectively. These reserves are able to support the current energy consumption for just over 50 years (Liew et al., 2014). While the timing of peak oil production remains uncertain, it has been predicted to occur within the next decade (Curtis, 2009). Natural gas peak production has been estimated to occur between 2025 and 2066 (Mohr and Evans, 2011).

Alternative energy sources have come into the foreground not only in the energy security discourse but also in terms of addressing anthropogenic climate change and global warming. Currently, the concentrations of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) exceed the highest concentrations recorded in ice cores over the past 800,000 years (IPCC, 2013). CO_2 is the single most important human-emitted greenhouse gas with emissions averaging 8.3 GtC yr^{-1} over the period 2002 to 2011. In 2011, 9.5 GtC was emitted representing a 54% increase in annual carbon emissions compared to 1990. The concentration of CO_2 in the atmosphere has risen steadily over the past few decades as illustrated in Figure 1.1.

The increase in greenhouse gas emissions has played a major role in contributing to a warming of 0.85 °C over the period 1880 to 2012 (IPCC, 2013). Whilst changes in extreme weather and climate events have been observed since 1950, the Fifth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC, 2013)

reports with high confidence the increase in likelihood of further changes in weather and climatic events in the late 21st century. These include:

- Heavy precipitation events. Increase in the frequency, intensity, and/or amount of heavy precipitation.
- Warm spells/heat waves. Frequency and/or duration increase over most land areas
- Increases in intensity and/or duration of drought
- Increased incidence and/or magnitude of extreme high sea level
- Increases in intense tropical cyclone activity

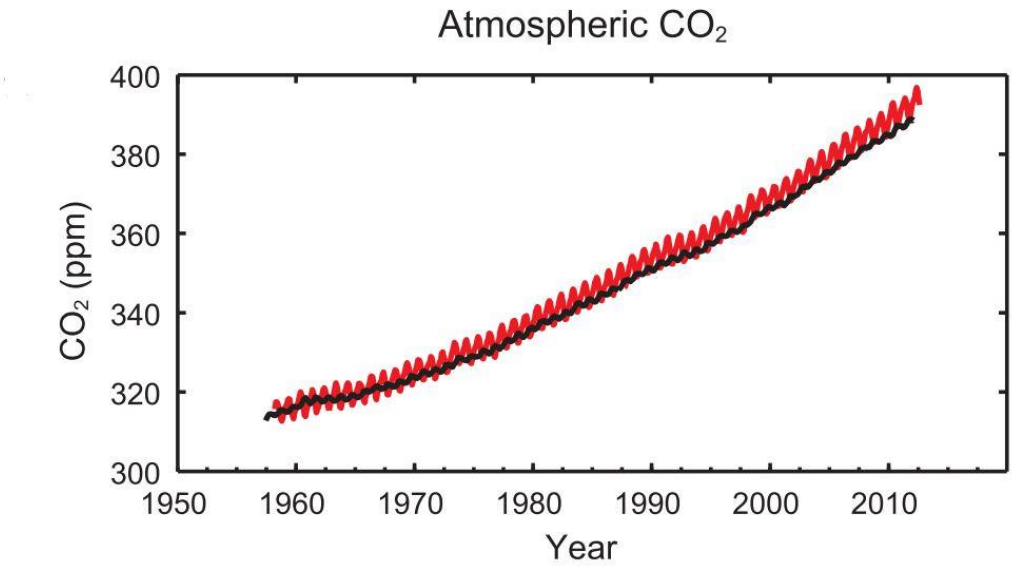


Figure 1.1 Multiple observed indicators of a changing global carbon cycle - atmospheric concentrations of carbon dioxide (CO_2) from Mauna Loa (red) and South Pole (black) since 1958 (IPCC, 2013)

Regardless of the scale of mitigation undertaken over the next two to three decades, additional adaptation will be required to reduce the impacts of climate change (IPCC, 2014). Whilst societies have managed the impact of weather and climate for

centuries, the vulnerability to climate change can be exacerbated by other factors such as poverty, conflict, unequal access to resources and incidence of disease.

1.1 Climate change mitigation

A wide variety of mitigation technologies is available to governments to help curb emissions in the sectors of energy supply, transport, buildings, industry, agriculture, forestry and waste. In the energy supply sector, some of the key mitigation technologies that are currently commercially available include nuclear power, renewable heat and power from hydro, solar, wind, geothermal and bioenergy, combined heat and power and carbon capture and storage. Other technologies that are projected to be commercialised before 2030 include carbon capture and storage for gas, biomass and coal fired technology, solar photovoltaics and advanced renewable energy including tidal and wave power.

No single technology can provide all the mitigation potential in any one sector and the burden falls on governments to ensure the correct policies are in place to promote uptake of mitigating technologies and also ensure barriers to uptake are removed. In the energy sector, some of the policies and measures shown to be effective include feed-in tariffs for renewable energy technologies, producer subsidies, renewable energy obligations and reduction of fossil fuel subsidies (IPCC, 2014).

In 2007, the European Council established a target of 20% of EU's energy to come from renewable sources. As a result, the 2009 Renewable Energy Directive (2009/29/EC) was implemented. This resulted in agreement of country 'shares' of the overall 20% target with the UK's share being 15% of its final energy consumption coming from renewable sources by 2020 including 10% of transport

energy coming from renewable sources by 2020. Table 1.1 highlights the progress of renewable sources in meeting the target. In 2013, renewable energy in the UK accounted for 5.2% of energy consumption. This highlights the scale of increase required from 2013 to 2020 which presents a huge challenge.

					Thousand tonnes of oil equivalent
Renewable Energy	**2009**	**2010**	**2011**	**2012**	**2013**
Electricity generation	2,153	2,420	2,795	3,448	4,414
Heating and Cooling	953	1,169	1,220	1,364	1,643
Transport biofuels	988	1,150	968	882	1,014
Total Final Consumption of Renewable Energy	4,095	4,739	4,983	5,694	7,072
Total Final Energy Consumption	136,887	143,223	130,830	134,990	136,470
Renewable Energy Consumption as a percentage of Gross Final Energy Consumption	3.0%	3.3%	3.8%	4.2%	5.2%

Table 1.1 Renewable sources data used to indicate progress under the 2009 EU Renewable Energy Directive - adapted from DECC's Digest of UK energy statistics (DECC, 2013).

The UK Renewable Energy Roadmap (DECC, 2011) states that approximately 90% of the generation necessary to meet the 15% target can be delivered from a subset of 8 technologies (listed in Table 1.2).

Renewable Energy	Central range for 2020 (TWh)
Onshore wind	24-32
Offshore wind	33-58
Biomass electricity	32-50
Marine	1
Biomass heat (non-domestic)	36-50
Air-source and ground-source heat pumps (non-domestic)	16-22
Renewable transport	Up to 48
Others (incl. hydro, geothermal, solar and domestic heat)	14
Estimated 15% target	**234**

Table 1.2 Renewable energy technology breakdown (TWh) for central view of deployment in 2020 - adapted from (DECC, 2011)

The technologies were chosen due to their relative cost effectiveness and potential for deployment. Electricity and heat from biomass and biofuels for renewable transport will all play a crucial role in meeting the 2020 target, curbing greenhouse gas emissions and decarbonising the UK's energy system.

1.2 Biofuels

Biofuels are solid, liquid and gaseous fuels derived from renewable sources such as biomass. Examples include bioalcohol, biodiesel, biocrude oil, biochar, biogas and biohydrogen. They have evolved from first to third generation biofuels based on the feedstock used. First generation biofuels are derived from food crops such as corn, wheat, sugar beet and oil seeds. Second generation biofuels are derived from lignocellulosic biomass and third generation biofuels are derived from algae. The main attraction to biofuels lies in their renewable, less toxic and carbon neutral nature when compared to fossil fuels. Biofuels offer a potential route for CO_2 mitigation as the carbon emitted is taken from the atmosphere during the biomass

growth. In addition, the combustion of biofuels releases less CO, NO_x, SO_x, and particulate matter compared to fossil fuel combustion (Bucksch and Egebäck, 1999).

Biofuels will play a more significant role in reducing emissions because the transport sector has seen less progress compared to electricity generation sector in terms of renewable sources (Table 1.3).

Table 1.3 indicates that whilst the percentage of transport energy from renewable sources increased by 70% over the five year period between 2009 and 2013, only 4.4% of transport energy came from renewable sources in 2013. The percentage of electricity from renewable sources doubled over the same five year period and represents 13.9% of the total electricity consumption in the UK.

The development of electric cars does offer the potential to curb emissions from the transport sector, however, the aviation and marine sectors are still far from being electrified. Powering heavy good vehicles, planes and ships by renewable energy though electricity and batteries does not look promising in the near future due to cost and weight and safety concerns of batteries. With the aviation sector set to grow from 241 million passengers per annum in 2007 to 465 million in 2030 (DfT, 2007), the development of sustainable biofuels is necessary to reduce the CO_2 emissions from the transport sector.

					Thousand tonnes of oil equivalent
	2009	**2010**	**2011**	**2012**	**2013**
Electricity generation component:					
Normalised hydro generation	430	419	439	446	440
Normalised wind generation	804	965	1,209	1,603	2,208
Electricity generation from renewables other than wind, hydro, and compliant biofuels	920	1,035	1,147	1,399	1,766
Electricity generation from compliant biofuels	-	-	-	-	-
Total renewable generation from all compliant sources	2,153	2,420	2,795	3,448	4,414
Total Gross Electricity Consumption	32,321	32,779	31,863	32,013	31,873
Percentage of electricity from renewable sources	**6.7%**	**7.4%**	**8.8%**	**10.8%**	**13.9%**
Transport component (excluding air transport):					
Road transport renewable electricity	0	0	0	0	1
Non-road transport renewable electricity	55	58	66	69	76
Biofuels (restricted to those meeting sustainability criteria from 2011)	988	1,150	968	882	1,014
Total electricity consumption in transport	347	350	351	352	353
Total petrol and diesel consumption in transport	38,105r	37,719	37,234	37,070	36,791
Total transport component numerator (including weighted components)*	1,044	1,209	1,034	1,405	1,666
Total transport component denominator (including weighted components)*	39,441	39,220	38,649	38,319	38,168
Percentage of transport energy from renewable sources	**2.6%**	**3.1%**	**2.7%**	**3.7%**	**4.4%**

*Some sustainable biofuels are double weighted in the numerator of this calculation, as specified by the Directive.

Table 1.3 Electricity and transport from renewable sources data used to indicate progress under the 2009 EU Renewable Energy Directive (adapted from DECC's Digest of UK energy statistics (DECC, 2013)).

1.3 First generation biofuels

There are three main types of first generation biofuels used commercially, namely, biodiesel (bio-esters), bioethanol and biogas. The renewed interest in blending biodiesel and bioethanol with fossil fuel for use as transportation fuel started in the 1980s despite the invention of vegetable oil fuelled engines in the 1900s (Janaun and Ellis, 2010). Currently, 5% of biodiesel is blended with diesel fuel and 10% of bioethanol is blended with gasoline (Liew et al., 2014). Biodiesel is produced through the transesterification of vegetable oils and residual oils and fats. During transesterification, triglycerides react with alcohol and generate biodiesel (esters of fatty acids) and glycerol as a high value byproduct (Meher et al., 2006). Bioethanol is produced by fermentation of feedstock rich in sugar or starch. Sugar containing crops include sugar cane, beet root, fruits and palm juice. Starch containing crops include wheat, barley, rice and corn. Biogas is produced from the anaerobic digestion of liquid manure and other digestible feedstock (Naik et al., 2010).

Both biodiesel and bioethanol make up over 95% of the UK renewable transport fuel mix with an average equal share over the past five years (Table 1.4). Only 29% of the UK transport biofuels came from UK sources for the year April 2014 – April 2015 (DfT, 2015). Since 2012, the largest source of biodiesel has been cooking oil from UK and the largest source of bioethanol has been corn from the US and Ukraine. The feedstock used for bioethanol production in the EU comprises wheat (70%), barley (15%) corn (10%), and rye (5%) (FAPRI, 2011). With such a heavy dependence on food crops for biofuel production, a food versus fuel debate has emerged with rising food prices linked to an increase in production of biofuels (Ajanovic, 2011).

In 2008, the cost of US wheat export increased by nearly 20% to \$440 ton^{-1} in the three month period between January and March. In addition, Thai rice export prices increased by 54% to \$562 ton^{-1} for the same period. This happened following a 181% increase in global wheat prices over the preceding 36 months and an 83% increase in overall global food prices for the same period (World Bank, 2008).

The rising trend in food prices in 2008 led to a response by the World Bank's lead economist of the Development Prospects Group, Donald Mitchell. After noting that almost all of the increase in global maize production in the four years between 2004 and 2007 went for biofuel production in the US, Mitchell (2008) pointed out that only a relatively small share (15%) of the increase was due to higher energy and fertiliser costs, attributing the majority of the increase to increased biofuel production. Collins (2008) used a mathematical simulation to report that 60% of the increase in maize prices between 2006 and 2008 was due to the increase in using maize for bioethanol production.

Counter arguments to the extent biofuels affect feedstock prices discuss factors such as oil price developments (Balcombe and Rapsomanikis, 2008) and recent strong economic growth in China (Rathmann et al., 2010), however, most studies agree that biofuels are increasing the price of food. The discrepancy lies in the estimates of how much the increase actually is. Other negative factors regarding first generation biofuels include a poor energy balance coupled with negative impacts on regional water sources, biodiversity and soil quality (Groom et al., 2008; Simpson et al., 2008) and the potential for increased greenhouse gases through emissions from land use change (Searchinger et al., 2008).

UK Transport Biofuels	2010/2011	2011/2012	2012/2013	2013/2014	2014/2015
Total volume supplied (million litres)	1,517	1,600	1,340	1,744	1,356
Total transport^	3.27%		3.00%	3.46%	3.54%
Total volume meeting sustainability requirements†	53.8%		99.6%	99.9%	75%
Biodiesel	59%	57%	37%	49%	50%
Bioethanol	41%	43%	59%	48%	49%
Biomethanol			5%	3%	1%
Largest source biodiesel (feedstock, country)	22% (Soy, Argentina)	19% (Cooking oil, Netherlands)	29% (Cooking oil, UK)	16% (Cooking oil, UK)	17% (Cooking oil, UK)
Largest source bioethanol (feedstock, country)	25% (Corn, US)	69% (Corn, US)	32% (Corn, US)	16% (Corn, Ukraine)	16% (Corn, Ukraine)
% UK feedstock	22%	12%	21%	19%	29%

^ road and off-road mobile machinery fuel
† Sustainability criteria set out in Renewable Transport Fuel Obligations Order 2007

Table 1.4 UK Renewable Transport Fuel Obligations 2010 - 2015 – summarised from Statistical releases publications (DfT, 2015).

1.4 Second generation biofuels

In order to overcome the main drawback of first generation biofuels from food sources, the development of second generation biofuels from lignocellulosic biomass has gained interest (Koçar and Civaş, 2013). Lignocellulosic biomass makes up the majority of the cheap and abundant non-food material available from plants. These include herbaceous plants, woody plants and agricultural and forestry residues that consist of cellulose (a glucose polymer), hemicellulose (mainly pentose sugar molecules) bound together by lignin (polymer of phenols) (Tyson et al., 2004).

There are three main conversion routes for biofuel production from lignocellulosic biomass – physical, thermochemical and biological. Pretreating the biomass reduces the energy requirement for the conversion routes by increasing the surface area, dries the biomass for downstream processing and degrades and breaks the lignin and hemicellulose structures for easier processing (see Agbor et al. (2011) for the fundamentals of biomass pretreatment).

Physical processing produces a solid biofuel through briquetting, pelletising and fibre extraction. Briquetting converts loose biomass (e.g. sawdust) into high density blocks and is done at high pressures (150 MPa) for biomass with high lignin content and at low pressures for lower lignin content (Liew et al., 2014). Pelletising extrudes the biomass and condenses it into pellet form of different sizes. Fibre extraction is used to process mesocarp fibre and empty fruit branch from palm based biomass. The fibre is extracted through pressing and shredding and is then packed into solid blocks (Mahlia et al., 2001).

Biological processing of lignocellulosic biomass involves the conversion of cellulose and hemicellulose to sugar, followed by fermentation for bioethanol

production. The biomass is pretreated to increase the sugar content and then subjected to saccharification and fermentation for high bioethanol yields. Several reviews have been published on the production of bioethanol from lignocellulosic biomass (Cardona and Sánchez, 2007; Cardona et al., 2010; Lin and Tanaka, 2006).

Thermochemical processing involves converting the whole biomass into energy, gas and liquid products through four routes – pyrolysis, liquefaction, gasification and combustion. The products are synthesized into chemicals or used directly as described in Figure 1.2.

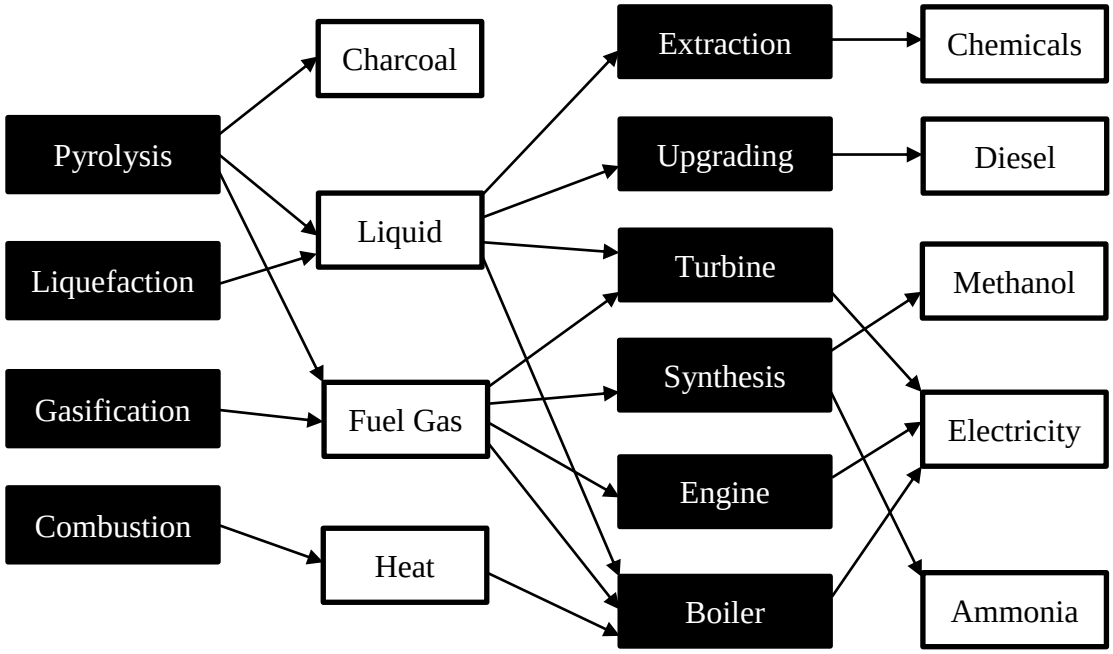


Figure 1.2 Thermochemical processes for bioenergy production from biomass - adapted from Zhang et al. (2010)

- Pyrolysis is thermal degradation process in the absence of oxygen to produce a biochar, bio-oil, and gaseous products. There are three types of pyrolysis routes – torrefacation, slow pyrolysis and fast pyrolysis.

Torrefaction involves heating the biomass to 230 - 300 °C in the absence of oxygen. This causes the biomass structure to alter chemically and produce acetic acid, methanol, H_2O, CO_2 and CO. The process increases the energy density of the biomass, reducing its weight and enhancing its commercial use for energy production (Basu, 2010). Slow pyrolysis involves heating the biomass at temperatures of 300 - 700 °C for 30 - 200 seconds in the absence of oxygen to produce a biochar. Fast pyrolysis involves heating the biomass at temperatures of 400 - 700 °C for 1 - 5 seconds to produce liquid fuels (bio-oil and biocrude) (Liew et al., 2014; Zhang et al., 2010). The liquid fuels are then further processed by hydrotreatment to produce naphtha and diesel.

- Liquefaction is mainly used for high lignin feedstock (woody material, saw dust) and involves heating to 250 - 350 °C and 5 - 20 MPa (Maldas and Shiraishi, 1997). The process depolymerises the biomass into smaller molecules which are unstable and reactive and they subsequently repolymerise into liquid products with a range of molecular weights. In order to improve the reaction kinetics and product yield, the liquefaction of biomass usually occurs with the aid of (i) a solvent (e.g. phenol), (ii) syngas (CO and H_2), and/or (iii) catalysts (sodium or potassium carbonate) (Liew et al., 2014).
- Gasification involves heating the biomass with partial oxygen, carbon dioxide and/or steam at high temperatures of 800 - 900 °C to a syngas (CO and H_2) and some CO_2 and CH_4. The syngas is used to produce fuels (e.g. gasoline through the Fischer-Tropsch process) and chemicals through

catalytic upgrading (e.g. methanol – an important feedstock for a large number of chemicals) (He and Zhang, 2011).

- Combustion (direct-combustion) is a process in which biomass is burned to generate heat. Combustion is an exothermic reaction between the hydrocarbons in the biomass and oxygen releasing water and carbon dioxide. It can be used as a standalone fuel or co-fired with fossil fuels in existing fossil fuel plants for electricity production. Co-firing has become the fastest and least expensive means for decreasing greenhouse gas emissions (Basu, 2006).

A major drawback to second generation biofuels from lignocellulosic biomass is the requirement for large arable lands and sufficient quantities of water and fertiliser for growth. In addition, introduction of invasive crop species to regions where biomass demands increase is a threat to local biodiversity (IEA, 2010). Another constraint is that the second generation biofuel industry is still in its infancy due to technological and financial barriers (Dyer et al., 2008; Low and Booth, 2007; Sims et al., 2010; Smith et al., 2013; Thompson and Meyer, 2013). Both the biological and thermochemical routes for conversion of lignocellulosic biomass remain unproven at the fully commercial scale with significant technical and environmental barriers to be overcome. For example, Sims et al., (2010) report that the biochemical route requires further advances in reducing the cost of pre-treatment (Eggeman and Elander, 2005), improving the efficacy of enzymes (Galbe et al., 2005; Mosier et al., 2005), lowering the production costs and improving overall process integration (Sheehan et al., 2004).

1.5 Third generation biofuels

Third generation biofuels are derived from algae. Algae harness energy via photosynthesis, capturing CO_2 and transforming it into organic biomass. Macroalgae (seaweeds) are diverse and abundant across the world's oceans and coastal waters and are rich in carbohydrates which are potential biofuels or biofuel precursors. Currently, seaweed usage is built around chemical extraction and production - including cosmetics and fertilizers. Microalgae are simple unicellular structures with high growth rates that can produce large amount of lipids for oil production.

Both macroalgal and microalgal biomass offer a renewable energy resource that is drawing significant interest from the research community (see Chapter 2) due to their advantages over first and second generation biofuels derived from terrestrial biomass. These advantages revolve around several aspects related to algae (U.S. DOE, 2010):

- Algal productivity can offer high biomass yields per acre of cultivation (Chisti, 2007);
- Algal cultivation does not compete with arable land and nutrients used for conventional agriculture;
- Algae can utilise waste water, produced water and saline water thus reducing competition for freshwater resources;
- Algae can recycle CO_2 emitted from power stations;
- Algal biomass is compatible with the integrated biorefinery vision for the production of fuels and valuable co-products (Fernando et al., 2006; Naik et al., 2010).

In terms of algal productivity, compared to terrestrial biomass, macroalgae has a faster growing rate due to no water limitations (Gellenbeck and Chapman, 1983) and a lesser effect with temperature variation. It also has a higher photosynthetic efficiency of 6 - 8% (FAO, 1997) compared to 1.8 - 2.2% for terrestrial biomass and ultimately 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). Microalgae has been reported to achieve light to biomass conversion efficiencies of 1 - 4% in conventional open pond systems (Hase et al., 2000) and significantly higher efficiencies in closed photobioreactors (e.g. 6.6% in coiled tubular reactors) (Morita et al., 2001, 2000; Tredici and Zlttelli, 1998).

1.5.1 Processing algae for fuel

Processing algae for fuel started in the late 1950s with the utilization of the carbohydrate fraction of algal cells for the production of methane by anaerobic digestion (Meier, 1955; Oswald and Golueke, 1960). More recently, microalgal biofuel is produced by the extraction of lipids and subsequent transesterification to biodiesel (Chisti, 2007; Meher et al., 2006; Schenk et al., 2008; Xu et al., 2006). One of the economic and energetic drawbacks of processing microalgae (and macroalgae in thermochemical routes) is the dewatering stage. Microalgae typically grow to a solid concentration of 1 - 5 g L^{-1} (Brennan and Owende, 2010). Since most lipid extraction techniques require a dry feedstock before transesterification, the energy input for dewatering can account for as much as 25% of the energy contained in the algae (Xu et al., 2011). Hydrothermal processing avoids the dewatering stage and processes the whole algae in hot compressed water.

The carbohydrates in macroalgae have potential for producing biofuels and whilst conversion has focused on biogas production by anaerobic digestion (Matsui and Koike, 2010), recent work has focused on utilising the carbohydrates 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.

1.5.2 Hydrothermal processing

Hydrothermal processing simulates the natural processes in nature over millions of years in generating fossil fuels. Fossil fuels are created by the transformation of organic matter under high pressures and temperatures over a long period of time. Coal is formed from terrestrial plants while oil and gas is formed from phyto- and zoo- plankton (Biller and Ross, 2012). Hydrothermal processing speeds up the natural pathways to form a renewable fossil fuel with the added flexibility of controlling the desired end product.

Hydrothermal processing involves processing the feedstock in hot compressed water with the aim of generating a higher energy density product by the removal of oxygen (Biller and Ross, 2012). The flexibility comes from the varying operating conditions

for the desired product. Algal biomass can be converted into a solid (biochar) through hydrothermal carbonization (HTC) at temperatures less than 200 °C with the product being co-fired with coal or used as biochar (Heilmann et al., 2010). Processing at temperatures between 200 - 375 °C – hydrothermal liquefaction (HTL) – produces a biocrude/oil which can be upgraded to various fuels and chemicals (Brown et al., 2010; Duan and Savage, 2011; Levine et al., 2010). Hydrogen and synthetic natural gas are produced from temperatures exceeding 375 °C through hydrothermal gasification (HTG) and the products directly combusted or further upgraded to hydrocarbons (Brown et al., 2010; Haiduc et al., 2009; Schumacher et al., 2011).

1.5.2.1. Hot compressed water as a reaction medium

Water is a cheap, abundant and environmentally pure solvent making it advantageous as a reaction medium compared to chemical solvents. When water is heated under pressure, its hydrogen bonds weaken and decrease in number resulting in a decrease in the dielectric constant. As such, the opportunities for water to take part in the reaction increase. This results in water acting as a catalyst, lowering activation energies ultimately facilitating reactions that would not occur at ambient conditions. Depending where in the phase diagram (Figure 1.3) the hydrothermal process conditions fall determines whether HTC, HTL, or HTG occurs.

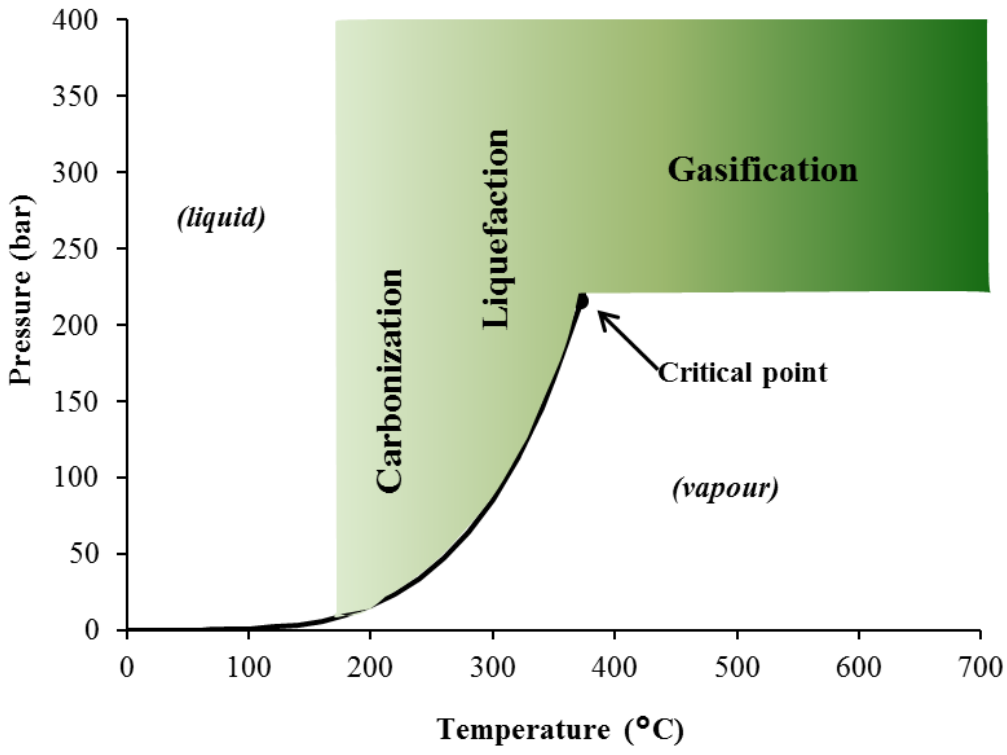


Figure 1.3 Hydrothermal processing conditions in the water phase (Perry and Green, 1997)

A summary of the reaction steps for the three hydrothermal processes is described in Figure 1.4. The carbonisation stage (~200 °C) increases the carbon content of the feedstock and lowers its oxygen and mineral content. Funke and Ziegler (2009) describe how this is achieved through dehydration, removal of carboxyl and carbonyl groups through decarboxylation and cleavage of ester and ester bonds through hydrolysis. The result is a coal like hydro-char or bio-char/coal which has a higher energy density that the starting feedstock.

HTL conditions (200 - 375 °C) allow the feedstock to decompose into smaller reactive molecules that repolymerise into oily compounds (Zhang et al., 2010). Based on several studies (Demirbas, 2010; Zhou et al., 2010; Zou et al., 2009), the main reaction steps during HTL of biomass are summarised as follows:

- Hydrolysis of biomass macromolecules (lipids, proteins, and carbohydrates in the case of algal biomass) into smaller fragments;
- Conversion of these fragments by, for example, dehydration into other, smaller compounds;
- Rearrangement via condensation, cyclisation, and polymerisation producing new oil-like components.

The main products from the HTL of biomass are a biocrude fraction and a water fraction (process water) that contains some polar organic compounds. In addition, a gaseous fraction (mainly CO_2) and a solid fraction are formed. Biocrude is a viscous crude-like oil with heating values around 30 - 38 MJ kg^{-1}. It can be upgraded by removal of oxygen and nitrogen through hydrotreating to a variety of high quality green fuels (Biller and Ross, 2012).

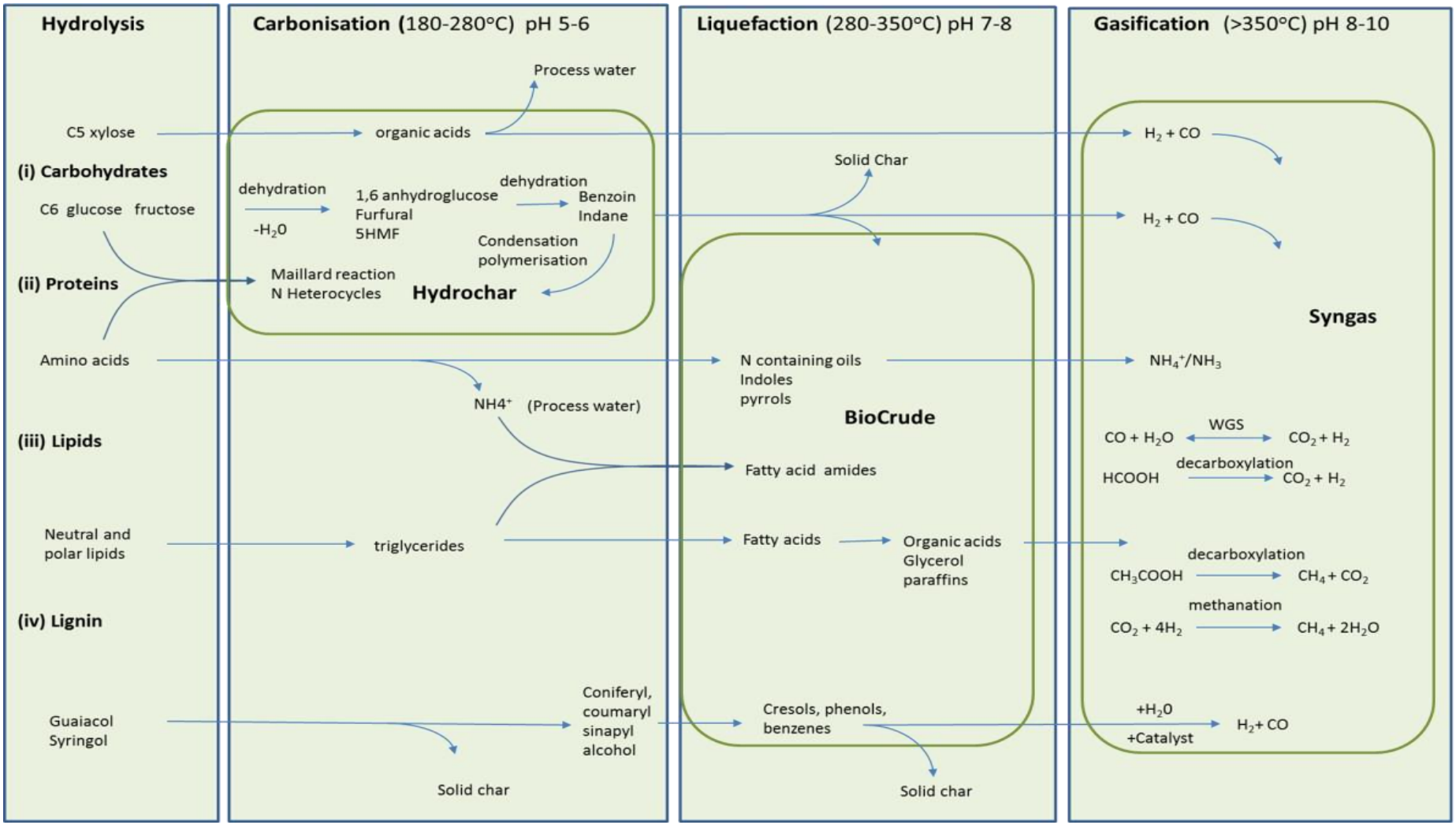


Figure 1.4 Summary of reaction steps during hydrothermal carbonisation, liquefaction and gasification (Biller and Ross, 2015).

The initial steps during HTG are similar to those summarised for HTL but the higher temperature and pressure conditions in the gasification stage (> 350°C) lead to the small fragments decomposing further to low molecular weight gaseous products. The gas consists of varying amounts of H_2, CO, CO_2, CH_4 and light hydrocarbon gases (C_2 - C_4). HTG produces process water that is low in organic content due to near complete gasification of the carbon in the feedstock to carbon in the gas product (Schmieder et al., 2000; Williams and Onwudili, 2006). The composition of the gas is determined by the gasification temperature with temperatures between 350 - 500 °C favouring CH_4 production and higher temperatures (> 500 °C) favouring H_2 production. Although, the selectivity towards CH_4 or H_2 can be influenced with the use of catalysts (Chakinala et al., 2010; J. A. Onwudili and Williams, 2013). When water's temperature and pressure exceed its critical point (T > 374 °C, P > 22.1 MPa), it changes to a state known as supercritical water and acts as a non-polar solvent with high diffusivity and transport properties. Hydrothermal gasification in supercritical water is known as supercritical water gasification (SCWG). SCWG technology is discussed in section 2.7.

1.5.2.2. The idealised integrated algal biomass hydrothermal system

Figure 1.5 describes an idealised integrated hydrothermal system for processing algal biomass. Whilst the system depicts a photobioreactor for microalgal growth (using recycled nutrients and CO_2), a similar concept can be described for macroalgal biomass with cultivation in closed tanks or marine environments. Biller and Ross (2012) summarise the operation of such a system as follows:

- Algae is grown, harvested and dewatered to produce a slurry with a higher solid content;

- The slurry is processed in hot compressed water (HTC, HTL or HTG);
- The desired primary energy product is separated;
- The nutrients in the process water are recycled for algal growth;
- The gaseous fraction mainly contains CO_2 (if HTC and HTL conditions are used in the reaction vessel) – the CO_2 can be recycled for algal growth;
- The solid residue which still contains some nitrogen and minerals can be used as a fertiliser, fuel or biochar.

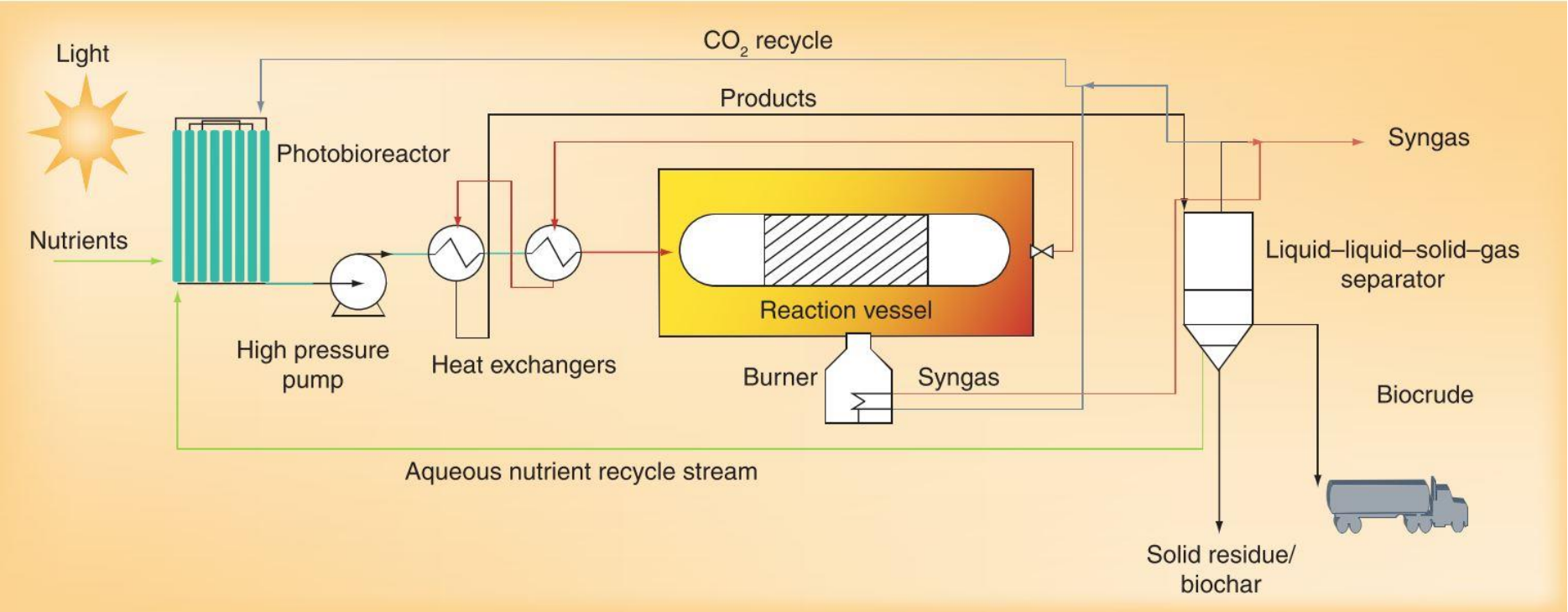


Figure 1.5 Integrated hydrothermal process with nutrient and CO_2 recycling for photosynthesis (Biller and Ross, 2012)

One of the advantages of the integrated hydrothermal processing of algae as illustrated in Figure 1.5 is that the nutrients in the process water and the CO_2 in the gaseous phase can be recycled for algal growth (Biller et al., 2012; Haiduc et al., 2009; Jena et al., 2011b; Onwudili and Williams, 2007). The proposed integrated hydrothermal process is still in its early research stages with most of the work carried out on a laboratory scale (Biller and Ross, 2011; Elliott et al., 2014a, 2013a; Haiduc et al., 2009; Jones et al., 2014; Liu et al., 2013; Ross et al., 2010; Stucki et al., 2009a; Zhu et al., 2013). Most of the research into hydrothermal processing has focused around HTL of microalgae (see Biller and Ross, (2012)) where the primary product is a biocrude. However, there has been increasing research into HTG (see the continuous microalgal HTG process proposed by Stucki et al., (2009) and the continuous macroalgal process by Elliott et al., (2014b)). The use of supercritical water gasification technology for the hydrothermal processing of macroalgae has several advantages based on the nature of the process and the composition of the feedstock (Chapter 2).

1.6 Research Objectives

The objective of this research is to study the hydrothermal gasification of macroalgae under supercritical water conditions for the production of gaseous fuel, mainly hydrogen and methane.

A series of experiments were carried out with the following objectives:

- Investigate the product distribution and composition from the supercritical water gasification (SCWG) of macroalgae.
- Analyse the influence of catalysts on the gaseous yield and gasification efficiency from the SCWG of macroalgae. The chosen catalysts (ruthenium, nickel, alkali reagents such as sodium hydroxide) have a proven track record in successfully catalysing hydrothermal gasification reactions – particularly using biomass and biomass model compounds.
- Study the effect of varying reaction parameters on the gaseous yield, gasification efficiency and energy recovery. Reaction parameters include:
    - SCWG temperature
    - Reaction hold time
    - Feed concentration (macroalgae concentration)
    - Catalyst loading
- Investigate the influence of feedstock composition on gaseous yields. The composition of macroalgae has a seasonal variation and harvests across the season were hydrothermally gasified to analyse the effect of seasonal variation on gaseous yields and energy output.

- Assess the potential of recycling nutrients following hydrothermal gasification of macroalgae to cultivate microalgae. The process water from SCWG was used in cultivation trials of microalgae.

With the majority of research into hydrothermal processing of algae focused on biocrude production from microalgae (see Chapter 2), the process water from the process has been identified as a rich source of organic carbon that requires treatment to reduce the chemical oxygen demand. The process water also contains significant amount of nutrients that can be recycled for algal cultivation benefiting process economics. Research has focused on the subcritical HTG of the process water to produce a biogas along with nutrient recycling.

The objectives of this research are to investigate the use of supercritical water gasification technology to upgrade the process water from microalgal HTL to maximise hydrogen production for biocrude hydrotreating. The nutrient content of the process water post SCWG is analysed to determine suitability of nutrient recovery for algal growth.

A series of experiments were carried out with the following objectives:

- Investigate the product distribution from the HTL of microalgae with different biochemical compositions and determine the organic carbon content of the process water.
- Investigate the effect of biocrude recovery (solvent extraction vs. gravity separation) on the quality of the biocrude and organic carbon content of the process water.
- Assess the upgrading of the process water through SCWG to maximise hydrogen production with the use of catalysts.

- Determine the process conditions required to generate sufficient mass of hydrogen for hydrotreating the biocrude.
- Determine the maximum hydrogen yield obtained through SCWG of the process water from microalgae HTL based on the selected process conditions.

2 Hydrothermal processing of algae for biofuels

This chapter provides:

- An introduction to macroalgae and microalgae's classification, cultivation and structure.
- A review on the hydrothermal processing of algae for fuel, focusing on hydrothermal liquefaction and hydrothermal gasification.
- A description of supercritical water gasification technology.

2.1 Macroalgae

2.1.1 Description

Macroalgae, also known as seaweed, is a group of eukaryotic photosynthetic marine organisms. Diverse and abundant in the world's oceans and coastal waters they are typically comprised of a blade or lamina, a stipe, and a holdfast for anchoring and support in marine environments (U.S. DOE, 2010). They have a low lipid content as a general rule (McDermid and Stuercke, 2003) but are high in carbohydrates that are potential biofuels or biofuel precursors. The following sections describe macroalgae's classification and cultivation with a focus on brown algae's structure and storage polysaccharides.

2.1.2 Classification

Following research in the early twentieth century[1], it was revealed that differences in pigmentation accompanied differences in storage products and cellular organisation. Thus a major reclassification of the groups followed with Smith (1950) grouping seven major categories or divisions in conformity with the International Code of Botanical Nomenclature – Cholorphyta, Euglenophyta, Chrysophyta, Phaeophyta, Pyrrhophyta, Cyanophyta, and Rhodophyta. However, Papenfuss (1946) argued that the names of the algal divisions should include *phyco* seeing as to use the designation "Chlorophyta" for the green algae precluded its use for other members of the plant kingdom with identical pigmentation and storage products (Bold and Wynne, 1978; Craigie, 1974). As such, the group names are Chlorophycophyta, Euglenophycophytam etc.

Broadly, seaweeds are defined according to their pigments e.g., brown seaweeds (*Laminaria, Fucus, Saragssum*), red seaweeds (*Gelidium, Palmaria, Porphyra*) and green seaweeds (*Ulva, Codium*) (SEI, 2009). The characteristics of the most common algal divisions (common names: green, brown, and red) are summarised in Table 2.1, highlighting the differences in pigments, stored food and cell wall composition between the three most common groups.

[1] For a history of the classification of the major groups of algae see Bold and Wynne (1978); Papenfuss (1955)

Division	Common Name	Pigments	Stored Food	Cell Wall	Flagellar Number	Habitat
Cholorophycophyta	Green algae	Chlorophyll *a*, *b*; *α*-, *β*-, and *γ*-carotenes + several xanthophylls; 2-5 thlakoids/stack[a]	Starch (amylase and amylopectin) (oil in some)	Cellulose in many (= *β* – 1, 4-gluco-pyranoside), hydroxyl-proline, glycosides; xylans and mannans; or wall absent; calcified in some	1, 2-8, many, equal, apical	freshwater, brackish water, saltwater, terrestrial (soil, rocks, etc)
Phaeophycophyta	Brown algae	Chlorophyll a, c; *β*-carotene + fucoxanthin and several other xanthophylls; 2-6 thylakoids/stack	Laminarin (= β – 1, 3-glucopyranoside, predominantly); mannitol	Cellulose, alginic acid, and sulphated mucopoly-saccharides, (fucoidan)	2, unequal, lateral	freshwater (very rare), brackish water, saltwater
Rhodophycophyta	Red algae	Chlorophyll a, (d in some Florideophycidae); R- and C-phycocyanin, allophycocyanin, R- and B-phycoerythrin. α- + β-carotene +several xanthophylls; thylakoids single, not associated	Floridean starch (glycogen-like)	Cellulose, xylans, several sulphated polysaccharides (galactans) calcification in some	Absent	freshwater (some), brackish water saltwater (most)

Table 2.1 Characteristics of green, brown, and red algae (Bold and Wynne, 1978)

2.1.3 Cultivation

Whilst the majority of Asian seaweed is cultivated, seaweed exploitation in Europe is currently restricted to manual and mechanised harvesting of natural stocks (SEI, 2009). Harvesting natural stocks to obtain seaweed biomass is common due to the natural population of seaweed being a significant resource. Depending on the temperature, brown seaweeds dominate in cold waters and reds in warmer waters. In the mid-90s, the global harvest of seaweed was equally split between natural harvest and cultivation by aquaculture. Approximately 3.6 million tonnes wet weight was naturally harvested in 1995, making up 48% of the global harvest – the balance produced by aquaculture (SEI, 2009). However, at the start of the 21st century, natural harvest of seaweed biomass only made up about 6% of the global resource, with over 15 million tonnes of seaweed produced by aquaculture in 2006 (FAO, 2006).

Cultivation methods for macroalgae can be done in offshore, near-shore, and open pond facilities. Large offshore seaweed farms were tested by the Marine Biomass Program in the U.S. through deployment of kelp on growth structures in deep waters off the coast of Southern California (U.S. DOE, 2010). In addition, modern prototypes for offshore growth of kelp, Laminaria hyperborean, have been successfully tested in the North Sea (Buck & Bucholz 2004; 2005). Near-shore coastal cultivation is already being exploited by countries like China, Japan and Chile, which have viable seaweed aquaculture industries. The artificial farming of seaweed has become a necessity in Asia due to demand overcoming the natural production in the food industry (Kain and Dawes, 1987). Kain and Dawes summarise the advantages of cultivating seaweed over natural production:

- Cultivating and harvesting seaweed offers a safer route by avoiding open seas which are prone to bad weather and storms.
- Harvesting of specific species without co-harvesting unnecessary and unwanted material.
- Harvesting seaweed of the same age and quality due to the controlled nature of the cultivation and harvesting.
- Potential to improve stock by genetic strain collection.

There still remains some limited control over the environment where seaweed can be artificially cultivated and harvested and as such, the sites have to be carefully chosen in order to meet the requirements for wave exposure, seabed suitability and nature of environment (rocky or sandy) (Lipkin, 1985). For a review on mass cultivation of macroalgae see Kerrison et al. (2015) and Kraan (2013)

2.1.4 Brown algae - Kelps

In this research, Phaeophyta - brown algae - commonly found around the British coasts and dominating the flora in temperate seas, is of particular interest. According to Bold & Wynne (1978), brown algae are an important assemblage of plants and are classified in about 265 genera with more than 1500 species (Davis et al., 2003). Their colour is derived from large amounts of carotenoid fucoxanthin contained in their chloroplasts and the presence of various pheophycean tannins. Their main characteristics are described in Table 2.1.

2.1.4.1. Structure

A typical brown algal cell is depicted in Figure 2.1. Typical algal cell walls of Phaeophyta are comprised of a fibrillar skeleton and an amorphous embedding matrix (Davis et al., 2003). The most common fibrillar skeleton material is cellulose (Figure 2.2). The Phaeophyta algal embedding matrix is predominately alginic acid or alginate (the salt of alginic acid – see Table 2.2) with a smaller amount of sulphated polysaccharide (fucoidan – see Table 2.2).

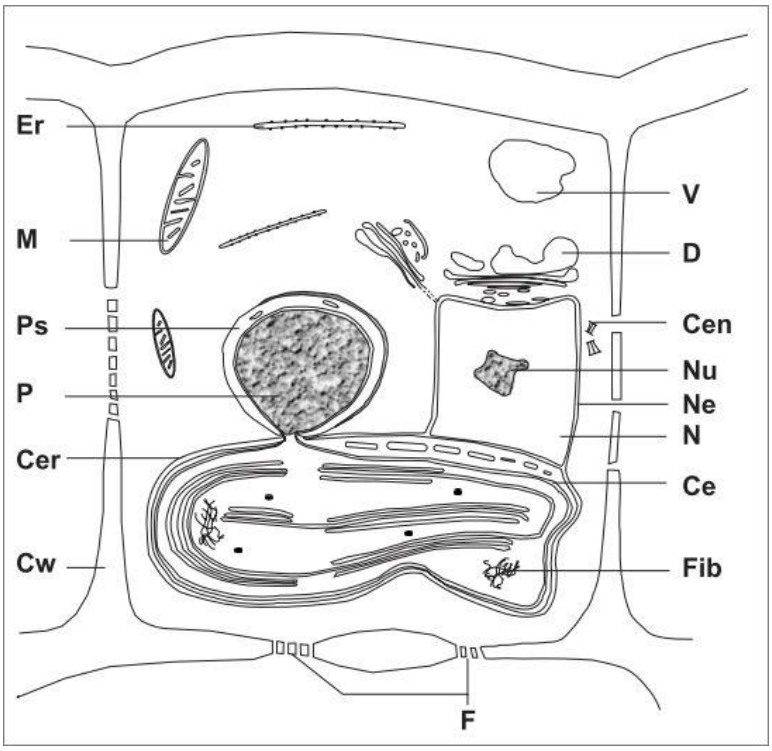


Figure 2.1 Schematic diagram of a brown algal cell (Bouck, 1965).

(Ce) Chloroplast envelope; (Cer) chloroplast endoplasmic reticulum; (Er) endoplasmic reticulum; (Ne) nuclear envelope; (Fib) DNA fibrils; (Nu) nucleolus; (N) nucleus; (P) premoid; (Ps) prenoid sac; (D) dictyosome; (M) mitochondrian; (V) vacuole; (F) plasmodesma pit field; (Cw) cell wall; (Cen) centrioles.

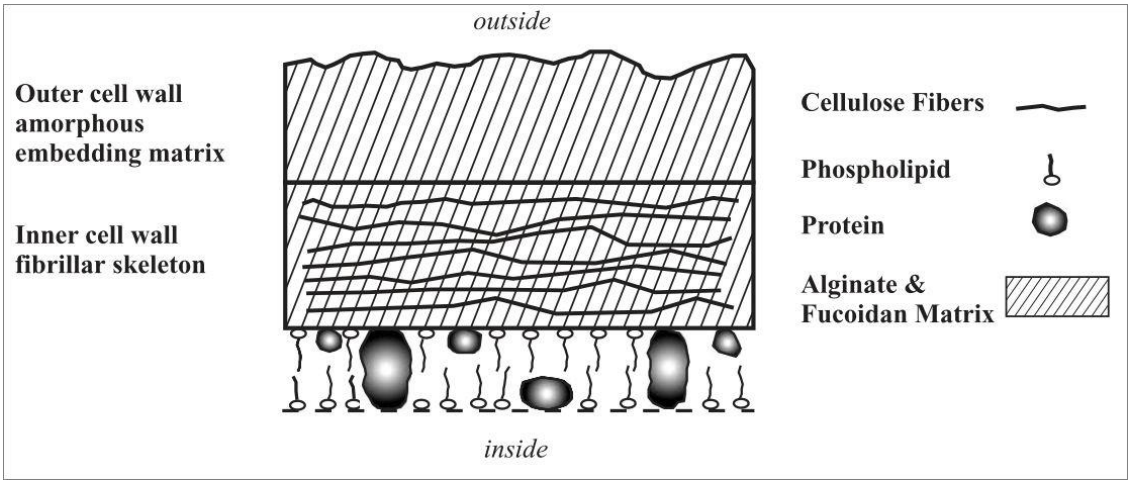


Figure 2.2 Cell wall structure in brown algae (Schiewer and Volesky, 2000)

2.1.4.2. Storage polysaccharides: mannitol and laminarin

Carbon is stored in monomeric compounds (e.g. mannitol) or in the polymeric state (e.g. laminarin) (Davis et al., 2003). Mannitol (Table 2.2) occurs in all brown algae (South and Whittick, 1987) and can constitute 30% dry weight (Volesky, 1970). It is the first accumulation product of photosynthesis and has osmoregulatory properties (Lee 1989; Percival 1967; in Davis et al. 2003). The second major storage product, laminarin (Table 2.2), was first characterised by Schmiedeberg in 1885 (Black, 1950a). It is made up of a mixture of polysaccharides and two types of chains exist: (i) 'M', with mannitol attached to the reducing end, and (ii) 'G', with glucose attached to the reducing end (Percival, 1967). Mannitol comprises about 2% of laminarin (Lewis and Smith, 1967).

According to Lewis & Smith (1967), the amount of mannitol found in members of the Phaeophyta is frequently large. Yields of 50% dry weight have been reported (Quillet 1957, for L. digitata), however, typical yields fall in the range of 5 - 25%. While the proportion of laminarin ranges between 2 - 34% dry weight of brown algae (Lewis and Smith, 1967).

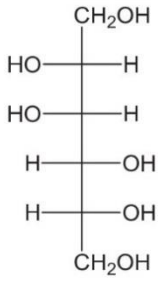
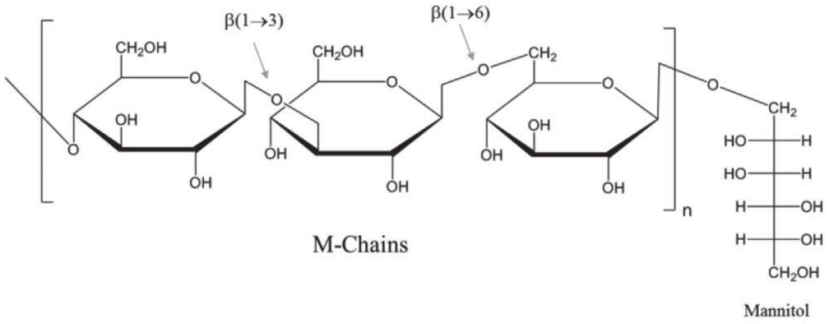
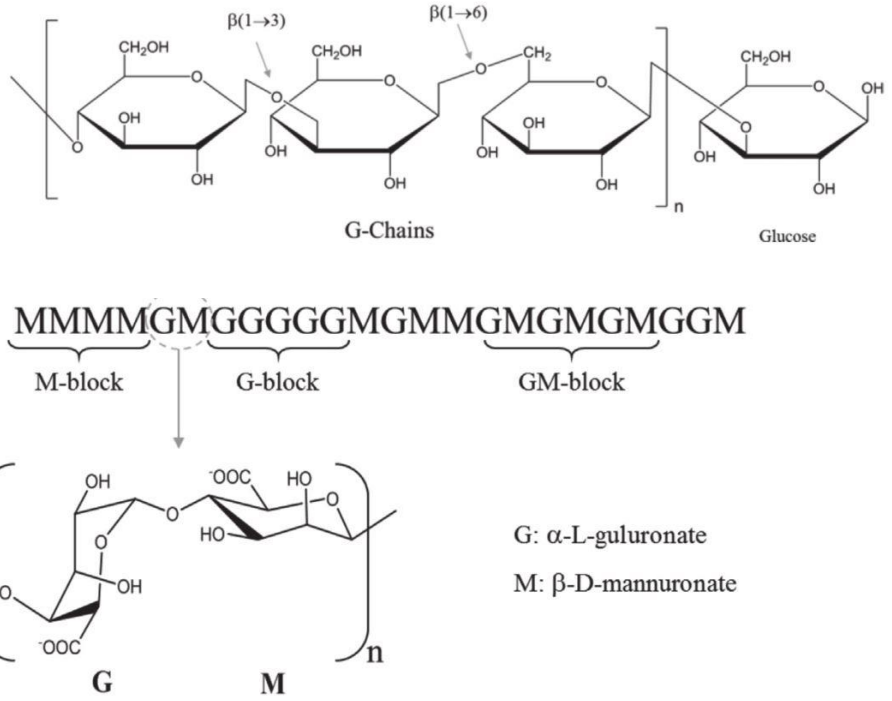
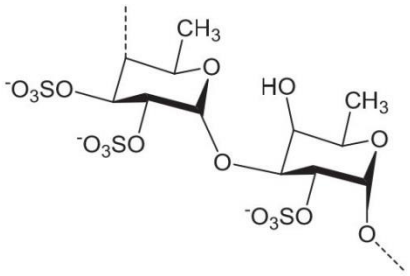
Carbohydrate	Chemical Structure
Mannitol	
Laminarin	
Alginate	
Fucoidan	

Table 2.2 Chemical structure of the main carbohydrates in brown algae - adapted from Anastasakis et al., (2011).

2.1.4.3. Extracellular polysaccharides: alginic acid and fucoidan

Alginic acid, found in all brown algae, was first isolated by Stanford in 1883 (Black, 1950a). It is found in the cell wall matrix and the mucilage or intercellular material as shown in Figure 2.2. It constitutes between 10 - 40% of the algal dry weight and its abundance depends on the depth and season in which the algae grow. A major polysaccharide in brown algae, alginic acid is a polymer of 5-carbon acids, D-mannuronic (M-block) and L-guluronic acid (G-block) (Table 2.2).

Fucoidan is the sulphated polysaccharide found in most brown algae. The compound was first isolated by Kylin (1915) who prepared and isolated L-fucose phenylhydrazone from the hydrolyzate (Percival, 1967). Dry mass percentages range from 5 - 20% and its presence in the cell walls of brown algae protects them from desiccation (Percival, 1979).

2.1.5 Species under investigation

In this study, four species of brown algae were chosen for investigation due to their wide distribution and abundance along British and European coasts. The four species are: *Laminaria digitata*, *Laminaria saccharina* (also known as and currently referred to as *Saccharina latissima*), *Laminaria hyperborea*, and *Alaria esculenta*.

- ***Laminaria digitata*** grows in rocky environments up to a depth of about 27.5 m and is widely distributed in the Northern Hemisphere and found in abundance in the British Isles coast along with the European seaboard from Norway to Spain (Drew, 1910). Vincent and Gravell (1986) describe *Laminaria digitata* as a large brown seaweed (commonly referred to as ‘kelp’ or ‘tangle’) with a thick cylindrical stipe and large ‘leaves’ or fronds. It also consists of a holdfast which helps the plant attach to rocks.

- ***Saccharina latissima*** is common across British coasts and grows in sheltered and rocky environments up to a depth of 27.5 m (similar to *Laminaria digitata*). Its structure is also similar to that of *Laminaria digitata* in that it consists of a holdfast, cylindrical stipe and fronds. However, the stipe is smaller (around 30 cm) and the lamina consists of a single long tapering lobe (Drew, 1910).
- ***Laminaria hyperborea*** grows on bedrocks in the North Eastern Atlantic, from Iceland to Norway to Portugal, between depths of 8 - 30 m and is rarely exposed in tides (Sjotun et al., 1993). Its length can reach up to 3.5 m and the stipe varies between 0.3 and 1.2 m and is hard and thick at the base (Dickinson, 1963). The stipe of Laminaria hyperborea is used as a raw material for the alginate industry.
- ***Alaria esculenta*** is widespread across the Northern hemisphere and grown along rocky shores with strong wave exposure (Kraan, 2013). It's generally smaller than the *Laminaria* species with a relatively small stipe of 15 cm but the blades can reach lengths of 4 m (Dickinson, 1963). Characteristic features of *Alaria esculenta* are the presence of a midrib and sporangia on the blades.

The chemical composition of the *Laminaria* species is presented in Table 2.3 (the chemical composition of *Alaria esculenta* was not available in the literature).

Parameter	***Laminaria digitata* (%)**	***Saccharina latissima* (%)**	***Laminaria hyperborea* (%)**	**References**
Ash	19 – 44 (blades) 29 – 42 (stipe) 22 – 43 (whole plant)	24 – 34	16 - 37 (blades) 32.5 – 36.5 (stipe)	(Black, 1950a, 1950b; Horn, 2000; Obluchinskaya, 2008)
Carbon	42 – 62	27.5 (blades) 27 (stipe)	63.7	(Chapman, 1970; Gevaert et al., 2001)
Alginate	14 – 25.7 (blades) 26.5 – 33.5 (stipe) 15 – 26.5 (whole plant)	33	18.5 – 38 (stipe) 8.5 – 33 (frond)	(Black, 1950a, 1950b; Kirby, 1953; Obluchinskaya, 2008)
Cellulose	3 – 5 (blades) 6 – 7.8 (stipe) 4 – 6 (whole plant)	4 – 5 (blades) 6.9 – 8 (stipe) 5 – 5.8 (thallus)	9.8 – 11.2 (stipe)	(Black, 1950a, 1950b; Horn, 2000)
Laminarin	0.5 – 28 (blades) 0.5 – 24.5 (whole plant)	9 – 14.3	1.5 – 32.4	(Black, 1950a, 1950b; Lamour and Black, 1954; Obluchinskaya, 2008)
Mannitol	3 – 29 (blades) 4 – 14 (stipe) 4 – 20 (whole plant)	13 – 17.8	6.1 – 25.7	(Black, 1950a, 1950b; Lamour and Black, 1954; Obluchinskaya, 2008)
Fucoidan	1.6 – 6.5	7.9 – 9.7	2 – 4 (stipe)	(Horn, 2000; Mabeau and Kloareg, 1987; Obluchinskaya, 2008)
Protein	4.5 – 14 (blades) 5.5 – 10 (stipe) 6.5 – 13 (whole plant)	18.1 (blades)	5.9	(Black, 1950a, 1950b; Lamour and Black, 1954; Mabeau and Kloareg, 1987)
Fat	-	1.2 – 1.36	0.77 – 1.67	(Chapman, 1970; Obluchinskaya, 2008)

Table 2.3 Chemical composition of macroalgal species

2.2 Microalgae

2.2.1 Description

Microalga is a microscopic organism that can grow in fresh, brackish, waste or salt water. There are two functional groups of microalga: (i) phototrophic, where the alga grows using CO_2 and sunlight via photosynthesis, and (ii) heterotrophic, where the alga requires an organic source of carbon for its growth. Both groups require water and nutrients for their growth.

Microalgae have been described as '*sunlight-driven cell factories*' (Chisti, 2007) that convert CO_2 to potential biofuels, foods, feeds and high value bioactives (Metting and Pyne, 1986; Schwartz et al., 1990; Walker et al., 2005).

2.2.2 Classification

Biologists have categorised microalgae based on their pigmentation, life cycle and basic cellular structure (Demirbas, 2010). The three main classes of microalgae in terms of abundance are:

- diatoms (*Bacillariophyceae*),
- green algae (*Chlorophyceae*),
- golden algae (*Chrysophyaceae*).

The cyanobacteria – blue-green algae – (*Cyanophyceae*) are also categorised as microalgae, for example, *Spirulina* (*Arthrospira platensis* and *Arthrospira maxima*).

Diatoms represent the largest group of biomass producers on earth and are the dominant life form in phytoplankton (Demirbas, 2010). Diatoms are unicellular organisms characterised by a silica shell. They exist singly although some join to form colonies. Diatoms are usually yellowish or brownish and are found in

freshwater, saltwater, soil and plant surfaces. Freshwater and saltwater diatoms show greatest abundance early in the year as part of a phenomenon known as ‘spring bloom’. This phenomenon occurs due to the availability of light and nutrients that have been regenerated during the winter.

Chlorophyceae are freshwater green algae that come in a variety of shapes and forms including unicellular species, filaments, colonies, and non-flagellate unicells.

Chrysophyceae are small flagellates that are yellow-brown in colour. Chrysophyceae are found as unicellular and multicellular organisms, although the unicellular is more common.

2.2.3 Cultivation

Photoautotrophic cultivation (requiring light) can be achieved in open-pond or photobioreactor systems. Open pond systems can be integrated into natural water systems such as lagoons and ponds but it is more common to use artificial systems such as raceway ponds. Photobioreactors involve the use of transparent tubes or plates to form the culturing environments. The advantages and disadvantages of both systems are summarised in Table 2.4.

System	Advantages	Disadvantages
Open ponds	• Lower capital costs • Easy maintenance • Evaporative cooling maintains temperature	• Subject to changes in temperature and light exposure (daily and seasonal) • Difficult to maintain monocultures due to contamination
Closed Photobioreactors	• Long term monoculture with no contamination • Less cleaning and maintenance • Allows higher cell concentrations	• Sophisticated systems have a high capital cost • Scalability issues • Temperature maintenance through cooling

Table 2.4 Comparative advantages and disadvantages of photoautotrophic microalgal cultivation systems - adapted from U.S. DOE, (2010).

Heterotrophic cultivation involves growing algae using a carbon source, such as sugars, instead of light to generate algal biomass. The benefits of heterotrophic cultivation include easy maintenance and relative ease in maintaining optimal conditions for production. There is potential to utilise inexpensive lignocellulosic sugars as the feedstock for algal growth. Xu et al. (2006) report that heterotrophic cultivation achieves high biomass concentrations that reduces the extent and cost of the infrastructure required to cultivate algae. However, a limitation of heterotrophic cultivation is that it competes for feedstock with other biofuel technologies.

2.2.4 Structure

The cell structures of a single celled cyanobacterium (*Cyanophyceae*) and a green alga (*Chlorophyceae*) are shown in Figure 2.3. In the green alga, the DNA and photosynthetic equipment are membrane bound. The cyanobacterium contains a network of thylakoid membranes referred to as the 'chromatoplast' and these are present in the peripheral region of the cell. Cyanobacterium also contains phycobilisomes (light harvesting protein complexes). The green alga however, has interconnected thylakoids which are more stacked. This bears a resemblance to plant cells with small nucleoids of DNA. The biochemistry of the green alga resembles that of plants and is capable of accumulating large quantities of lipids (Thompson, 1996)

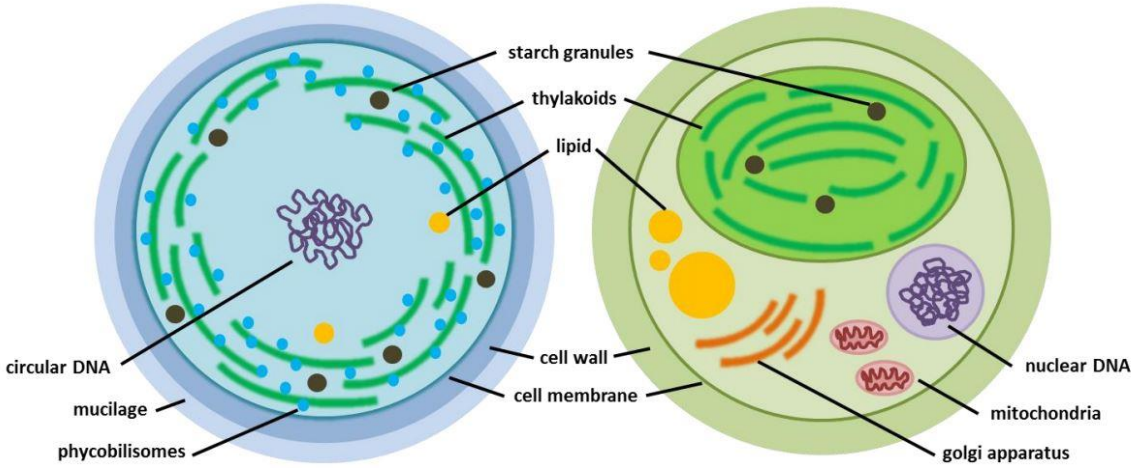


Figure 2.3 Generalised cell structure of *Cyanophyceae* (left) and *Chlorophyceae* (right) - adapted from Barsanti and Gualtieri, (2006)

Microalgae produce lipids, carbohydrates, proteins and nucleic acids in varying compositions depending on the strain and culture conditions (Banerjee et al., 2002; Metzger and Largeau, 2005). The lipid content is the primary component for biodiesel production (Biller et al., 2011; Levine et al., 2010; Williams and Laurens, 2010) and the lipid fraction can vary between 5 and 80% (Chisti, 2007). Table 2.5 summarises the biochemical content of a range of microalgal species.

Species	**Protein**	**Carbohydrates**	**Lipids**	**Nucleic acid**
Scenedesmus obliquus	50-56	10-17	12-14	3-6
Scenedesmus quadricauda	47	-	1.9	-
Scenedesmus dimorphus	8-18	21-52	16-40	-
Chlamydomonas rheinhardii	48	17	21	-
Chlorella vulgaris	51-58	12-17	14-22	4-5
Chlorella pyrenoidosa	57	26	2	-
Spirogyra sp.	6-20	33-64	11-21	-
Dunaliella bioculata	49	4	8	-
Dunaliella salina	57	32	6	-
Euglena gracilis	39-61	14-18	14-20	-
Prymnesium parvum	28-45	25-33	22-38	1-2
Tetraselmis maculata	52	15	3	-
Porphyridium cruentum	28-39	40-57	9-14	-
Spirulina platensis	46-63	8-14	4--9	2-5
Spirulina maxima	60-71	13-16	6-7	3-4.5
Synechoccus sp.	63	15	11	5
Anabaena cylindrica	43-56	25-30	4-7	-

Table 2.5 Biochemical composition of microalgal species (adapted from (Becker, 1994)).

2.3 Hydrothermal liquefaction of algae (HTL)

2.3.1 Batch microalgal HTL

The first reports on HTL of microalgae date back to the early 1990s at the National Institute for Resources and Environment in Tsubaka, Japan (Dote et al., 1994; Inoue et al., 1994; Minowa et al., 1995). Using a batch reactor, the group studied the HTL of *Botryococcus braunii* and *Dunaliella tertiolecta* with a high concentration of dry matter algae mass, 50 wt.% and 78.4 wt.% respectively. At a temperature of 300 °C, they reported a biocrude yield of 37 wt.% and 57 – 64 wt.% respectively for the two microalgal species. The biocrude yields were found to be higher than the lipid content of the two algal species resulting in the conclusion that the biocrude was also being formed by the protein and carbohydrate fractions too. *Botryococcus braunii* was processed in a stirred reactor for 1 hour at 200 - 340 °C. At higher temperatures, the nitrogen content of the biocrude increased suggesting the onset of protein breakdown. Following on from the early studies in the 1990s, several researchers have investigated the HTL of microalgae. A summary of biocrude yields from recent (non-catalytic) microalgal HTL is presented in Table 2.6.

Species	Temperature (°C)	Holding time (min)	Algal concentration (%)	Biocrude yield (%)	References
Tetraselmis sp.	310 - 370	5 - 60	16	65	(Eboibi et al., 2014)
Chlorella vulgaris, *Spirulina* sp., *Porphyridium cruentum*, *Nannochloropsis oculata*, *Chlorogloeopsis fritschii*, *Scenedesmus dimorphus*	300 - 350	60	10	35	(Biller and Ross, 2011; Biller et al., 2011)
Nannochloropsis sp.	200 - 500	60	5.5	43	(Brown et al., 2010)
Spirulina platensis	100 - 380	0 - 120	10 - 50	40	(Jena et al., 2011b)
Spirulina sp., *Scendesmus* sp.	300	30	20	45	(Vardon et al., 2012, 2011)
Chlorella pyrenoidosa	200 - 300	0 - 120	20	39	(Yu et al., 2011a, 2011b)
Desmodesmus sp.	175 - 450	5*-60	7-8	49	(Garcia Alba et al., 2012; Torri et al., 2012)

Table 2.6 Summary of recent non-catalytic microalgal HTL - adapted from Biller and Ross, (2012)

The effect of operating conditions (temperature, reaction time, algal concentration) and algal biochemical composition on the HTL of microalgae has been the focus of several studies (Brown et al., 2010; Chakinala et al., 2010; Jena et al., 2011a; Yu et al., 2011b). Jena et al., (2011a) studied the effect of operating conditions on the HTL of *Spirulina platensis* in a 1.8 L stirred batch reactor. The HTL conditions varied from 200 - 380 °C with holding times up to 120 min and an algal concentration of 10 - 15 wt.%. The authors found that the highest biocrude yield (39.9%) was obtained at 350 °C, 60 min hold time and an algal concentration of 20 wt.%. The biocrude had a HHV of 35.3 MJ kg^{-1}. Torri et al., (2012) argue that whilst higher temperatures might favour higher biocrude yields and deoxygenation of the biocrude, the biocrude obtained at higher temperatures might not be usable directly as a fuel due to its compositional complexity. The authors studied the composition of biocrude at different temperatures and concluded that HTL at relatively low temperatures (below 250 °C) maximise the yield of lipids and algenan derivatives in the oil while harsher conditions (300 - 375 °C) cause cellulose and proteins to break down resulting in amino acid derivatives and carbohydrate derivatives in the oil – thus increasing the nitrogen content of the oil. Therefore, with regards to temperature and algal HTL, if lipid-rich oil is preferred then temperatures should not exceed 250 °C. If heavier crude-like oil is preferred then temperatures as high as 350 - 375 °C should be used. The variation in holding time and algal concentration during microalgal HTL had less effect on the oxygen and nitrogen content of the biocrude product.

Alternatively, rather than lowering the operating conditions, if a biocrude of lower nitrogen and higher lipid content is desired, then the protein fraction can be removed prior to HTL. This ties in with the algal biorefinery concept where advances have

been made recently with the development of a novel two step sequential HTL technology (Chakraborty et al., 2012; Miao et al., 2012). In their study, Chakraborty et al. developed a process for extracting the value added polysaccharides (carbohydrates) from *Chlorella sorokiniana* prior to HTL. The first process involved hydrothermal treatment at 160 °C to produce a polysaccharide rich water phase. The polysaccharides were extracted by precipitation with ethanol and the remaining algal residue was processed at 300 °C to produce a biocrude. The advantages of the two step process included: (i) the subsequent yield of biocrude was 5% higher compared to direct HTL of *Chlorella sorokiniana*, (ii) the biochar yield was reduced by 50%, and (iii) the second-step HTL required a lower temperature (240 °C) to achieve similar yields observed from direct HTL of *Chlorella sorokiniana* at 300 °C. As such, the energy input for the two step process was calculated to be 15 MJ less per kg of biocrude compared to direct HTL of *Chlorella sorokiniana*.

A similar biorefinery approach was adopted by (López Barreiro et al., 2014) where the quality of biocrude was assessed after extracting lipids and after extracting proteins in micro-autoclave experiments. The authors found the results promising in terms of extracting the proteins prior to HTL due to obtaining a biocrude with lower nitrogen content and a valuable co-product stream of amino acid concentrates.

Yu et al., (2011) studied the effect of temperature and holding time on the biocrude yield from the HTL of the low lipid microalga, *Chlorella pyrenoidosa*. The authors argue that high lipid algae and the associated culturing conditions result in lower biomass productivities and the alternative approach would be to culture fast growing low lipid algae and hydrothermally process it into a biocrude through HTL. With an algal concentration of 20% they achieved the highest biocrude yields (39%) at

280 °C and a holding time of 120 min. The elemental composition of the biocrude was not presented, however, the HHV of the biocrude was 35.4 MJ kg^{-1} increasing to 38.5 MJ kg^{-1} at 300 °C and 30 min hold time suggesting a lower oxygen and nitrogen content in the biocrude.

Brown et al., (2010) studied the effect of temperature on the HTL of *Nannochloropsis* sp. At a holding time of 60 min. High yields of biocrude (43%) were reported at HTL temperatures of 350 °C. The biocrude had a HHV of 39 MJ kg^{-1} and the process had an energy recovery of 78% (see section 2.6 for energy recovery).

Biller and Ross, (2011) investigated the influence of the biochemical composition of microalgae on the composition of the biocrude. The algae investigated ranged from high carbohydrate (*Poryphyridium cruentum* - 40 wt.%), high protein (*Spirulina* sp. - 65 wt.%) to high lipid and ash (*Nannochloropsis* sp. – 32 wt.% and 26 wt.% respectively). The algal species were investigated alongside seven carbohydrate, protein and lipid model compounds to compare the HTL behaviour at 350 °C. The results indicated the tendency of biocrude production to follow the trend: lipids > protein > carbohydrate, with the highest oil yield reported from the HTL of the high lipid species *Nannochloropsis oculata* (35% biocrude) and medium lipid, high protein *Chlorella vulgaris* (36% biocrude). A summary of the analysis of the biocrude from the study is presented in Table 2.7.

Species	C (%)	H (%)	N (%)	S (%)	O* (%)	HHV (MJ kg^{-1})
Chlorella	70.7	8.6	5.9	0	14.8	35.1
Nannochloropsis	68.1	8.8	4.1	0	18.9	34.5
Porphyridium	72.8	8.5	5.4	0.3	13.3	35.7
Spirulina	73.3	9.2	7	0	10.4	36.8

*by difference

Table 2.7 Ultimate analysis and HHV of the biocrudes produced from HTL at 350 °C, 60 min hold time (Biller and Ross, 2011).

Based on the non-catalytic studies of microalgal HTL, a high biocrude yield (~35%) is obtained. The biocrude has a HHV around 35 MJ kg^{-1} and is highly viscous with relatively high nitrogen and oxygen content. Researchers have incorporated catalysts during HTL to increase the biocrude yield and lower the heteroatom content in order to improve the fuel quality and its capability for combustion and upgrading. A summary on catalytic microalgal HTL is presented in Table 2.8.

Catalytic HTL has focused on the use of sodium carbonate (Na_2CO_3) as a homogeneous catalyst. Early work in the 1990s generated mixed results for the effect of catalytic HTL. With the use of 5 wt.% Na_2CO_3, the biocrude yield from *B. braunii* increased by 5% at 300 °C but decreased by 10% at 200 and 340 °C. A decrease in the oxygen content of the biocrude was observed at 200 °C, however, the oxygen content increased at higher temperatures (Inoue et al., 1994). Similar concentrations of Na_2CO_3 were used in a study by Yang et al., (2004). The authors found that the effect of catalyst was stronger at lower temperatures and shorter hold times.

Ross et al. (2010) investigated microalgal HTL using two alkali and two organic acids: Na_2CO_3, KOH, formic acid and acetic acid. Their results indicated that the use of organic acids improved the flow properties and lowered the boiling point of the biocrude. In addition, the authors noted the effect alkali and acidic homogeneous catalysts had on different biochemical composition feedstocks. Na_2CO_3 was more effective in the HTL of carbohydrates and the high carbohydrate rich *P. cruentum* resulted in higher biocrude yields compared to both acid catalysed and non-catalysed reactions. However, due to the promotion of saponification reactions with the use of alkali catalysts on high lipid algae, significantly less biocrude yields were observed. Model protein compounds were investigated and exhibited the highest biocrude yields and HHVs in water alone. As such, the conclusions from the study indicated that high carbohydrate algae should be processed in alkali and high protein and high lipid algae processed in water or formic acid.

Species	Catalyst	Catalyst concentration (%)	Atmosphere	Oil yield (%)	References
Botryococcus braunii *Dunaliella tertiolecta*	Na_2CO_3	0-5	N_2	22-64	(Dote et al., 1994; Minowa et al., 1995)
Microcystis viridis	Na_2CO_3	5	N_2	25-34	(Yang et al., 2004)
Dunaliella tertiolecta	Na_2CO_3	0-10	Air	26	(Shuping et al., 2010)
Chlorella vulgaris *Spirulina* sp. *Nannochloropsis oculata* *Porphyridium cruentum*	Na_2CO_3, KOH, Formic acid, Acetic acid	1 Molar	Air	~20	(Biller and Ross, 2011; Ross et al., 2010)
Nannochloropsis sp.	Pd/C, Pt/C, Ru/C, Ni/SiO_2-Al_2O_3, CoMo/y-Al_2O_3, Zeolite	50	He/H_2	35-58	(Duan and Savage, 2011)

Table 2.8 Summary of catalytic microalgal HTL - adapted from Biller and Ross, (2012)

The effect of homogeneous catalysts on biocrude yields do not appear to be significant (Biller and Ross, 2012) and with the added difficulty in recovering the catalyst, research into heterogeneous catalysts could potentially have advantages over homogeneous catalysts. Duan and Savage (2011) investigated the use of palladium, platinum, ruthenium, nickel, cobalt-molybdenum on carbon-alumina support and a zeolite during microalgal HTL. Every catalyst increased the biocrude yield from *Nannochloropsis* sp. The maximum yield achieved was 57% with the use of palladium (20% higher than the non-catalysed experiment). The effect on the heteroatom content of the biocrude compared to non-catalysed runs was negligible. Contrary to the work done by Biller et al. (2011) with heterogeneous catalysts where significant deoxygenation of the biocrude was achieved resulting in a larger HHV.

2.3.2 Batch macroalgal HTL

The work on macroalgal HTL is limited compared to microalgal HTL. A summary of recent work on both catalytic and non-catalytic macroalgal HTL is presented in Table 2.9.

Species	Temperature (°C)	Catalyst concentration (%)	Time (min)	Algal concentration (%)	Oil yield (%)	References
Laminaria saccharina	250 - 375	-	15 - 120	2 - 20	19	(Anastasakis and Ross, 2011)
Laminaria saccharina	250 - 375	KOH (0 - 100%)	15 - 120	2 - 20	4-19	(Anastasakis and Ross, 2011)
Enteromorpha prolifera	220 - 320	Na_2CO_3 (5%)	5 - 60	13	23	(Zhou et al., 2010)
Enteromorpha prolifera	290	Acetic acid	20	33.3	28	(Yang et al., 2014)
Laminaria saccharina	350	-	15	10	79	(Bach et al., 2014)

Table 2.9 Recent studies on catalytic and non-catalytic macroalgal HTL

Anastasakis and Ross (2011) investigated the HTL of *Laminaria saccharina* at different conditions – with and without catalysts. Results indicated the optimum reaction condition at 350 °C, 15 min hold time and an algal concentration of 10%, producing a biocrude yield of 19.3%. The biocrude had a HHV of 36.5 MJ kg^{-1} with high heteroatom content (4.9% N and 5.4% O). A carbon and nitrogen balance showed that half the carbon ended up in the biocrude with the remaining half equally split between the other product fractions (solid residue, process water and gas products). 40% of the nitrogen was found in the biocrude with the remainder in the process water. The study concluded that the process water could be further processed by fermentation due to the presence of organic carbon and used as a fertiliser due to the presence of a large amount of potassium and other minerals. In addition, the use of alkali catalyst (KOH) in varying concentrations resulted in a lower biocrude yield and an increase in the water soluble products.

Similar HTL work was carried out on *Enteromorpha prolifera* by Zhou et al. (2010) with the use of Na_2CO_3. The biocrude yield was 23% at 300 °C, 30 min hold time, and 5% Na_2CO_3. The biocrude had a HHV of 30 MJ kg^{-1} and was analysed and reported as a complex mixture of ketones, aldehydes, phenols, alkenes, fatty acids, esters, aromatics, and nitrogen containing heterocyclic compounds. Acetic acid was the main component of the water-soluble products in the process water.

Yang et al. (2014) studied the HTL of undried *Enteromorpha prolifera* at varying conditions and found that HTL at 290 °C, 20 min hold time and an algal concentration of 33.3% produced the highest biocrude yield of 28.4%. The biocrude had a HHV of 29.5 MJ kg^{-1} and was found to be a mixture of fatty acids, ketones, alkenes and 5-methyl furfural. The main components of water soluble organics in the process water were pyridines, carboxylic acids and glycerol. Yang et al. also

experimented with acid catalysts (0.02 M sulphuric acid and 0.2 M acetic acid) and found that the content of ketones in the biocrude significantly increased while the alkenes disappeared. In addition, the flow properties of the biocrude were improved on addition of acidic catalysts.

Bach et al. (2014) investigated the HTL of *Laminaria saccharina* at very high heating rates (585 °C min^{-1}). This resulted in much higher biocrude yields (79%) with a significantly higher HHV of 36 MJ kg^{-1}. Bach et al. also experimented with the addition of KOH and found a slight increase (~2%) in biocrude yield. They concluded that the difference in heating rate has a stronger effect on biocrude yield compared to catalyst addition.

2.3.3 Continuous microalgal HTL and biocrude upgrading

Recent studies on microalgal HTL in continuous reactor systems have confirmed the general trend observed in batch experiments (Elliott et al., 2013b; Jazrawi et al., 2013). Jazrawi et al. studied the continuous processing of *Chlorella* and *Spirulina* from a 15 - 30 L hr^{-1} plug flow type reactor unit across a range of algal concentrations (1 - 10%), temperatures (250 - 350 °C), hold times (3 - 5 min) and pressures (15 - 20 MPa). The maximum biocrude yield was 42% using an algal concentration (*Chlorella*) of 10% at 350 °C and 3 min hold time. The study established that while continuous processing confirms the general trends observed in batch studies, the maximal yields obtained through continuous processing are achieved in much shorter reaction hold times. This is down to the uncertainties in heating and cooling times in batch reactors which affect the reported reaction timescale.

The elemental analysis and HHV of the biocrude from the continuous HTL of *Chlorella* and *Spirulina* from Jazrawi et al. (2013) is presented in Table 2.10. The heteroatom content is significantly high (O 12 - 21%, N 2.6 - 7.9%, S 0.4 - 3.1%). Higher processing temperatures led to a decrease in oxygen content but an increase in nitrogen content (as established in batch studies – due to the breakdown of protein (Jena et al., 2011a; Torri et al., 2012). The carbon fraction in the process water is as high as 60%. However, as the algal concentration increases, the carbon fraction in the process water decreases. The continuous reactor performed better in terms of pressure controllability at higher processing temperatures and hold times. The authors found that less severe processing conditions caused difficulties with the control valve due to large particle sizes and higher solid yields.

	Temp (°C)	Hold time (min)	C (%)	H (%)	N (%)	S (%)	O* (%)	HHV (MJ kg^{-1})
Chlorella								
1 wt.%	250	3	70.3	4.8	2.6	0.4	21.9	27.9
	275	3	65.9	9.0	4.3	0.8	20.0	31.6
	300	3	64.1	7.8	7.5	1.5	19.1	29.6
	300	5	67.6	8.2	6.3	2.1	15.8	31.7
5 wt.%	300	3	69.5	8.9	7.2	-	14.4	33.2
	350	3	67.9	8.9	7.9	-	15.3	32.5
10 wt.%	300	3	69.1	8.7	7.8	0.9	13.5	33.0
	350	3	70.7	8.8	7.7	0.8	12.0	33.8
Spirulina								
1 wt.%	250	3	65.8	8.5	3.5	0.5	21.7	30.7
	275	3	62.3	7.3	6.7	1.1	22.5	28.0
	300	3	64.3	8.4	7.5	1.3	15.4	32.0
	300	5	68.3	8.3	6.9	1.1	15.4	32.0

Table 2.10 Elemental analysis and HHV of biocrudes from the continuous HTL of *Chlorella* and *Spirulina* at different processing conditions (Jazrawi et al., 2013)

The produced biocrude from batch and continuous algal HTL tends to be viscous and tar-like with a significant amount of heteroatoms – oxygen, nitrogen and sulphur. Therefore, it is not directly suitable for storage, transport and use as a transport fuel. Attempts at catalysing the HTL process to improve the quality of the biocrude produced involved the use of alkali (Na_2CO_3 and KOH) and organic acids (formic and acetic) (Biller and Ross, 2011; Ross et al., 2010). Results indicated that the use of organic acids improved the flow properties of the biocrude and lowered its boiling point. However, Duan and Savage (2011) point out that their studies on catalytic HTL of microalgae suggest that the quality of the biocrude is largely insensitive to the presence or identity of a catalyst and as such, separate upgrading of the biocrude through hydrotreating might be more suitable.

Hydrotreating involves processing the algal biocrude with hydrogen over a catalyst. Hydrogenation reactions convert oxygen, nitrogen and sulphur to H_2O, NH_3 and H_2S respectively. The amount of hydrogen required for hydrotreating depends on the amount of oxygen, nitrogen and sulphur in the biocrude. Baker and Elliott, (1988) describe treatment of HTL oils from woody biomass but a comparison with algal biomass cannot be drawn due to the negligible amounts of nitrogen in woody biomass compared to algal biomass. Frank et al. (2012) resorted to a stoichiometric calculation to calculate the hydrogen demand for hydrotreating and calculated a hydrogen demand of 0.023 - 0.060 g H_2 $g^{-1}_{biocrude}$ based on a biocrude containing 71% C, 9.2% H, 11% O and 5.7% N.

Jones et al. (2014) reported biocrude yields from the continuous HTL of *Nannochloropsis* and *Chlorella* consisting of C (77%), H (9 - 10%), O (6 - 8%), N (4 - 6%), S (0.3 - 0.7%). The biocrudes were investigated for hydrotreating and required 0.0375 - 0.043 g H_2 $g^{-1}_{biocrude}$. . Zhu et al. (2013) reported 0.05 g H_2 $g^{-1}_{biocrude}$ for the upgrading system of lipid extracted HTL oil.

The parameters used in the base case of a life cycle assessment of bio-jet fuel from HTL of microalgae (Fortier et al., 2014) included a minimum value of 0.0235 g H_2 g^{-1}_{feed} and a maximum value of 0.0399 g H_2 g^{-1}_{feed}. The parameters altered for the optimised case included a hydrogen consumption of 0.0276 g H_2 g^{-1}_{feed} as a nominal value. These were calculated based on the conversion of an algal biocrude with a similar elemental composition content to those reported by Jones et al., (2014).

Elliott et al. (2013b) studied the continuous HTL of wet *Nannochloropsis* slurries followed by catalytic hydrotreating to form liquid hydrocarbon fuel. In addition, the process water was catalytically gasified to produce a biogas. As opposed to batch studies and Jazrawi's continuous study on microalgal HTL that recover the biocrude using a solvent, Elliot et al. recovered the biocrude without the use of solvent by using gravity. This was achieved by separating the solids then routing the products into a dual liquid collecting system where the condensed liquids were collected under pressure. The liquid product was then drained into holding jars where the lighter biocrude fraction and heavier process water fraction formed two separate layers. The continuous system was operated at 350 °C and 20 MPa with an algal concentration of 17 - 35%. A carbon balance indicates that most of the carbon is recovered in the biocrude (50.3 - 81.8%) with a large fraction in the process water (15.2 - 43.9%). The carbon in the gaseous phase (1.8 - 5.1%) is mainly CO_2 with

small amounts of CH_4, H_2 and NH_3 and a small amount of carbon is found in the solid fraction (0.1 - 1.7%).

The biocrude was hydrotreated at 13.6 MPa in a fixed-bed catalytic reactor in two stages. The biocrude and excess hydrogen were fed at the top of the reactor and passed downward through the bed. In the first stage (top quarter of the reactor), the temperature of the reactor was lower (125 - 170 °C) with a liquid hourly space velocity (LHSV) of 0.66 $L_{biocrude}\ L^{-1}_{catalyst}\ hr^{-1}$. The partially hydrotreated biocrude then proceeded into the high-temperature stage (405 °C) with a LHSV of 0.14. The catalyst in both stages was a molybdenum sulphide catalyst with cobalt promotion on a fluorinated-alumina support. The hydrogen consumption for hydrotreatment was 0.027 - 0.045 g $H_2\ g^{-1}_{biocrude}$ and the elemental analysis of the biocrude pre- and post- hydrotreatment is summarised in Table 2.11.

	C (%)	**H (%)**	**N (%)**	**S (%)**	**O* (%)**
HTL biocrude	47.6 – 52.0	6.6 – 7.5	4.8 – 5.8	0.62 – 1.6	21.7 – 26.7
Upgraded biocrude	79.5 – 84.6	13.3 – 14.2	0.05 – 0.25	0.05 – 0.5	0.8 – 1.7

* by difference

Table 2.11 Elemental analysis of biocrude and upgraded biocrude following continuous HTL of *Nannochloropsis* (Elliott et al., 2013b)

The result of hydrotreatment was near complete desulphurisation and denitrogenation and an almost oxygen free hydrocarbon blend. Analysis of the upgraded product by gas chromatography – mass spectrometry (GC-MS) showed that the volatile components of the hydrotreated product were a mixture of light cyclic hydrocarbons, aromatic and naphthenic, as well as longer chain alkanes

suggesting lipid structure transformation. All detectible compounds from the hydrotreated product were less than C_{40}. In addition, the hydrotreated product fell primarily in the diesel range (defined as less than 10% boiling below 180 °C and less than 10% boiling above 350 °C) with 80 - 85% of the product blendable into the diesel pool.

Based on the Elliot et al. (2013) study on continuous microalgal HTL followed by hydrotreatment of the biocrude, and other studies (theoretical), the hydrogen requirements for treating a typical microalgal biocrude produced by HTL are summarised in Table 2.12.

H_2 consumption ($kg\ kg^{-1}_{biocrude}$)	**References**
0.05	(Zhu et al., 2013)
0.063	(Fisk et al., 2009)
0.032 – 0.040	(Fortier et al., 2014)
0.038 – 0.043	(Jones et al., 2014)
0.027 – 0.045	(Elliott et al., 2013a)
0.026 – 0.060	(Frank et al., 2012)

Table 2.12 Hydrogen consumption for hydrotreatment of microalgal HTL biocrude

In terms of hydrotreating the algal HTL biocrude, Jones et al. (2014) discuss that the biocrude would ideally be transported to a centralised upgrader that accepts oil/biocrude from multiple sites to realise commercial economies of scale. However, initial upgrading may be required to process the algal biocrude to achieve oxygen, nitrogen and sulphur levels that could be tolerated in a conventional plant. In

addition, Frank et al., (2012) discuss that algal HTL biocrude may not be stable enough for transporting without at least partial upgrading.

In a process design and economics study of algal HTL including upgrading (Jones et al., 2014), a hydrotreater and hydrogen plant are co-located with the algal HTL unit on an algae farm site (see Figure 2.4). The hydrogen plant is a conventional natural gas based steam reformer and its capital cost is 11% of the total installed capital cost for the microalgae HTL and upgrading system.

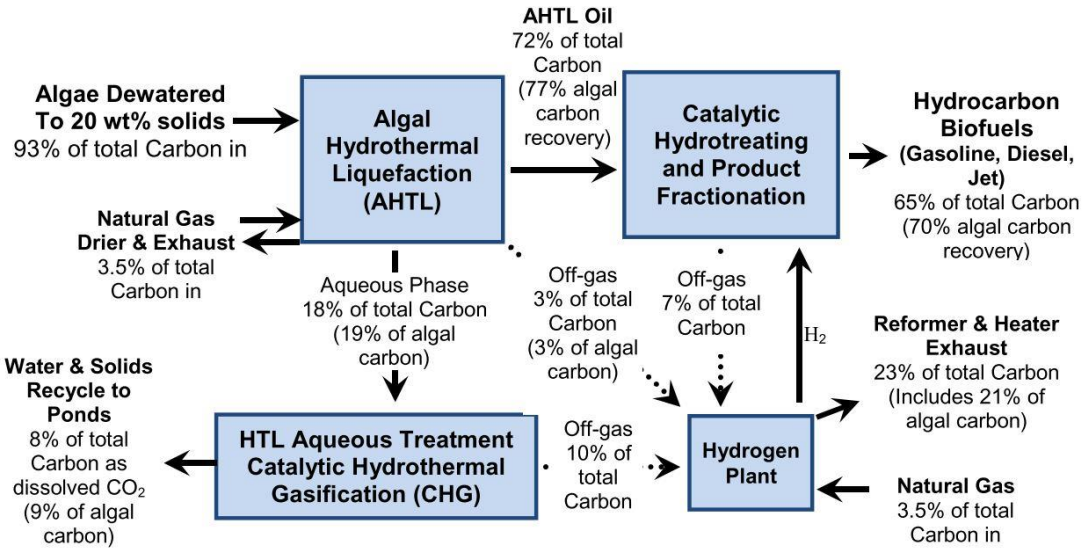


Figure 2.4 Block flow diagram of AHTL conversion process showing carbon balance (Jones et al., 2014)

The flow diagram in Figure 2.4 shows a carbon balance for the proposed algal HTL process. 70% of the algal carbon ends up in the liquid fuel following hydrotreatment and 19% in the process water post liquefaction. Due to the significant flow of organic material into the process water, recovery and/or reuse of the process water is essential for the economical processing of algae by HTL. In addition, the recycling of nutrients in the process water from algal HTL for algae cultivation is essential in

biofuel production due to the high energy, cost, and carbon emissions associated with nutrient production (see section 2.5 for nutrient recovery). The aqueous fraction ranges between 30 - 50% of the product composition, and can be as high as 68% as demonstrated in the HTL of *Spirulina* (Biller et al., 2012). Due to the high nitrogen content, the process water has a carbon to nitrogen ratio that makes it unsuitable for anaerobic digestion (Fricke et al., 2007). Therefore, unless the nitrogen content is reduced by precipitation for example (Uludag-Demirer and Othman, 2009), anaerobic digestion is being replaced by catalytic hydrothermal gasification (CHG) as an alternative for algal HTL (see Figure 2.5) (Elliott et al., 2014a; Frank et al., 2012).

Experimental results by Jones et al. (2014) on CHG of the process water following HTL of *Nannochloropsis* and *Chlorella* produced a biogas of approximately 70% CH_4 and 25% CO_2. The cost of the CHG unit is 32% of the total installed capital cost for the microalgae HTL and upgrading system. CHG of the aqueous was demonstrated by Elliott et al. (2013), where the process water was hydrothermally gasified in the presence of ruthenium catalyst to produce a biogas (~60% CH_4, 30% CO_2, 5% NH_3, and 2% H_2). The chemical oxygen demand of the water was reduced by 98.8 - 99.8%.

Guan et al. (2012b) studied the HTG of microalgae for the aim of supplying H_2 for catalytic upgrading or hydrotreating the algal biocrude in an algal biorefinery. A similar concept can be realised with HTG of the process water post HTL with studies suggesting further research into the conversion of the process water into hydrogen. Jones et al. (2014) and Jazrawi et al. (2013) suggest further research into converting the organics in the process water (using catalysts) to increase hydrogen production or fuel precursor species (e.g. syngas). An opportunity for hydrogen

production can be realised by increasing the temperature and pressure of the HTG process to supercritical water conditions. This study investigates upgrading the process water from HTL through catalytic HTG under supercritical water conditions to maximise hydrogen production for biocrude hydrotreating (see section 2.7 for a description of supercritical water gasification).

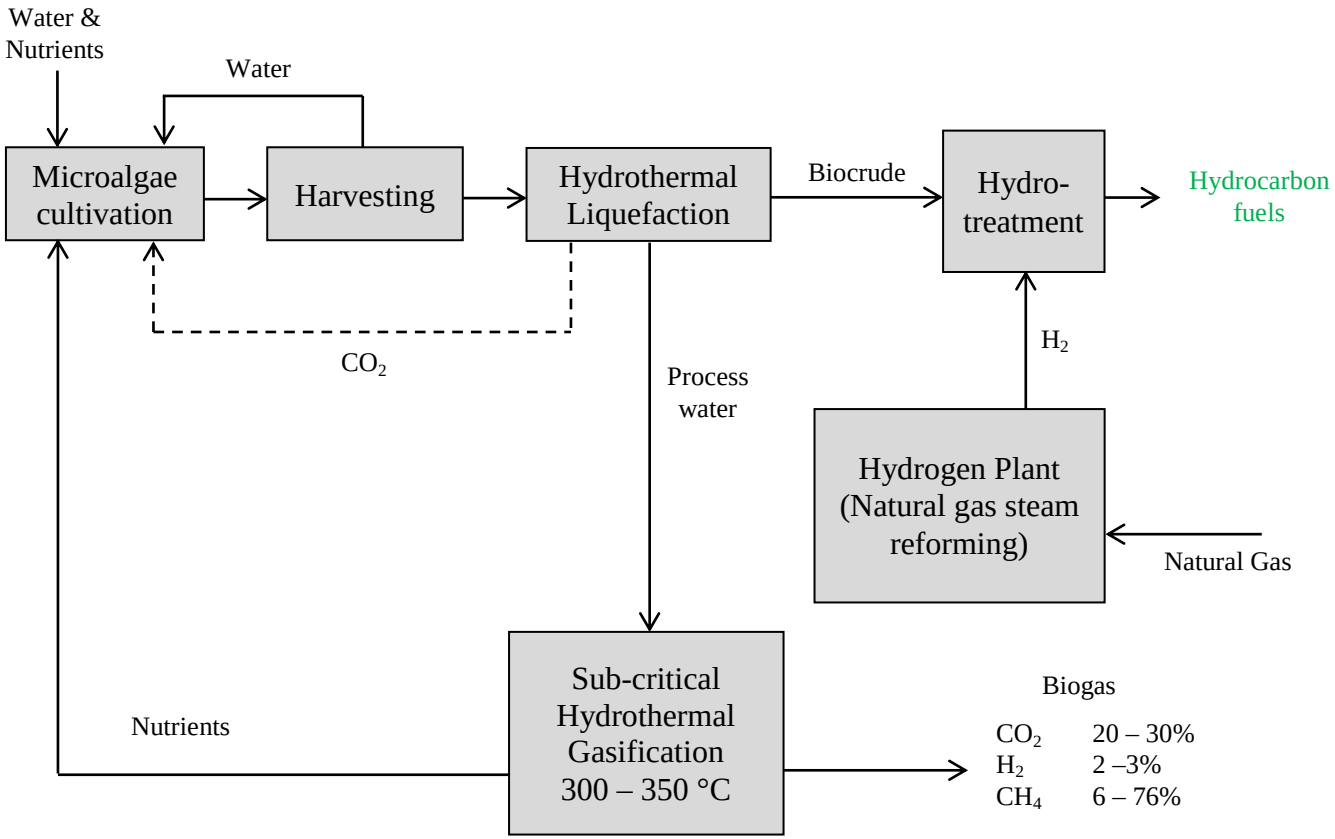


Figure 2.5 Schematic layout of HTL of microalgae with sub –critical HTG of the process water for biogas production

2.4 Hydrothermal gasification of algae

HTG occurs in the higher temperature region of the hydrothermal processing range described in Figure 1.3. The initial steps during HTG are similar to those for HTL but the higher temperature and pressure conditions in the gasification stage (> 350°C) lead to the smaller fragments (intermediates) decomposing further to low molecular weight gaseous products. The gas consists of varying amounts of H_2, CO, CO_2, CH_4 and light hydrocarbon gases (C_2 - C_4). HTG produces process water that is low in organics due to near complete gasification of the carbon in the feedstock to carbon in the gas product (Schmieder et al., 2000). The high solubility of the intermediates in water at HTG conditions significantly inhibits tar and coke formation (Williams and Onwudili, 2006). In addition, another advantage of HTG is the production of a 'cleaner' fuel compared to HTC and HTL where inorganic metals and heteroatoms are present in the desired product, biochar and biocrude respectively. This is particularly beneficial in processing high protein microalgae for example where large amount of nitrogen is found in the biocrude if processed by HTL. The HTG gas product requires less cleaning efforts and causes less corrosion during downstream processing.

Research on algal HTG has focused on microalgae with limited research on macroalgae. The following sections describe the studies on algal HTG.

2.4.1 Microalgal HTG

A summary of studies on catalytic and non-catalytic microalgal HTG is presented in Table 2.13. Minowa and Sawayama (1999) first investigated the catalytic HTG of *Chlorella vulgaris* with the aim to produce methane and recycle the process water for algal cultivation. Using nickel, they produced 37.5 vol % CH_4 and 10 vol % H_2

with a carbon conversion to gas of 70%. They found that the nitrogen in the microalga was converted to ammonia during gasification and the recovered process water in which ammonia was dissolved could be used as a nitrogen nutrient for algal growth. Tests on algal cultivation using the process water supported the concept however algal growth was only one eighth that compared to growth in standard culture medium due to a lack of phosphorus.

Chakinala et al. (2010) also investigated the catalytic and non-catalytic HTG of *Chlorella vulgaris*. They found that HTG had higher gasification efficiency with higher temperatures and lower algal concentrations. The maximum gasification efficiency for non-catalytic HTG was found to be 75% at 600 °C with a holding time above 4 min. The catalysts investigated included Ru/TiO_2, $NiMo/Al_2O_3$, $PtPd/Al_2O_3$, $CoMo/Al_2O_3$, and nickel wire. The gasification efficiency during catalytic HTG increased from 14 to 82% when the temperature increased from 400 to 700 °C with the highest gasification efficiencies observed using nickel. The highest H_2 yields were observed under catalytic HTG using ruthenium. It was also observed that complete gasification could be achieved using ruthenium at 700 °C and a hold time of 2 min or 600 °C with excess catalyst.

Species	Catalyst	Temperature (°C)	Hold time (min)	Algal conc. (%)	Carbon conversion (%)	References
Nannochloropsis sp.	None	450 - 550	0 - 80	1-15	30 - 60	(Guan et al., 2012a)
Spirulina platensis	Ru/C, Ru/ZrO_2	400	30 - 360	2.5 - 20	20 - 100	(Stucki et al., 2009a)
Chlorella vulgaris	Ru/TiO_2, $NiMo/Al_2O_3$, $PtPd/Al_2O_3$, $CoMo/Al_2O3$, Ni wire	400 - 700	1-15	7	15 - 100	(Chakinala et al., 2010)
Chlorella vulgaris	$Ni/SiO_2/Al_2O_3$	350	0	12	35 - 70	(Minowa and Sawayama, 1999)
Phaeodactylum tricornutum	Ru/C	400	12 - 67	2.5 - 13	68 - 74	(Haiduc et al., 2009)
Chlorella vulgaris *Spirulina platensis*	Ni/Al_2O_3, NaOH	500	30	6.67	57 - 79	(Onwudili et al., 2013)

Table 2.13 Summary of catalytic and non-catalytic microalgal HTG.

Stucki et al. (2009) proposed a theoretical continuous system for the HTG of microalgae. Due to high content of heteroatoms in the microalgae – which can poison catalysts – the authors suggest preheating the algal slurry prior to gasification to precipitate the salts. The heteroatoms will be split off during preheating forming inorganic ions (ammonium from N, sulphide from S, and phosphate from P) which are separated as salts before the remaining slurry enters the catalytic HTG reactor. The concept is to capture all the nutrients before the organic fraction enters the reactor and then use the nutrients for algal cultivation. A series of batch experiments were conducted with *Spirulina platensis* to test the effect of heteroatoms on catalyst poisoning and the gasification efficiency. The catalysts used were ruthenium on activated coconut carbon (Ru/C) and ruthenium on zirconia (Ru/ZrO_2). The catalyst to algae ratio was varied from 0.1 to 8.1, with excess catalyst used in some experiments on the basis that a fraction of the catalyst is sacrificed as adsorbent for the heteroatoms (especially sulphur). Results indicated that complete gasification was achieved with the highest catalyst loadings. Yields of methane came close to the chemical equilibrium calculated yields at 43.5 vol % but this was only achieved with high catalyst loadings due to catalyst poisoning at lower catalyst to algal ratios. The authors suggest there are still challenges to overcome concerning catalyst poisoning and propose their pre-separation continuous model as a potential solution.

2.4.2 Macroalgal HTG

Hydrothermal gasification of macroalgae is of particular interest due the process being tolerant to the high ash content of macroalgae. On top of the advantages HTG provides (cleaner fuel, low tar/coke formation), the HTG of macroalgae has an additional benefit in that the alkali salts have a catalytic effect resulting in higher hydrogen yields and better gasification efficiencies (Sınağ et al., 2003). In addition,

supercritical water, at temperatures and pressures that exceed its critical point (>374 °C and >22.1 MPa), acts as a non-polar solvent with high diffusivity and transport properties. The dielectric constant decreases and hydrogen bonding becomes weaker. Therefore, it behaves like an organic solvent becoming miscible with small organic compounds and gases in a single fluid phase with no interphase mass transport processes that slow reaction rates (Savage, 1999). As such, reactions proceed quickly and completely due to no limitation in interface mass transfer. In addition, supercritical water reduces coke formation and extends catalyst life through solubilising and diluting the reaction intermediates which act as precursors for coke formation (Byrd et al., 2007; Kruse, 2008; Williams and Onwudili, 2006). High gasification efficiencies and hydrogen yields make supercritical water a beneficial medium in hydrothermal processing of algae compared to other processes. A description of supercritical water gasification is provided in section 2.7.

The work on macroalgal HTG is limited and a summary is provided in Table 2.8. Compared to terrestrial biomass, Schumacher et al., (2011) report higher gasification efficiencies and H_2 yields from the gasification of four macroalgae species; however they do not report percentage carbon conversion from feed to gas or gasification efficiencies. In addition, their work does not explore any catalyst use. The composition of gases from the HTG of various macroalgal species is presented in Figure 2.6. At a temperature of 500 °C, hold time of 60 min, and algal concentration of 5%, Schumacher et al. produced 12 and 13 g of H_2 $kg^{-1}_{macroalgae}$ from *L. digitata* and *A. esculenta* respectively.

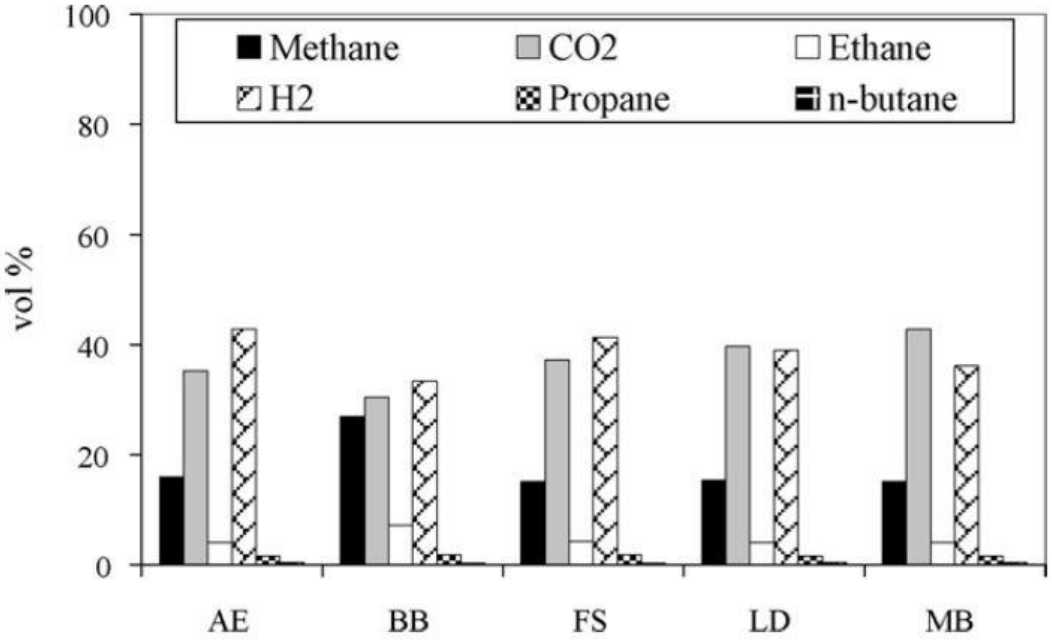


Figure 2.6 Composition of gases from the HTG of macroalgal species at 500 °C, 6% algal concentration and 60 min hold time. (Schumacher et al., 2011)

(AE: *Alaria esculenta*, BB: *Bifurcaria bifurcata*, FS, *Fucus serratus*, LD: *Laminaria digitata*, MB: mixed species from Black sea).

Species	**Catalyst**	**Temp (°C)**	**Hold time (min)**	**Algal conc. (%)**	**Carbon conversion (%)**	**References**
Fucus serratus, Laminaria digitata, Alaria esculenta, Bifurcaria bifurcata	None	500	60	5	NA	(Schumacher et al., 2011)
Saccharina latissima	Ni/Al_2O_3, NaOH	500	30	6.67	72-93	(Onwudili et al., 2013)

Table 2.14 Summary of catalytic and non-catalytic macroalgal HTG.

Onwudili et al. (2013) reported the compositional analyses of products from the catalysed and non-catalysed supercritical water gasification (SCWG) of two microalgae, *Chlorella vulgaris* and *Spirulina platensis*, and a macroalga, *Saccharina latissima*. Results from the catalytic HTG of *S. latissima* produced 30 g H_2 $kg^{-1}_{macroalgae}$ in the presence of sodium hydroxide. In addition, previous work yielded 20.4 g H_2 $kg^{-1}_{macroalgae}$ and 102 g CH_4 $kg^{-1}_{macroalgae}$ 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 *Nannochloropsis*. By comparison, the authors found that the carbohydrate-rich macroalgae produced more hydrogen gas than the two microalgae species, thereby highlighting the potential of hydrothermal gasification of macroalgae for hydrogen and methane production. In addition, they highlighted the possibility of recycling the liquid residuals for microalgae cultivation.

Further research is required on macroalgal HTG to understand the effects of temperature, algal concentration, holding time and different catalysts on HTG products and gasification efficiency. In addition, the seasonal variation in biochemical composition and its effect on HTG products should be studied and the recycling of nutrients from the process water post HTG for algal cultivation needs to be demonstrated.

2.5 Nutrient recycling

The process water from hydrothermal processing of algae has been found to be rich in nitrogen, phosphorus, carbon and potassium - nutrients which are essential for algal growth (Grobbelaar, 2004). The potential of recycling nutrients, especially nitrogen, phosphorus and potassium, post hydrothermal processing to cultivate algae is significant due to the cost associated with supplying these nutrients for large scale algal growth. The fossil fuel energy input for the production of these nutrients is significantly large and would reduce the life cycle energy balance of algal biofuels. Phosphorus, in particular, requires large amounts of energy for its extraction from phosphorus rock. In addition, current estimates predict peak phosphorus reserves may be depleted in 50 - 100 years (Cordell et al., 2009).

The cultivation of algae using wastewater effluents from various industrial and agricultural farms is extensively reported in the literature and the production of algal biomass coupled with wastewater treatment is well established (An et al., 2003; Aziz and Ng, 1992; Chinnasamy et al., 2010; Tarlan et al., 2002; Wang et al., 2010; Woertz et al., 2009). Limited information is available on the use of process waters (process water) from hydrothermal processing of biomass for algal cultivation. Minowa and Sawayama (1999) were the first to recognise and demonstrate the potential to cultivate *Chlorella vulgaris* using the nutrient rich process water obtained from HTG of the same microalga. They found that nitrogen in the microalga was converted to ammonia, which was distributed in the process water. Whilst the cultivation of Chlorella was not as high compared to growth in standard growth media, the authors demonstrated the potential to blend the process water from HTG with standard media to enhance algal growth.

Phenols are toxic compounds to microalgae and alter the structure and function of membranes due to hydrophobic interactions causing partitioning of lipophilic compounds into the membrane (Leonard and Lindley, 1999). Studies by Nakai et al. (2001) and Scragg (2006) have demonstrated the inhibitory effects of phenols on algal growth (Jena et al., 2011b). In testing the effect of phenol on the growth of *Chlorella vulgaris*, Scragg reports that the microalga was inhibited by phenol concentrations of 100 - 400 ppm.

High concentrations of acetate in the process water may be beneficial due to mixotrophic growth, thus increasing biomass productivity (Bhatnagar et al., 2011). However, nickel concentrations as low as 0.85 ppb have an inhibitory effect on the growth of algae (Spencer and Nichols, 1983) due to accumulation on the cell surface by adsorption and acting as a barrier for nutrient uptake (Bordons and Jofre, 1987). In testing the effect of nickel on algae growth, Haiduc et al. (2009) report adverse effects at nickel concentrations of 1, 5, and 10 ppm with complete inhibition of cell division at 25 ppm.

In a detailed study of nutrient recycling from algal hydrothermal processing, Biller et al. (2012) investigated the growth of *Scenedesmus dimorphus*, *Chlorella vulgaris*, *Spirulina platensis* and *Chlorogleopsis fritschii* from their respective process waters from HTL. Process water dilutions of 50, 100, 200, 400 and 600x were used to avoid growth inhibition and to achieve similar concentrations of nitrogen to that found in standard growth media. The four microalgal species reproduced in the process water from HTL but different dilutions resulted in strain specific growth curves. It was found that 200 - 400x dilutions resulted in optimum growth. The process water was analysed post HTL and post cultivation and it was found that effective nitrogen, phosphorus and potassium recycling was possible without any additional nutrient

supplementation. In addition, all four species used acetate present in the process water as a substrate for mixotrophic growth which in the case of *Chlorella vulgaris* and *Chlorogleopsis fritschii* resulted in higher biomass yields compared to cultivation in standard growth media.

The potential to recycle nutrients following hydrothermal processing of macroalgae has been suggested but never demonstrated. In a study on the HTG of a macroalga, *Saccharina latissima*, and two microalgae, *Chlorella vulgaris* and *Spirulina platensis*, Onwudili et al. (2013) found high concentrations of potassium, phosphate and ammonium in the process water. In addition, the concentration of potassium in the process water was eight times higher following HTG of the macroalga compared to the two microalgal species due to the high ash content of the macroalgae. Macroalgal HTG produced the lowest concentration of phenols compared to microalgal HTG in the study.

2.6 Energy recovery

Energy recovery, Eq (1), is an expression of how much chemical energy of the feedstock is recovered in the desired product from hydrothermal processing.

$$\textbf{\textit{Energy recovery}}\ (\%) = \frac{\textbf{\textit{HHV product}}\ (MJkg^{-1}) * \textbf{\textit{mass of product}}\ (kg)}{\textbf{\textit{HHV algae}}\ (MJkg^{-1}) * \textbf{\textit{mass of algae}}\ (kg)} \quad \textbf{(1)}$$

The energy recoveries from algal HTC, HTL and HTG research papers are presented in Table 2.15.

Hydrothermal process	Temperature (°C)	Energy recovery (%)	ΔT (T_2-T_1) 1 kg H_2O (MJ)	References
Carbonisation	203	76	0.8	(Heilmann et al., 2010)
Liquefaction	350	88	1.6	(Brown et al., 2010)
	350	59	1.6	(Anastasakis and Ross, 2011)
	350	75 - 112	1.6	(Duan and Savage, 2011)
	300	71	1.3	(Garcia Alba et al., 2012)
Gasification	400	70	2.1	(Stucki et al., 2009a)
	550	58	3.2	(Guan et al., 2012a)

Table 2.15 Energy recovery and heating energy for hydrothermal processing of algae - adapted from Biller and Ross, (2012).

In processing microalgae by HTG, Guan et al. achieved a 58% energy recovery at 550 °C whilst Stucki et al achieved 70% energy recovery at 400 °C with the use of ruthenium catalysts. The use of catalysts increased the carbon conversion and gasification efficiency thus increasing the yield of syngas (see section 2.7.5 for more details on catalytic HTG). Catalytic HTL led to energy recoveries over 100% (Duan and Savage, 2011). This is explained by the biocrude containing lower oxygen than the feedstock and the transfer of hydrogen from the water to the biocrude during HTL.

Whilst the energy recovery percentage is important to consider, another factor is the energy required to heat the reactants to the process temperature. This energy requirement varies significantly based on the process (HTC, HTL or HTG). To assess the varying energy input requirements, Biller and Ross (2012) calculated the energy required to heat 1 kg of pure water to the respective reaction temperature of the studies presented in Table 2.15. The energy required for HTG is double that for HTL and triple that for HTC. For HTL, an increase in 50 °C results in 20% more energy input.

Specifically for HTG, improvements in efficiencies or yields by raising reaction temperatures (e.g. from 400 to 550 °C) 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 process at both temperatures against the net gain in energy recovered. To do this, the energy required to heat the algae up to the reaction temperature (E_I or Energy Input) can be calculated using Eq (2) (adapted from Xu et al., (2011)):

$$\boldsymbol{E_I = W_{H2O} * \left(\Delta H_{H2O}^{T1} - \Delta H_{H2O}^{T0}\right) + W_{cell} * C_{ps}(T_2 - T_1)} \qquad \textbf{(2)}$$

where w_{H_2O} is the mass of water fed (kg), T_1 is the reaction temperature (K), T_0 is the ambient temperature (K), $\Delta H^T_{H_2O}$ is the enthalpy of water at a certain temperature, W_{cell} is the mass of the algae (kg), C_{ps} is the average specific heat of the algae, T_2 is the temperature when the reaction will start.

The energy of the product gas (E_O or Energy Output), can be simply estimated from the sum of the mass of each gaseous component (M_n) multiplied by its calorific value (CV_n):

$$\boldsymbol{E_O = \sum(M_1 * CV_1, M_2 * CV_2, \ldots\ldots M_n * CV_n)} \qquad \textbf{(3)}$$

The percentage increase in E_I can be compared with the percentage increase in E_O to determine whether an increase in temperature results in a net energy gain. However, other considerations, particularly regarding the mechanical requirements of the reactor to operate at high temperatures, are of immense importance in a complete process. The algal concentration in the slurry is an important process consideration. If more algae is heated per unit mass of water and more product is formed then the energy efficiency becomes more favourable due to less energy required to heat a higher solid concentration.

2.7 Supercritical water gasification (SCWG)

When water's temperature and pressure exceed its critical point (T > 374°C, P > 22.1 MPa), it changes to a state known as supercritical water (SCW) and acts as a non-polar solvent with high diffusivity and transport properties (Figure 1.3). Hydrothermal gasification in supercritical water is known as supercritical water gasification (SCWG). At such conditions, water can be compressed from gas-like to liquid-like densities. The new dense fluid has properties that differ remarkably from its subcritical state. Kruse (2008) describes how in no other solvent can the properties near or above the critical point be changed more significantly as a function of pressure and temperature than in water. Physiochemical characteristics such as density, dielectric constant and ion product change significantly when water reaches and exceeds its critical point.

This section will provide a description of the physiochemical characteristics of SCW and describe the SCWG of biomass including use of catalysts, effect of operating parameters, scale up of the technology and challenges associated.

2.7.1 Physiochemical characteristics

2.7.1.1. Density

Loppinet-Serani et al. (2010) describe how the density of the liquid phase decreases and the density of the vapour phase increases when a biphasic water system is heated from 25 °C. On reaching the critical point, the two densities are equal and a homogeneous medium is achieved. Above the critical point, the density of supercritical water can be changed from high (liquid-like) to low (gas-like) without any phase transition by varying the pressure and temperature as illustrated in Figure 2.7.

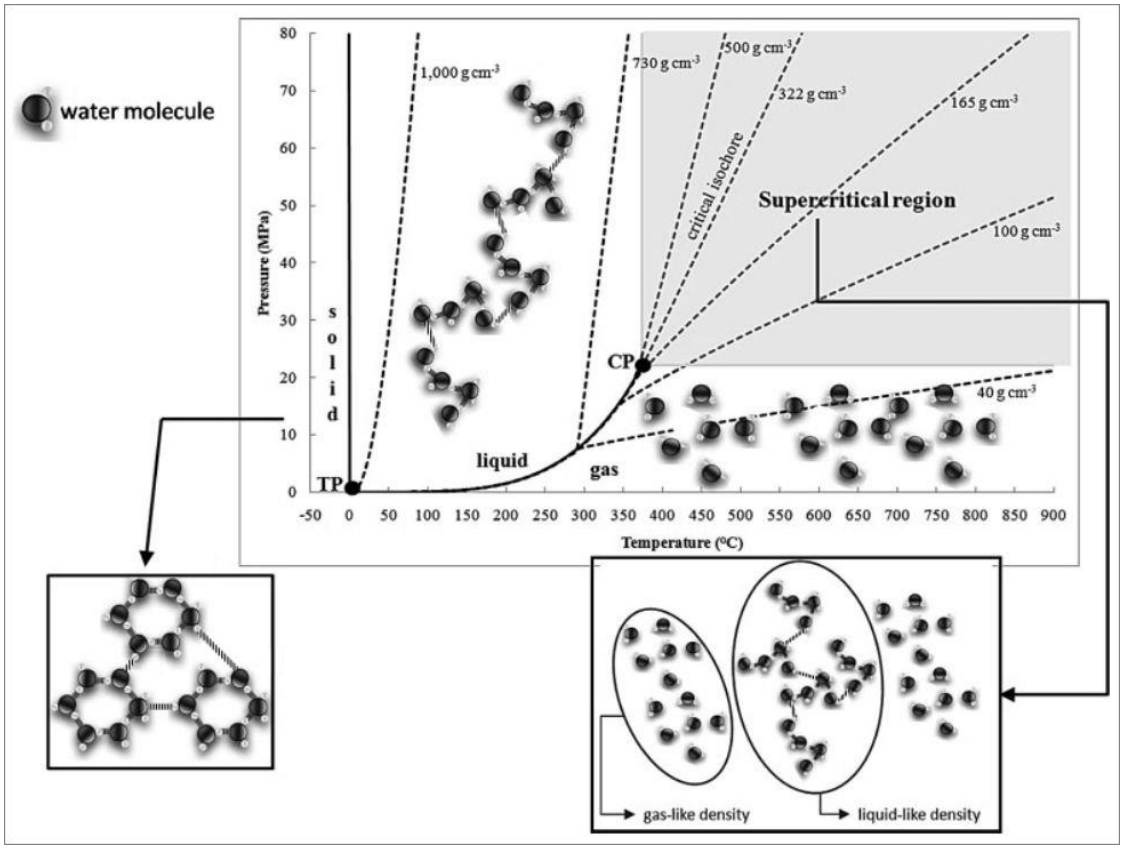


Figure 2.7 Pressure-temperature phase diagram of pure water (TP is the triple point and CP is the critical point) - adapted from Loppinet-Serani et al. (2010).

Figure 2.7 illustrates that a change in pressure by 20 MPa can alter the fluid density by one order of magnitude; an increase in temperature of 200 °C reduces the fluid density by four times (Loppinet-Serani et al., 2010).

2.7.1.2. Dielectric constant (ε)

Cochran et al. (1992) report that the number of hydrogen bonds per water molecule at the critical point is about one third the number observed in pure ambient water. The decrease in hydrogen bonds results in a decrease in the dielectric constant ε of liquid water from 80 at room temperature and pressure to 6 at the critical point (Figure 2.8). The dielectric constant reflects the polarity and solvent ability of water. As such, a lower dielectric constant allows the dissolving of non-polar compounds

in water. Supercritical water behaves like an organic solvent in that organic compounds become highly soluble and completely miscible. In addition, gases are also miscible and therefore supercritical water provides a highly beneficial medium and environment for reactions as the chemistry is conducted in a single fluid phase rather that a multiphase system under conventional conditions (Savage, 1999). A single phase reaction medium allows a higher concentration of reactants to be attained along with no interphase mass transport processes to hinder reaction rates.

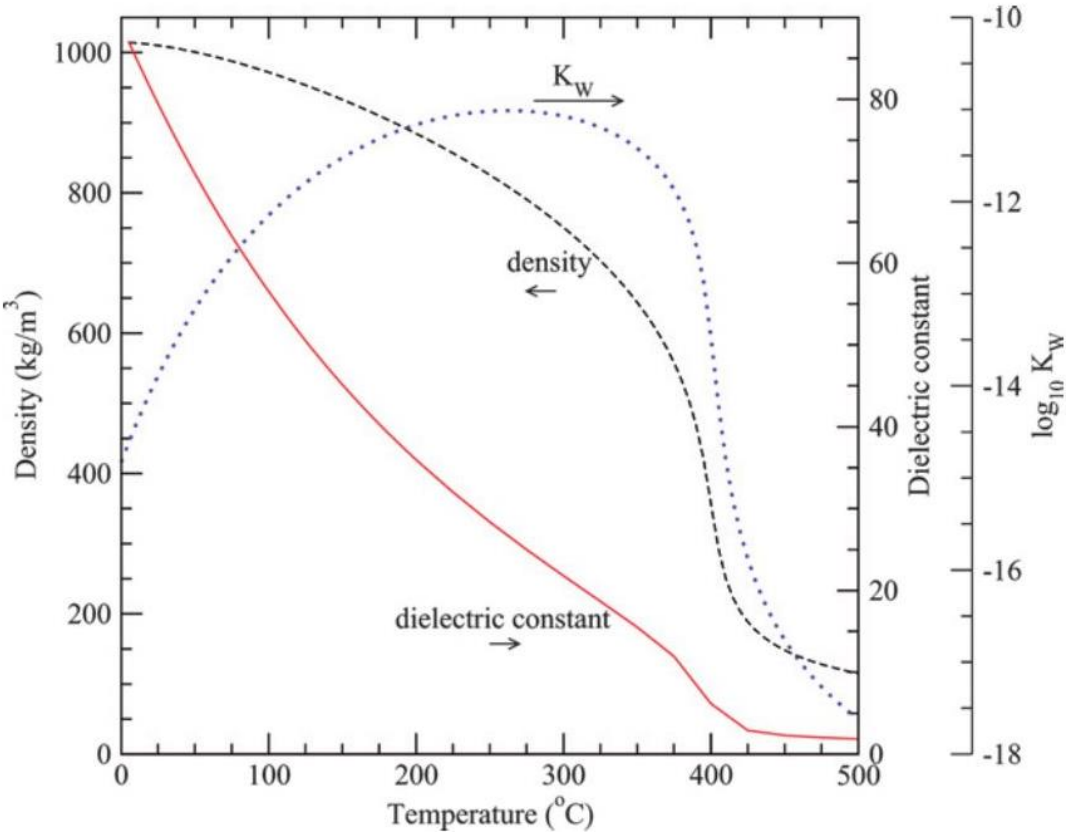


Figure 2.8 Density, dielectric constant and ionic product, K_w, of water at 30 MPa as a function of temperature (adapted from Peterson et al., (2008)).

2.7.1.3. Ion product Kw

The dissociation equilibrium of water (Eq 4) is characterized by the ion product K_w.

$$H_2O \leftrightarrow H^+ + OH^- \quad (4)$$

As water approaches the critical point, the ion product is approximately three orders of magnitude higher compared to ambient liquid water. It has a higher H^+ and OH^- ion concentration and therefore is an effective medium for acid- and base-catalysed reactions. Savage (1999) highlights that the dissociation of water near the critical point generates enough H^+ ions that some acid-catalysed organic reactions proceed without any external acid source. Upon exceeding the critical point, K_w radically decreases by nine orders of magnitude at 600 °C and 25 MPa. At such conditions of high temperature and low density, supercritical water becomes a poor medium for ionic chemistry.

2.7.2 Role of water in reaction

2.7.2.1. Water as a participant in reactions

SCW water participates and contributes in hydrolysis reactions by producing acids or alkalis in the presence of salts which have an influence on bond scission of organic compounds (Guo et al., 2010). The intermediates formed from biomass degradation have double bonds that are able to repolymerise but due to the single phase aqueous medium, the probability of combining via condensation reactions to form coke and tar is significantly reduced. Rather, the frequency of intermediates colliding with water is much higher and as such, tar and coke formation is reduced (Kruse, 2008).

2.7.2.2. Resource of hydrogen

At high temperatures, the intramolecular and intermolecular hydrogen bonds weaken making water a hydrogen resource. Kuhlmann et al. (1994) and Park and Tomiyasu (2003) conducted hydrothermal reactions of hydrocarbons and organic compounds using heavy water (deuterium oxide – D_2O) which contains the hydrogen isotope deuterium instead of the common protium isotope found in water (H_2O). They both found that deuterium atoms in the product with Park and Tomiyasu (2003) indicating that all the H in the product gas came from water. Further studies by Kruse et al. (2000) in SCWG of pyrocatechol found that the hydrogen yields increases in proportion to the contribution of water in the reaction process (i.e. lower feed concentrations). Furthermore, water promotes hydrogen production through the water-gas shift reaction. The water-gas shift reaction of carbon monoxide and water is the key reaction in the conversion of biomass to hydrogen (see section 2.7.4).

2.7.3 Advantages of supercritical water gasification

The thermophysical properties of supercritical water vary continuously above the critical point over much larger ranges compared to the variation in ambient liquid water. This allows for the possibility of altering temperature and pressure to tune the properties of the reaction medium to optimal values for a given chemical transformation (Savage, 1999). The significant change in the physical properties of water by changing the temperature and pressure can facilitate the efficient separation of product steams and thus reduce the energy consumption for product purification (Peterson et al., 2008). On top of being able to optimise reactions, supercritical

water offers many advantages over conventional gaseous and liquid reaction methods:

- High reaction rates lead to gaseous products with high concentrations (Kruse et al., 2005).
- Reactions proceed quickly and completely due to no limit of interphase mass transfer resistance (Kritzer and Dinjus, 2001).
- Post reaction separation of water and products can be achieved by altering temperature and pressure. This avoids separation through distillation or extraction (Savage, 2009, 2000).
- High pressure of the gaseous product makes it easy for transportation, usage, carbon capture and further purification (Guo et al., 2010) and hydrogen is produced at high pressure making it ready for downstream commercial use (Basu, 2010).
- Higher dispersivity and better heat transfer is achieved in reactions with supercritical water as the medium (Loppinet-Serani et al., 2008).
- Supercritical water reduces coke formation and extends catalyst life through solubilising and diluting the intermediates formed during hydrothermal processing which act as a precursor for coke formation (Byrd et al., 2007; Kruse, 2008; Williams and Onwudili, 2006).
- Heteroatoms like sulphur and nitrogen are not present in the gaseous product but rather leave the reactor in the process water thus avoiding expensive gas cleaning. Inorganic impurities being insoluble are also easily removed (Basu, 2010).

2.7.4 SCWG of biomass and the influence of main operating parameters

Several studies have been published on the non-catalytic SCWG of biomass and model compounds:

- Glucose (Kabyemela et al., 1999; Lee et al., 2002; Williams and Onwudili, 2005, 2006);
- Methanol (Boukis et al., 2006; Gadhe and Gupta, 2007);
- Cellulose (Kabyemela et al., 1998; Matsumura et al., 1999; Yoshida and Matsumura, 2001);
- Lignin (Antal et al., 2000; D'Jesús et al., 2006; Kabyemela et al., 1998);
- Biomass compounds (Antal, et al., 2000; Guan et al., 2012a; Kruse, 2009; Stucki et al., 2009a; Williams and Onwudili, 2006; Yan et al., 2006);
- Organic waste/water (Gasafi et al., 2008, 2007; Sricharoenchaikul, 2009)

Guo et al. (2007) provide an overall simplified net reaction of the SCWG of biomass (Eq 5) where x and y represent the molar ratios of H/C and O/C in biomass respectively.

$$\boldsymbol{CH_x + (2-y)H_2O \rightarrow CO_2 + (2-y+\frac{x}{2})H_2} \quad \textbf{(5)}$$

The main intermediate and interacting/competing reactions during SCWG of biomass are the steam reforming reaction (Eq 6), water gas shift reaction (Eq 7) and methanation reaction (Eq 8).

$$\boldsymbol{CH_xO_y + (1-y)H_2O \rightarrow CO + \left(1-y+\frac{x}{2}\right)H_2} \quad \textbf{(6)}$$

$$\boldsymbol{CO + H_2O \leftrightarrow H_2 + CO_2} \quad \textbf{(7)}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad (8)$$

In terms of hydrogen production from the SCWG of biomass, the water gas shift reaction is favoured and the methanation reaction must be restrained. In a study of SCWG of glucose, Lee et al. (2002) observed that the yield of CO is high in the early stages of SCWG and as the temperature increased beyond 650 °C, the concentration of CO decreased and the concentration of H_2 increased due to beginning of the water gas shift reaction.

2.7.4.1. Influence of temperature

Figure 2.9 shows the equilibrium gas yields of SCWG of sawdust as a function of reaction temperature at 25 MPa. This was predicted by thermodynamic calculation code on the chemical equilibrium of sawdust SCWG (Guo et al., 2010; Lu et al., 2007; Yan et al., 2006). Figure 2.9 illustrates that temperature has a significant effect on biomass gasification in SCW. This was demonstrated experimentally by Xu et al. (1996) in completely gasifying 1 M glucose at 600 °C but producing a thin layer of dark brown oil-like at 580 °C. At the chemical equilibrium state, the yields of H_2 and CO_2 increase with increasing temperature but the yield of CH_4 decreases. Sealock et al. (1993) report that high temperatures drive the methane steam reforming reaction (Eq 6) to increase the hydrogen yield.

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \quad (9)$$

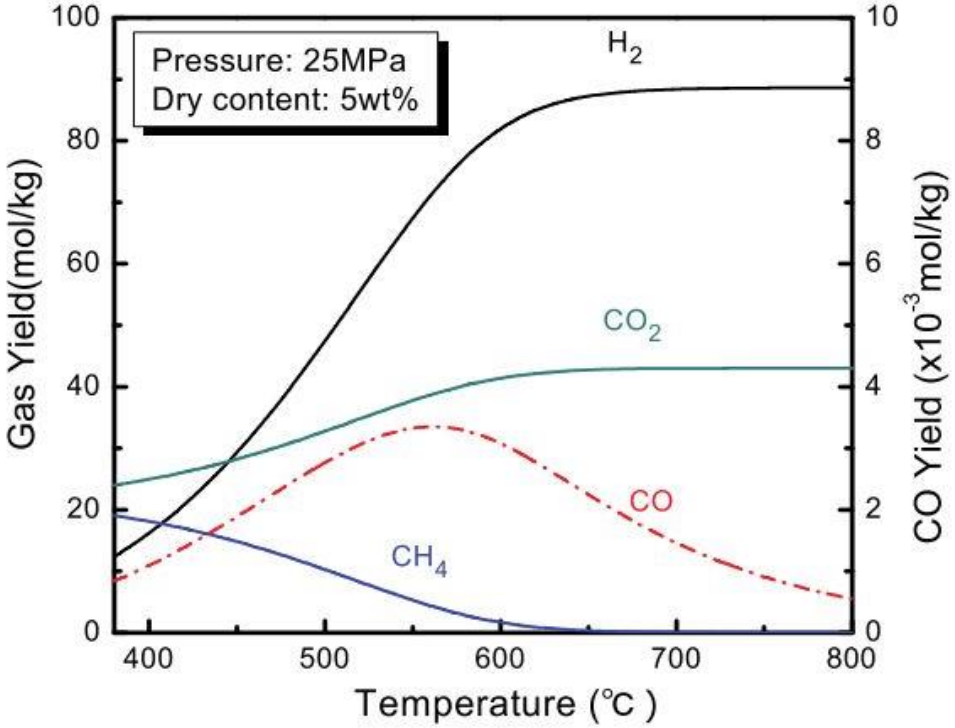


Figure 2.9 Equilibrium gas yields of SCWG of 5 wt.% sawdust with change of temperature - adapted from Guo et al., (2010).

During the SCWG of 0.6 M glucose at 28 MPa and 30 second hold time, Lee et al. (2002) demonstrated that temperature has an important effect on the gasification efficiency . Gasification efficiency (GE) is defined as the percentage conversion of carbon or hydrogen in the feedstock (original biomass) to gaseous products. Carbon gasification efficiency (CGE) continues to increase as the temperature increases, reaching 100% above 700 °C. Hydrogen gasification efficiency (HGE) increases with temperature and increases beyond 100% at 740 °C which clearly demonstrates the role of water as a reactant in SCWG and a source of hydrogen.

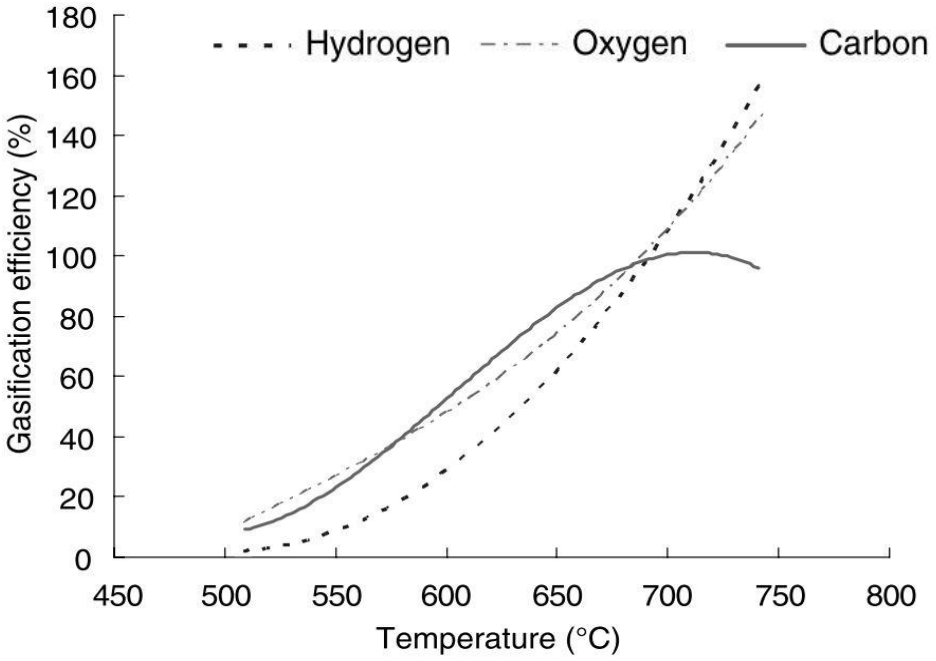


Figure 2.10 Effect of temperature on gasification efficiency - adapted from Lee et al., (2002).

High temperature ranges (550 - 700 °C) for biomass SCWG do not need catalysts for complete gasification of the biomass. A hydrogen rich gas is mainly produced from operation at such high temperatures (see Figure 2.9). However, to improve the economic efficiency of SCWG and maintain complete or high gasification efficiencies, catalysts are employed to lower operating temperatures. Operating temperatures can be lowered to ~500 °C for moderate SCWG producing a methane rich gas with some hydrogen and to around or below 374 °C (critical point of water) for low or sub-critical water gasification producing methane and C_2 - C_4 gases. As such, SCWG can be classified into three broad categories: high, moderate and low (Azadi and Farnood, 2011; Basu, 2010; Peterson et al., 2008). The selectivity towards hydrogen and/or methane production can be achieved through catalyst selection (Onwudili and Williams, 2013). A detailed description on catalytic SCWG in provided in section 2.7.5.

2.7.4.2. Influence of pressure

The influence of pressure on biomass SCWG is complex however several studies note than no significant effect is realised with increasing pressure during biomass SCWG. Studies by Kruse et al. (2003) and Lu et al. (2006) showed no major effect of pressure on carbon conversion or product distribution. The density, dielectric constant and ion product of SCW increase as the pressure increases. Consequently, the hydrolysis rate and ion reaction rate increase and free radical reactions are restrained. In addition, high pressure favours the water gas shift reaction, thereby increasing the hydrogen yield. However, the studies on pressure and equilibrium gas yields from biomass SCWG show no significant effect of an increase in pressure (Figure 2.11).

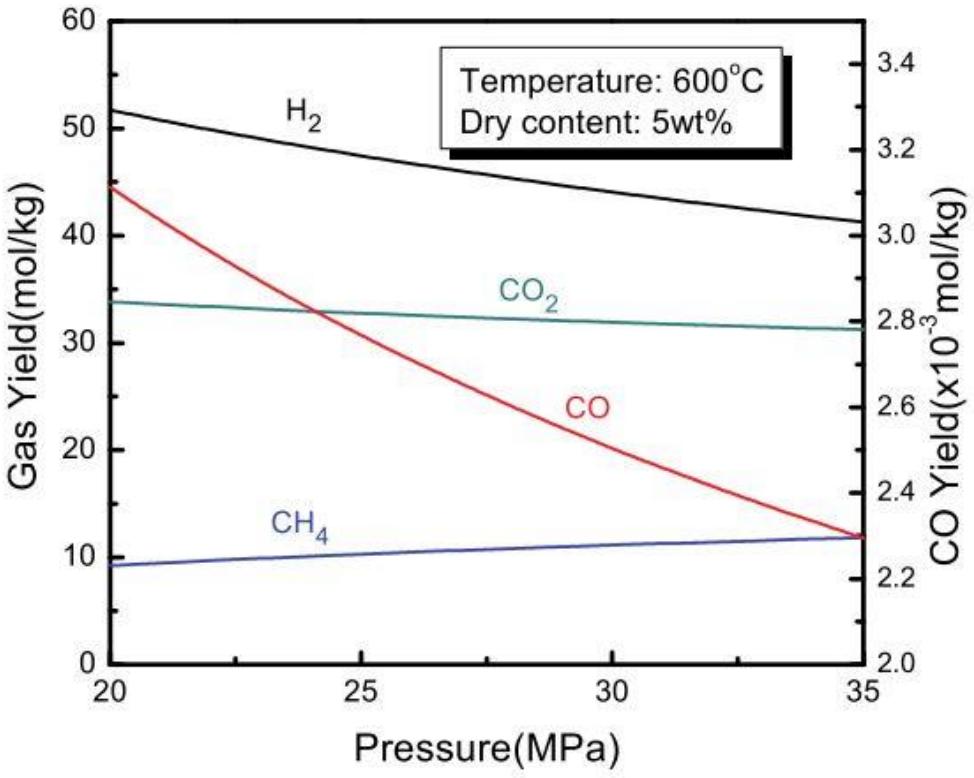


Figure 2.11 Equilibrium gas yields of SCWG of 5 wt.% sawdust with change of pressure - adapted from Guo et al., (2010).

Studies have also indicated that the hydrogen yield and gasification efficiency are not affected by changes in pressure around the critical point of water but an increase in pressure at higher pressures (~30 MPa) causes a slight increase in hydrogen yield and gasification efficiency (Demirbas, 2004).

2.7.4.3. Influence of biomass concentration

The effect of biomass concentration on equilibrium gas yield is presented in Figure 2.12. The gas product mainly consists of H_2 and CO_2 at low biomass concentrations. As the biomass concentration increases, an increase in the concentration of CH_4 is observed as both H_2 and CO_2 yields decrease. Based on thermodynamic calculations, Prins et al. (2005) reported the gasification efficiency of biomass SCWG rapidly declines as the biomass concentration exceeds 50% (Basu, 2010). Experimental data, however, indicates that the gasification efficiency drops when the biomass concentration increases beyond 2% (Schmieder et al., 2000). Based on studies using glucose and wood, the biomass concentration can be categorised into (i) low (< 2%) with a GE of 92 - 100%, (ii) medium (2 - 10%) with a GE of 60 - 90% and (iii) high (> 10%) with a GE of 68 - 80% (Basu, 2010; Mozaffarian et al., 2004).

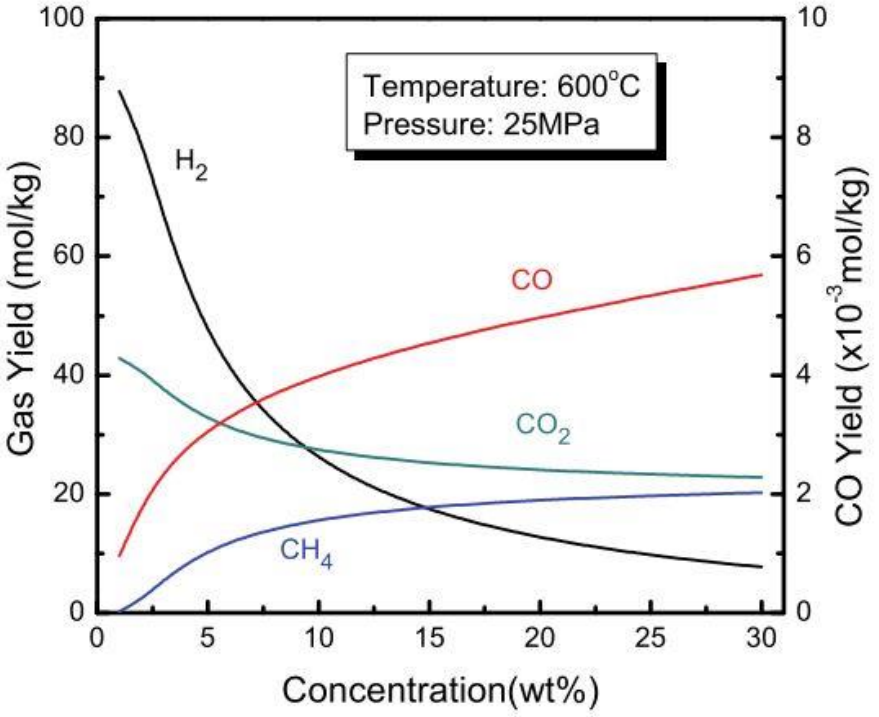


Figure 2.12 Equilibrium gas yields of SCWG of 5 wt.% sawdust with change in biomass concentration - adapted from Guo et al. (2010).

Despite lower biomass yields achieving high GEs, the need to gasify biomass at high concentrations is essential to achieve a thermal efficiency high enough to establish an economic process. As such, high temperatures, high heating rates and catalysts are used to achieve high GEs at high biomass concentrations.

2.7.4.4. Influence of heating rate

Several studies have demonstrated that higher heating rates lead to higher yields of gaseous products and higher gasification efficiencies (Fang et al., 2004; Hashaikeh et al., 2006; Sinag et al., 2004; Xiaodong Xu et al., 1996; Zhong et al., 2002).

One of the main reasons for increased gaseous yields and higher gasification efficiencies is the reduction in the formation of tar and char with higher heating

rates. Xu et al. (1996) found that higher heating rates reduced tar formation and ultimately reduced catalyst deactivation resulting in higher gas yields. During the gasification of cellulose, Fang et al. (2004) observed that a heating rate of 1.3 - 2.3 °C s^{-1} resulted in a homogenous reaction compared to a lower heating rate of 0.18 °C s^{-1} that resulted in a heterogeneous reaction with interference of char and dissolved compounds. Sınağ et al. (2004) demonstrated that a heating rate of 3 °C min^{-1} led to higher gas yields during the SCWG of glucose compared to a heating rate of 1 °C min^{-1}.

2.7.4.5. Influence of holding time

The effect of holding time on the SCWG of 2% rice husk, sawdust and carboxymethyl cellulose was studied at 650 °C and 25 - 30 MPa (Lu et al., 2006; Mettanant et al., 2009). Results indicated that a longer hold time allowed for a better yield of gaseous products with the amount of organic carbon in the process water decreasing as the hold time increased. In the experiments with 2 % rice husk, the yield of hydrogen doubled as the hold time increased from 10 to 60 min. Whilst longer hold times is favourable for biomass SCWG, the optimum hold time, beyond which no further improvement in GE is observed, depends on the other operating parameters such as temperature, biomass concentration and biomass particle size.

2.7.5 Catalytic SCWG of biomass

Catalysts are a potential solution to maintain high gasification efficiencies during SCWG while operating at lower temperatures to realise economic efficiency. Whilst various catalysts have been used for thermochemical conversion of biomass (see Azadi and Farnood, (2011), Yanik et al., (2008)), the selection of catalysts for SCWG needs to be carefully considered due to properties of the supercritical medium and high pressures involved in the process. Generally, four types of catalysts have been used for biomass SCWG: alkali metals, activated carbon, transition metals and metal-oxides.

2.7.5.1. Alkali metals

The catalytic effect of alkali metal catalysts in accelerating the water gas shift reaction during biomass SCWG has been confirmed by various studies (Kruse et al., 2000; Onwudili and Williams, 2009; Watanabe et al., 2003; Yanik et al., 2008). Examples of alkali metal catalysts include Na_2CO_3, $KHCO_3$, K_2CO_3, $Ca(OH)_2$, NaOH and KOH.

The catalytic effect of KOH on the SCWG of industrial organic waste was demonstrated by García Jarana et al. (2008). Results indicated that the water gas shift reaction was accelerated through the addition of KOH with formic acid being the intermediate product in the reaction process (Eq 10). The production of H_2 and CO_2 was due to the decomposition of formic acid.

$$CO + H_2O \leftrightarrow \text{"HCOOH"} \leftrightarrow H_2 + CO_2 \quad (10)$$

Watanabe et al. (2003) studied the effect of NaOH on SCWG of formaldehyde. The authors found that H_2 production increased four times through the addition of NaOH

and the production of coke was effectively inhibited. Similar results on inhibition of coke formation during SCWG of glucose were reported by Onwudili and Williams (2009). The use of NaOH prevented the adherence of glucose particles to the reactor walls due to NaOH scouring the reactor surface as a surfactant. As such, no tar deposition or char formation was observed compared to experiments without NaOH. The addition of NaOH prevented the formation of furfural and 5HMF during SCWG of glucose. Rather, glucose was broken down to ketones, aldehydes, carboxylic acids and their alkylated and hydroxylated derivatives. These compounds indicated the suppression of the dehydration and polymerisation pathways, ultimately producing more hydrogen in the product gas as the temperature of SCWG was achieved. The promotion of hydrogen production using NaOH was presumed to occur through two processes: (i) the decarbonylation of hydroxylated carbonyl compounds to produce CO and simpler carboxylic acids with the CO then reacting to produce H_2 through the water gas shift reaction, and (ii) the reaction of sodium salts of simpler carboxylic acids with water to form H_2 and sodium bicarbonate (Onwudili and Williams 2009). In both processes, the removal of CO_2 as Na_2CO_3 appeared to have enhanced H_2 production by pushing forward the water gas shift reaction. Similar CO_2 capture effects were observed in the addition of $Ca(OH)_2$ during SCWG of cellulose at 500 °C and 20 min hold time (Guo et al., 2007). CO_2 was captured as $CaCO_3$ by Eq (11) as follows:

$$\boldsymbol{CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O} \qquad \textbf{(11)}$$

Increased H_2 production during SCWG of cellulose has also been observed using K_2CO_3 as a catalyst (Sinag et al., 2004). The catalytic mechanism for K_2CO_3 for SCWG biomass gasification is summarised as follows (Onsager et al., 1996):

$$K_2CO_3 + H_2O \rightarrow KHCO_3 + KOH \quad (12)$$

$$KOH + CO \rightarrow HCOOK \quad (13)$$

$$KOOCH + H_2O \rightarrow KHCO_3 + H_2 \quad (14)$$

$$2KHCO_3 \rightarrow H_2O + K_2CO_3 + CO_2 \quad (15)$$

$$CO + H_2O \leftrightarrow \text{"HCOOH"} \leftrightarrow H_2 + CO_2 \quad (16)$$

The overall reaction (16) is obtained by the integration of the reactions (12 - 15) which is similar to the mechanism in reaction (10) that accelerates the water gas shift reaction through using KOH to catalyse the SCWG of industrial organic waste.

2.7.5.2. Activated carbon

Activated carbon from natural sources such as trees, plants, shells, coal and wood has been used to catalyse SCWG reactions with high effect. Examples include spruce wood charcoal, macadamia shell charcoal, coal activated carbon and coconut shell. The carbon is treated in high temperature inert gas, CO_2, and/or steam to tailor its properties for use as a catalyst support or as a standalone catalyst. Treatment at moderate temperatures with an active atmosphere results in the production of activated carbon with an ultra-high surface area. The pore size and surface area of activated carbons vary between 0.5 - 1 nm and 800 - 1500 $m^2\ g^{-1}$ respectively (Azadi and Farnood, 2011).

Xu et al. (1996) studied the effect of activated carbon catalysts on the SCWG of organic feedstocks (glucose, glycerol, celloboise, depithed bagasse liquid extract, and sewage sludge). They found increases in the carbon gasification efficiency,

water gas shift reaction and methanation reaction with complete gasification of glucose (22 wt.%) at 600 °C and 34.5 MPa. Complete conversion of the biomass feedstock (bagasse liquid extract and sewage sludge) was also achieved at similar conditions. Deactivation of the catalyst was observed after four hours of operation but carbon gasification efficiencies remained near 100% with the operation of swirl at the reactor entrance.

Studies have argued that the use of activated carbon in low to moderate SCWG does not enhance the rate of gasification significantly and useful data on catalytic SCWG with activated carbon can only be obtained in the high temperature region (Yamaguchi et al., 2009). Due to high gasification efficiencies at high temperatures, a comparison between non-catalytic SCWG and activated carbon catalysed SCWG is challenging (Azadi and Farnood, 2011). Nevertheless, Azadi and Farnood point out that the gas product following activated carbon catalysed SCWG in continuous reactors contains significantly lower amounts of CO. In addition, separation and recovery of the activated carbon catalyst is an important consideration during catalyst selection – a drawback in homogeneous alkali metal catalysts. Successful recovery of activated carbon catalysts has been demonstrated in a continuous pilot scale SCWG for poultry manure (Yanagida et al., 2009).

2.7.5.3. Transition metals

In researching catalytic SCWG, both supported and unsupported forms of transition metals have been used. Unsupported catalysts come in the form of powders and wires with low specific surface areas and skeletal structures (e.g. Raney catalysts).

2.7.5.3.1 **Unsupported catalysts – powders and wires**

The majority of the research into catalytic SCWG using transition metals has used the supported form of the catalyst. The main aim of using metals and metal oxides in powder and wire form is to demonstrate and establish the inherent ability of the metal/metal oxide to catalyse SCWG reactions. Further research is also done to establish whether the unsupported form of catalyst can actually be used in large scale SCWG processes. Studies have been published on the SCWG of organics using nickel (Elliott et al., 1993; Fang et al., 2008), Inconel (Chakinala et al., 2010), ruthenium (Savage and Resende, 2010), ruthenium oxide (Izumizaki et al., 2005; Park and Tomiyasu, 2003; Yamamura et al., 2009) and platinum (Shabaker et al., 2003).

2.7.5.3.2 **Unsupported catalysts – Raney (skeletal) catalysts**

Raney catalysts have a spongy structure and are formed by leaching out aluminium from a metal aluminium alloy (e.g. nickel) (Nishimura, 2001). Raney nickel has a specific surface area ranging from 50 - 100 m^2 g^{-1} and its low cost and high activity in SCW medium makes it highly attractive (Azadi et al., 2009; Erlt et al., 1999). Raney nickel has been used to catalyse the SCWG of various feedstock; glucose, glycerol, sawdust, coal and corncob (Azadi et al., 2009; Huber et al., 2003; Li et al., 2010; Waldner and Vogel, 2005). In all cases, the gas yields improved with the use of Raney nickel. In addition, when various catalysts were used on the same feedstock, Raney nickel resulted in one of the highest conversions. However, its hydrothermal stability in SCW has been questioned due to sintering and deactivation during SCWG.

Waldner and Vogel (2005) studied the catalytic SCWG of woody biomass at 300 - 410 °C and 12 - 34 MPa. At a hold time of 90 min, complete gasification was obtained using Raney nickel catalysts. However, the catalyst surface was covered with carbon deposit and the catalyst was found to be deactivated over time in a 50 hour experiment in a continuous flow reactor.

Raney nickel catalysts have considerable capability in cleaving C - O bonds and consuming a portion of the produced H_2 to produce a CH_4 rich gas. If H_2 production is favoured, then two approaches can be utilised (Azadi and Farnood, 2011):

(i) The reaction time (or weight hourly space velocity) can be optimised for maximum hydrogen production before methanation reactions start. This may result in incomplete carbon conversion which ultimately leads to reactor clogging due to tar formation over time.

(ii) The surface chemistry of Raney nickel can be modified with small quantities of tin in order to retain its C - C cleaving ability but retard C - O cleaving. This has been demonstrated to increase hydrogen to methane ratios (Huber et al., 2003; Shabaker et al., 2003).

2.7.5.3.3 **Supported catalysts – nickel**

A summary of SCWG experiments with supported nickel catalysts is presented in Table 2.16. With the low cost of nickel and its extensive application in the petrochemical industry, researchers have introduced nickel into SCWG to get a better understanding of its hydrothermal ability and stability (Guo et al., 2010; Osada et al., 2006; Sato et al., 2006; Sharma et al., 2007). Whilst the studies found that nickel can increase the conversion of biomass, sintering and deactivation were unavoidable using both supported and unsupported forms.

Research by Elliott (2008) demonstrated that Ni catalyst is inevitably limited by its life performance (<100 hours) due to physical and chemical structural changes in the catalyst support. The Ni crystallite sintered in both batch and continuous experiments. Although Ni crystallites may sinter in SCW, the long term activity of supported Ni catalysts is closely related to the stability of the carrier in SCW. Research has shown that stable supports in SCW include: activated carbon (Elliott et al., 1993; Lee and Ihm, 2009), carbon nanotubes (Azadi et al., 2010a; Taylor et al., 2009), α - Al_2O_3, rutile TiO_2 and monoclinic ZrO_2 (Elliott et al., 1993). Silica, alumina (except α - Al_2O_3), MgO, cubic ZrO_2, silica-alumina, alumina-silicate and most zeolites were found to be unstable in SCW (Azadi and Farnood, 2011; Elliott et al., 1993).

Feed (conc %)	**Ni (%) / Support**	**Reactor**	**Temp (°C) / Hold time (min)**	**CGE (%)**	**H_2 (mmol/g)**	**CH_4 (mmol/g)**	**Reference**
Cresol (10%)	62 / SiO_2 – Al_2O_3	Batch	350 / 100	54	1.5	21	(Elliott et al., 1993)
Cresol (2%)	48 / ɣ - Al_2O_3	Cont.	350 / -	99	1	40	(Elliott et al., 1994)
Cellulose (14%)	50 / SiO_2 – Al_2O_3	Batch	350 / 30	70	14	6.8	(Minowa and Ogi, 1998)
Lignin (5.5%)	20 / MgO	Batch	400 / 120	15	5	2.5	(Furusawa et al., 2007)
Glucose (9%)	20 / ɣ - Al_2O_3	Batch	400 / 20	33	10.5	2.5	(Lu et al., 2010)
Glucose (11%)	16 / C	Cont.	650 / -	98	13.6	6.2	(Lee and Ihm, 2009)

Table 2.16 Summary of catalytic SCWG using supported nickel catalysts.

Nickel's catalytic performance can be improved by adding trace elements such as Cu, Ag, Sn, and Ru in the Ni catalyst in order to suppress hydrothermal crystallite growth – as demonstrated by Elliott et al. (2006). Results indicated the increased activity and lifetime through addition of Ru with proven continuous tests over six months.

2.7.5.3.4 **Supported catalysts - ruthenium**

Ruthenium has been observed to be a very active catalyst in SCWG with low metal loadings still producing high catalytic activity (Elliott et al., 2006). Ruthenium has a higher metal dispersion compared to nickel because ruthenium has (i) a lower metal loading on the support (typically around or below 5%), (ii) limited surface mobility and (iii) better resistance against sintering due to its high melting point and milder reduction temperature. A summary of SCWG experiments with supported ruthenium catalysts is presented in Table 2.17.

Feed (conc %)	Ru (%) / Support	Reactor	Temperature (°C)	Hold time / WHSV (min h^{-1})	CGE (%)	H_2 (mmol g^{-1})	CH_4 (mmol g^{-1})	Reference
Cresol (10%)	5 / ɣ - Al_2O_3	Batch	350	90	89	0.6	34.8	(Elliott et al., 1993)
Cresol (2%)	5 / Al_2O_3	Continuous	350	-	100	0.4	13	(Elliott et al., 1994)
Glucose (6%)	5 / C	Continuous	360	1.2	82	3.2	8.8	(Azadi et al., 2010b)
Spirulina platensis (5%)	2 / C	Batch	400	60	45	2.7	4	(Stucki et al., 2009a)
Spirulina platensis (10%)	2 / ZrO_2	Batch	400	63	25	2.4	2.6	(Stucki et al., 2009a)
Cellulose (5%)	2 / TiO_2	Batch	400	15	74	2.7	13.4	(Hao et al., 2005)
Lignin (3.3%)	2 / TiO_2	Batch	400	180	97	2.6	28.5	(Osada et al., 2007a)
Lignin (3.3%)	5 / C	Batch	400	60	80	2.4	23.6	(Osada et al., 2007b)
Lignin (3.3%)	5 / C	Batch	450	60	100	4.1	27.7	(Yamaguchi et al., 2009)
Glycerol (5%)	5 / ɣ - Al_2O_3	Continuous	800	2.5	93	70.6	3.7	(Byrd et al., 2008)

Table 2.17 Summary of catalytic SCWG using supported ruthenium catalysts.

In the catalytic SCWG of lignin and cellulose using ruthenium, high H_2 selectivity was observed at 400 °C (Osada et al., 2004) The intermediate compound formaldehyde was rapidly decomposed to CH_4, CO_2 and H_2 in the presence of ruthenium. The absence of a catalyst resulted in formaldehyde being converted to methanol and CO_2. The catalytic mechanism for ruthenium can be summarised as follows (Montassier et al., 1991):

- Oxygenated compounds containing hydroxyl groups adsorb to the catalytic Ru surface predominantly through one or more oxygen atoms;
- The reactant undergoes dehydrogenation on the catalyst surface followed by cleavage of C - C or C - O bonds;
- Cleavage of C - C bonds leads to syngas production which is subjected to the water gas shift reaction and possible methanation reactions;
- Cleavage of C - O bonds leads to the production of organic acids and alcohols;
- Very low levels of organic carbon in the process water post SCWG suggests that an intermediate alcohol or organic acid is formed from C - O cleavage which is further reacted to gaseous products.

In a study on SCWG of spruce sawdust, Vogel et al. (2007) studied several catalysts and the best performance was achieved by Raney nickel, 1% Ru/TiO_2 and 2% Ru/C. These catalysts were further tested for their long term stability in a continuous test rig using a mixture of five organic compounds that represent hydrolysed wood. Results showed that Raney nickel and even a Ru doped Raney nickel sintered after a short period of time and 1% Ru/TiO_2 was not active enough. 2% Ru/C was

hydrothermally stable for more than 200 hours at 400 °C and 30 MPa with space velocities of 1.6 - 33 $g_{organics}$ $g^{-1}_{catalyst}$ hr^{-1}. The authors also tested the effect of sulphur on the catalyst activity by adding small amounts of sodium sulphate to the reactor (8 ppm of sulphate at the entrance of the reactor). They found that catalyst began to deactivate gradually due to the irreversible bonding of the sulphate anion to surface ruthenium.

Osada et al. (2007b) studied the effect of sulphur on supercritical catalytic gasification of lignin where they concluded that sulphur poisoned the active sites for C - C bond breaking and methanation reaction but did not block sites for the water-gas shift reaction. The shift in the selectivity of the gas products to hydrogen during catalyst re-use may be related to catalyst deactivation due to sulphur poisoning. More recently, Guan et al. (2012a) demonstrated the deactivation of Ru/C catalyst during the SCWG of the microalga *Nannochloropsis*. They found that subsequent re-use of the catalyst resulted in poorer gas yields due to loss of catalytic activity and traced the problem to the sulphur content of the microalga. Onwudili and Williams (2013) also showed that hydrogen yields increased while methane yields decrease during hydrothermal gasification of glucose using spent Ru/Al_2O_3 catalyst, which agreed with the observations of Osada et al.

In a study on the SCWG of lignin using Ru catalyst, Osada et al. (2007a) investigated the deactivating effect of sulphur on ruthenium catalyst. A 2 wt.% Ru/TiO_2 catalyst was soaked in aqueous sulphuric acid then dried (labelled: S - Ru/TiO2). SCWG of lignin was carried out at 400 °C, 37 MPa, 180 min hold time with a biomass concentration of 3.33%. In the presence of Ru/TiO_2, lignin was completely gasified with a CGE of over 97%. The CGE decreased to 21% when S - Ru/TiO_2 was used. The sulphur doped Ru catalyst (S - Ru/TiO_2)

caused a decrease in the number of active sites leading to the formation of tetrahydrofuran (THF)-insoluble products, namely char. The reaction pathway of SCWG of lignin over the sulphur doped ruthenium catalyst is presented in Figure 2.13.

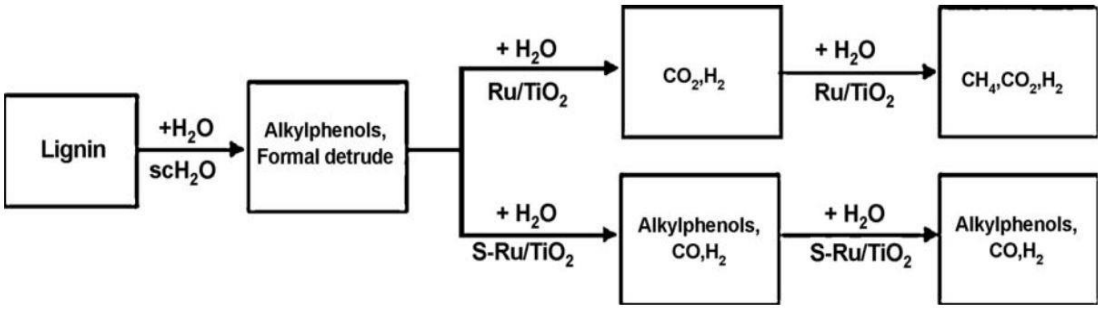


Figure 2.13 Reaction pathway of SCWG of lignin over a supported ruthenium catalyst containing sulphur (Osada et al., 2007a)

Over Ru/TiO_2, conversion of lignin to low molecular weight compounds such as formaldehyde and alkylphenols (C - C bond breaking) occurs through hydrolysis and decomposition followed by the formation of gaseous products (H_2, CO and CO_2). Some of these gases then react to form methane via the methanation reaction over the Ru/TiO_2 catalyst. Over S - Ru/TiO_2 however, the C - C breaking and methanation reaction were inhibited by the adsorption of sulphur atoms on the ruthenium metal surface. However, the formaldehyde reaction and water gas shift reaction still proceeded over S - Ru/TiO_2 resulting in a higher hydrogen yield compared to methane.

The blocking of active sites by sulphur was investigated by Waldner et al. (2007) to determine the catalyst deactivation mechanism. Four possible ruthenium catalyst deactivation mechanisms were suggested as described in Figure 2.14: (i) dissolution

of ruthenium and carry-out of the system, (ii) sintering of the crystallites and loss of active metal surface area, (iii) precipitation of sodium sulphate leading to physical blockage of the active sites, or (iv) irreversible chemical bonding of sulphate to Ru(III), masking the active sites. Experiments were carried out by the authors to determine the governing mechanism. The authors found that sulphate bonded irreversibly with the active sites (mechanism (iv)).

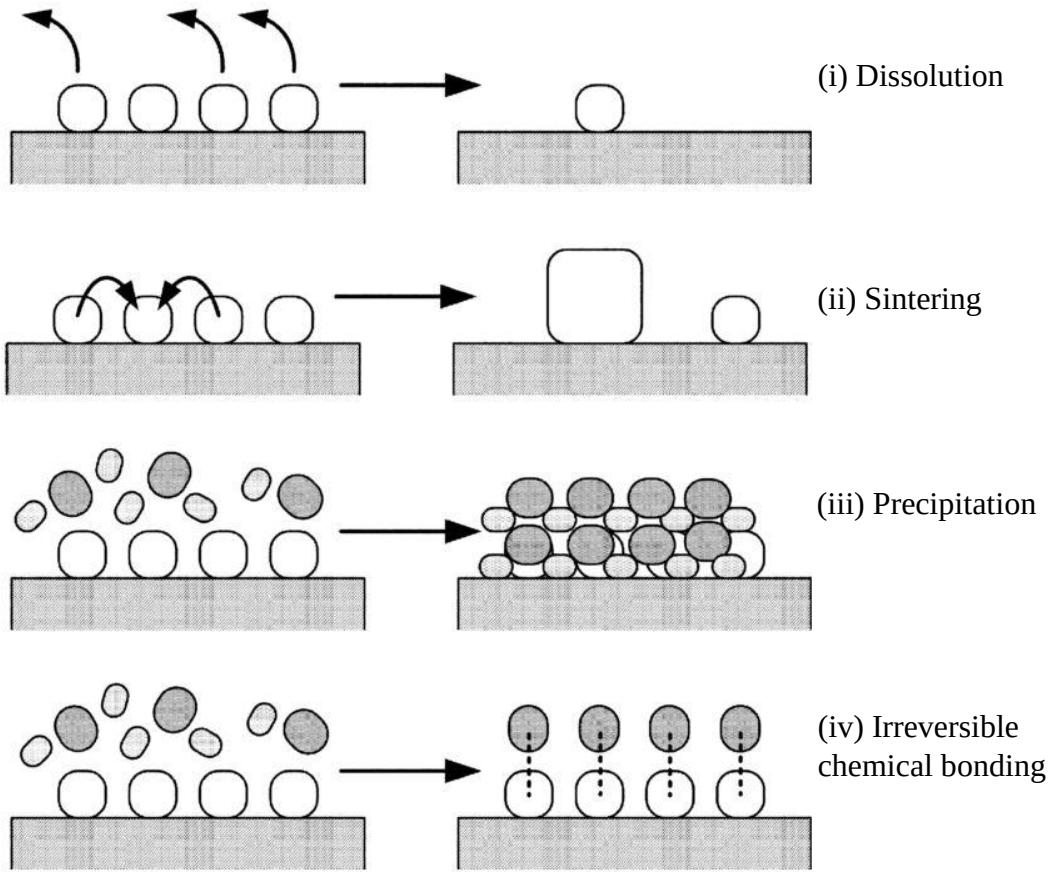


Figure 2.14 Four possible ruthenium catalyst deactivation mechanisms - adapted from Waldner et al. (2007)

A potential solution to catalyst deactivation is to remove the sulphur from the feed in a hydrothermal salt separator prior to passing the feed to the catalytic reactor. Stucki et al., (2009b) propose a novel process based on the idealised integrated

hydrothermal system (Figure 1.5) where diluted CO_2 emissions from fossil fuel flue gas are used to grow microalgae. The microalga is then converted through catalytic SCWG with a salt separator placed before the catalytic reactor to prevent catalyst poisoning. The nitrogen and sulphur in the microalga are expected to form NH_3 and H_2S respectively. The authors propose precipitating both NH_3 and H_2S as ammonium and sulphide salts from SCW in their appropriate pH ranges before the algal feed enters the catalytic SCWG reactor. SCW demonstrates a very low solubility for salts and a reverse flow gravity separator is proposed to continuously separate the precipitated salts from the supercritical fluid stream as demonstrated in Figure 2.15.

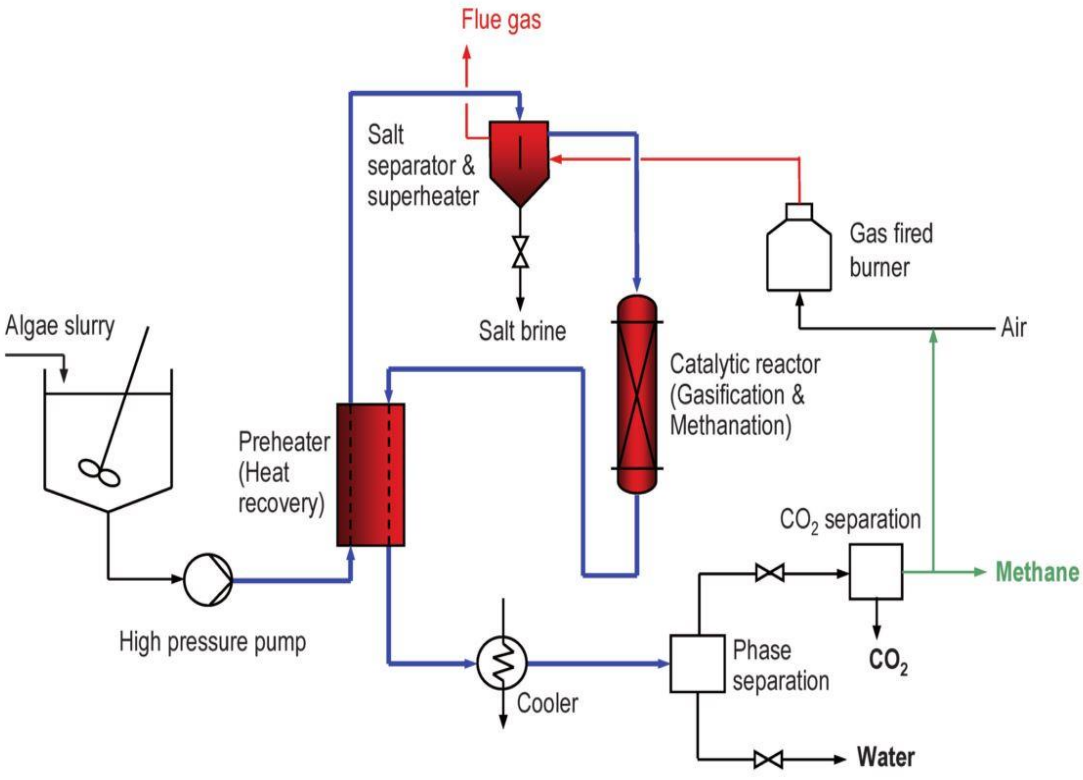


Figure 2.15 Catalytic SCWG of algal slurry with salt separation (Stucki et al., 2009a)

2.7.5.3.5 **Metal oxides**

Only a few metal oxides have been used to catalyse SCWG of biomass. Their advantage lies in their easy recovery following the reaction compared to homogeneous alkali catalysts. CaO improved the hydrogen yield from SCWG of lignite at 500 - 600 °C and 20 - 30 MPa. The hydrogen yield increased from 135 ml g^{-1} to 345 ml g^{-1} in the presence of CaO (Zhang et al., 2010). This can be explained by CaO capturing the produced CO_2 from biomass SCWG to form carbonates thus accelerating the water gas shift reaction for increased hydrogen production. ZrO_2 was also found to increase the hydrogen yield from the SCWG of glucose (Watanabe et al., 2002). Red mud is a byproduct from the aluminium production industry and has also been used as a catalyst for SCWG (Yanik et al., 2008). It contains large amounts of iron oxides (30 - 60%) and smaller quantities of CaO and Na_2O and has been found to accelerate the water gas shift reaction and increase hydrogen production – although the increase is not as high compared to alkalis (NaOH for example).

2.7.6 Status of technology and challenges

The SCWG of biomass has been intensively researched over the last two decades with the influence of reaction parameters, different ingredients of biomass as well as different catalysts all being investigated (Kruse, 2009; Matsumura et al., 2005; Savage, 2009, 2000, 1999; Schmieder et al., 2000; Yanik et al., 2008).

In the mid-2000s, a process development pilot plant with a throughput of 100 kg hr^{-1} was constructed at Froschungszentrum Karlsruhe, Germany, for the SCWG processing of biomass and organic wastes. The plant can operate up to 700 °C and 35 MPa and the components subjected to high temperatures are made of a

nickel based alloy. A schematic of the VERANA test facility (German acronym for 'experimental facility for the energetic exploitation of agricultural matter') is presented in Figure 2.16.

The biomass is crushed and the water content is adjusted to reflect the desired biomass concentration for the reactor. The slurry is pressurised using membrane pumps and heated through a tube-in-tube heat exchanger. The temperature of the slurry can be further heated in a 'pre-heater' that may be integrated or bypassed.

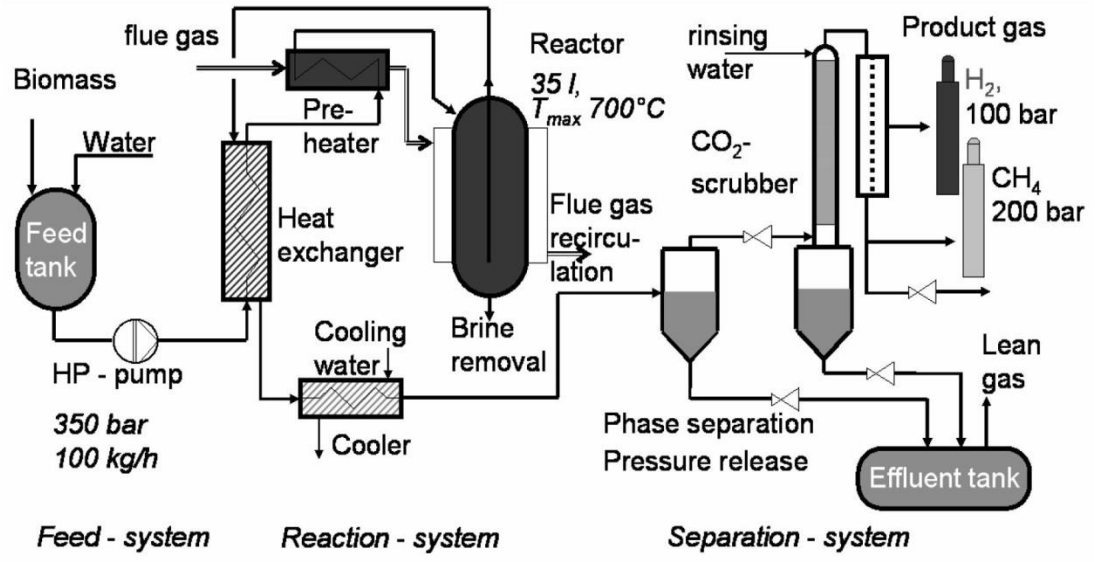


Figure 2.16 Pilot plant for SCWG of biomass ("VERANA"), simplified flow sheet - adapted from Boukis et al. (2005)

SCWG takes place in a vertical 'thick tube' reactor with a relatively large diameter (internal diameter: 110 mm; reactor length: 3.5 m). Both the pre-heater and reactor are fired by hot flue gas from a propane boiler. Following SCWG, the product is cooled in a heat exchanger and further cooled in an additional cooler. Separation of the gas and liquid phase occurs under pressure maintaining a large part of the CO_2 dissolved in the process water. The H_2 rich gas phase is depleted of any CO_2 in a

scrubber resulting in a final combustible gas half consisting of hydrogen and the remaining half consisting of hydrocarbons (mainly methane with some ethane and propane). The H_2 product gas is then expanded and burnt in a flare or filled into pressurised cylinders for use by directly coupled gas motors of fuel cells for example. Using this process, the SCWG of ethanol, pyroligeneous acid and corn silage was demonstrated for hydrogen production (Boukis et al., 2005). The carbon gasification yield was 97 - 98% in the case of ethanol and pyroligeneous acid and 90% in the case of corn silage with a heat transfer efficiency higher than 80%. In all cases the mass balance of the chemical elements could be closed.

The study highlighted potential challenges in the development of SCWG plans and resulting in further research into the application of improved process layouts to prevent plugging and to enhance reliability and economics of the process. Other studies have also highlighted challenges that need to be resolved to achieve commercialisation of SCWG of biomass (Basu, 2010; Guo et al., 2010; Kruse, 2008). These include corrosion, pumping of the feedstock and the large heat input/requirement for SCWG.

2.7.6.1. Corrosion

In a SCWG reactor where temperatures and pressures are high, water becomes highly corrosive. Halogens, sulphur and phosphorus present in feedstocks are converted to mineral acids such as HCl, H_2SO_4 and H_3PO_4. SCW containing these acids in the presence of oxygen can be extremely corrosive to stainless steels and nickel-chromium alloys (Friedrich et al., 1999). Similar results were observed in experiments with zoo mass in a continuous stirred reactor where corrosion was found due to the sulphur contained in the biomass (Kruse et al., 2005).

However, Kruse (2008) argues that whilst corrosion in SCWG experiments was observed, it is relatively weak corrosion and a solution to the problem will be found similar to how corrosion issues in supercritical water oxidation (SCWO) processes were resolved (Boukis et al., 2001; Chen et al., 2006; Kritzer et al., 2000).

Marrone and Hong (2009) provide a detailed review on corrosion control methods in SCWO and SCWG processes. The authors summarise key areas in the process susceptible to corrosion and the common types of corrosion encountered and anticipated. The authors propose corrosion control approaches in SCWG plants such as:

- Using a vortex/circulating flow reactor to contact between corrosive species and solid surfaces.
- Use of nickel based alloys or stainless steel (high corrosion resistant materials) for material construction.
- Optimising process conditions by reducing the temperature of SCWG to 400 °C instead of 600 °C for example. This would allow the use of other corrosion control methods such as coatings or liners that would not be applicable at high temperatures.

2.7.6.2. Pumping the feedstock

The feeding of wet solid biomass which is fibrous and varying in composition presents a challenge in the scaling of SCWG processing. Slurry pumps have been used to feed solid slurries into high pressure reactors but they have not been tested to feed biomass slurries into supercritical reactors that operate at ultra-high pressures.

The main challenge associated with the reactor feed system is the high pressure of the reactor (> 22 MPa). The feeding of biomass into a high pressure reactor presents difficulties due to the fibrous solid and granular nature of the biomass. Unlike most SCWG studies using water soluble organics such as glucose, digested sewage sludge and wastewater (Byrd et al., 2007; Di Blasi et al., 2007; Lee et al., 2002), fibrous biomass does not flow well through an augur or gear pump and it is difficult to transform it into a uniform slurry for pumping through impellers (Basu, 2010) The irregular size and low shape factor of biomass makes it particularly difficult to flow and as such pulverisation becomes necessary for pumping the biomass.

To overcome pumping issues, Antal, et al. (2000) investigated the use of additives and emulsifiers to make pumpable slurries. The authors used corn starch gel via a 'cement pump', sodium carboxymethyl cellulose and xanthan to improve the flow properties of biomass. However, in large scale industrial applications, the large scale use of emulsifiers is impractical (Basu, 2010).

2.7.6.3. Heat input, efficient recovery and process economics

SCWG requires a large heat input due to its high reaction temperature. The heat requirement affects the energy conversion efficiency and the recovery of heat is crucial to the viability of SCWG technology. Without efficient heat recovery from the product gas, the external energy input may exceed the energy produced making the process a net energy consumer. Gasafi et al. (2008) conducted an economic analysis for a SCWG plant for processing sewage sludge for hydrogen production. The costs are divided into (i) feed preparation, (ii) heat exchanger, (iii) reactor, and (iv) purification. Figure 2.17 compares the investment costs for a SCWG plant based on estimates from the literature.

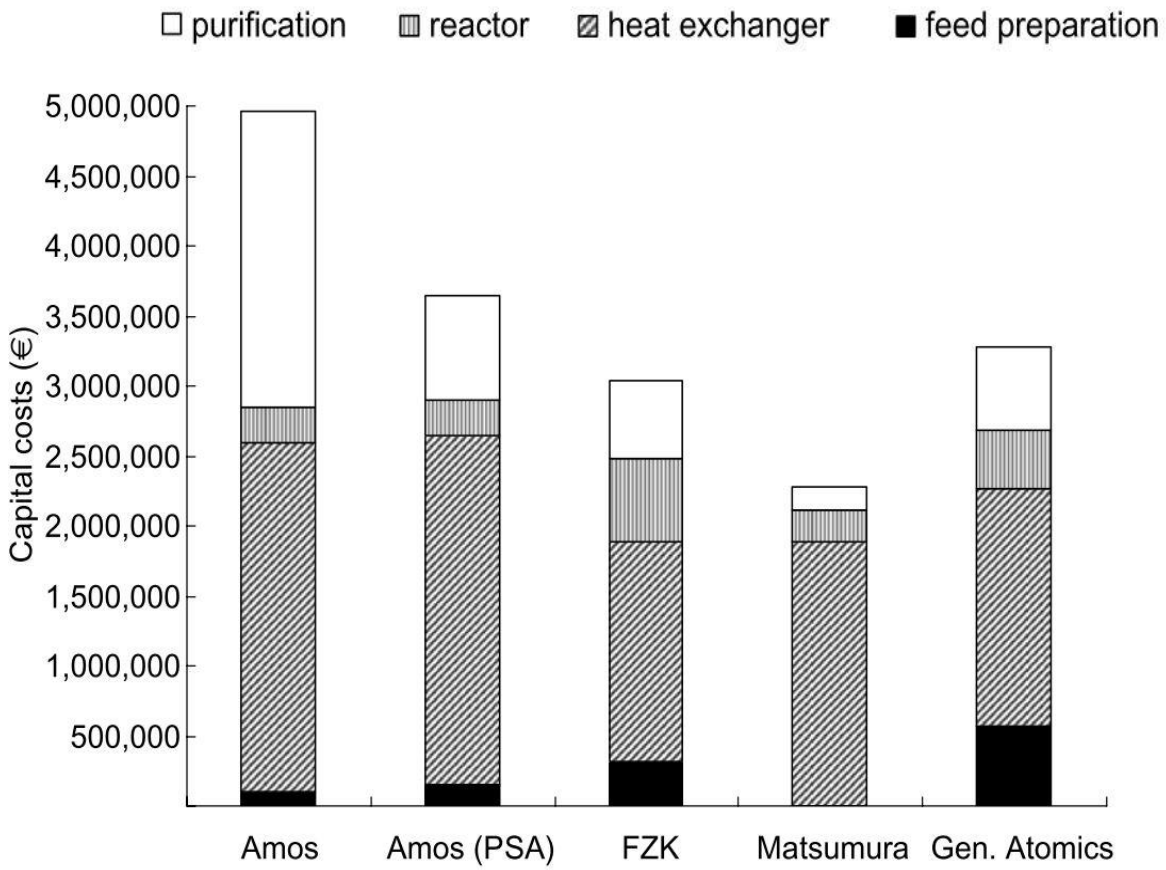


Figure 2.17 Investment cost of SCWG plant designs based on a throughput of 5000 kg per hour of sewage sludge, based on a 245 € $t^{-1}_{dry\ matter}$ and a hydrogen production cost of 2.3 € GJ^{-1} - adapted from Basu (2010) and Gasafi et al. (2008).

Heat recovery exchangers represent 50 - 60% of the total capital cost of a SCWG plant making it a critical component. The viability of SCWG processes depends on the ability of the feedstock to obtain as much of its enthalpy as possible from the sensible heat of the product through efficient heat exchangers. If the heating rate of the heat exchanger is low, coke and tar formation will take place. To overcome such problems, the VERANA pilot plant mixed the concentrated biomass feed with high temperature pure water (Boukis et al., 2007).

A potential solution to coke and tar formation was proposed by Kruse and Faquir (2007). The authors proposed SCWG in a reaction process where a continuously stirred tank reactor (CSTR) is followed by a tubular reactor in order to benefit from 'active hydrogen' formation in the CSTR due to its backmixing (Yakaboylu et al., 2015). 'Active hydrogen' is the hydrogen formed during the intermediate stages of the water gas shift reaction and suppresses tar and coke formation. In addition, the authors point out that gas yields increase when the CSTR is combined with a tubular reactor.

2.7.6.4. Scaling up and implications

Kruse (2008) discusses the implications of plant size on the economics of a SCWG plant, focusing on the transportation of biomass with a high water content which is very expensive and energy consuming. In addition, an important consideration in SCWG is the low feed concentration to achieve high gasification efficiencies and as such, there is a trade-off between low feed concentrations and handling costs (including pretreatment and preparation). Boukis et al. (2006) report the use of a sludge pump in a 100 kg h^{-1} pilot plant however, the solids had to be ground to less than 1 mm in particle size and pretreated before pumping.

In terms of processing macroalgae, a potential solution to reducing pumping issues is to pre-treat the macroalgae and hydrolyse the carbohydrates into the aqueous phase through direct hydrolysis or microwaving for example. Further discussion on pretreatment is discussed in section 8.1.

3 Methodology

3.1 Introduction

This chapter provides a description of the samples, instruments and equipment used in the study. A description of the algal species, reactants (including catalysts) and experimental conditions used during hydrothermal processing is detailed. The techniques used for product analysis are also described.

3.2 Algal species

3.2.1 Macroalgal species

The selected macroalgal species formed part of the Supergen Bioenergy II Programme (Anastasakis 2011) which investigated the use of macroalgae for bioenergy, focusing on all the steps from production of biomass to delivery of a valuable energy product. The four species, *Saccharina latissima*, *Laminaria digitata*, *Laminaria hyperborea* and *Alaria esculenta* were selected due to their wide distribution and abundance along British and European coasts. In addition, their selection was based on proven trials of seeding and high growth rates. The species were harvested off the West Coast of Scotland near Oban at Easdale, Clachan Sound and Barnacarry Bay.

The harvested macroalgal samples were not washed to prevent any changes to their chemical composition. The samples were freeze dried then ground by a Retch PM100 ball mill and sieved to a particle size of < 90 μm before analysis and hydrothermal processing.

The proximate and ultimate analysis of the macroalgal species used in the study are summarised in Table 3.1 (as cited in Anastasakis, (2011)).

		Sample name	Harvest date	Moisture (%)	Ash (%)	C (%)	H (%)	N (%)	S (%)	O* (%)	HHV (MJ kg^{-1})
Chapter IV	Seasonal Variation	*S. latissima*	07/01/2009	5.42	44.0	25.9	3.29	2.17	0.87	23.7	9.58
			17/04/2009	4.37	31.8	30.2	4.23	2.54	0.68	30.5	11.7
			30/07/2009	6.44	23.4	32.5	4.46	1.14	0.63	38.0	12.2
			16/10/2008	4.07	33.6	29.7	4.13	1.64	0.98	30.0	11.5
	Summer harvest	*S. latissima*	15/07/2008	5.93	36.2	29.1	4.24	2.18	0.43	28.3	12.2
		L. digitata	26/07/2009	4.27	20.5	32.9	5.41	1.79	n.d.	39.4	13.3
		A. esculenta	22/07/2008	7.95	24.8	34.9	4.52	2.50	n.d.	33.3	13.5
		L. hyperborea	16/07/2009	5.66	28.3	31.8	4.57	1.60	0.90	32.8	12.6
Chapter V		*L. hyperborea*	16/10/2008	8.52	20.84	35.2	4.57	1.35	0.64	37.39	13.4

Table 3.1 Proximate and ultimate analysis of macroalgal species

	Sample name	Moisture (%)	Ash (%)	C (%)	H (%)	N (%)	S (%)	O* (%)	HHV (MJ kg^{-1})	Protein (%)	Carbohydrate (%)	Lipid (%)
Chapter VI	*Chlorella vulgaris*	5.20	6.40	53.6	7.3	9.2	0.5	29.4	23.2	46	36	15
	Pseudochoricystis ellipsoidea	3.22	0.77	61.4	9.2	2.7	-	26.6	27.3	19	35	33
	Spirulina platensis	7.80	7.60	54.4	7.6	10.9	0.83	26.3	21.2	65	20	5

Table 3.2 Proximate and ultimate analysis of microalgal species, including biochemical composition

3.2.2 Microalgal species

Samples of *Chlorella vulgaris, Pseudochoricystis ellipsoidea* and *Spirulina platensis* were obtained from commercial sources. *Pseudochoricystis ellipsoidea* was obtained from the DENSO Corporation (Kariya, Japan). *Spirulina platensis* was obtained from Naturally Green Ltd. (Reading, UK), where it is traded as health food supplements. *Chlorella vulgaris* was obtained from Sunrise Nutrachem Group, Qingdao Sunrise Trading Co., Ltd. (China).

The three microalgal strains were selected due to their varying range in biochemical composition. *Pseudochoricystis ellipsoidea* is a high lipid strain and *Spirulina platensis* is low lipid, high protein strain. The proximate and ultimate analysis of the microalgae including the biochemical composition is listed in Table 3.2 (as cited in Biller, (2013)).

3.2.3 Catalysts

Three different loadings of ruthenium alpha-alumina (Ru/Al_2O_3) catalyst were 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 1.7 nm.

Nickel catalyst on hydrothermally stable alumina support in the form of cylindrical pellets, were supplied by Johnson Mattey, UK and used as received. The catalyst has a BET surface area of $\geq 70\ m^2\ g^{-1}$ with 5 wt.% nickel content.

Sodium hydroxide pellets were obtained from Sigma-Aldrich UK and used as gasification additive. The required mass of sodium hydroxide was added to the reactor to achieve the required concentration of sodium hydroxide.

3.3 Hydrothermal processing

3.3.1 SCWG Reactor

SCWG experiments were performed in a 75 ml batch non-stirred Inconel reactor, Parr Instrument Co., Moline, Illinois, USA with a maximum operating temperature and pressure of 600 °C and 45 MPa respectively. The reactor's inner diameter is 25 mm and it has a wall thickness of 9.53 mm. The reactor was heated by a 1.5 kW ceramic knuckle heater and the reactor temperature was monitored by J-type thermocouple (accuracy ± 1 °C) held in a thermowell at the bottom of the reactor. The operating pressure was measured with a pressure gauge (accuracy ± 0.05 MPa) mounted on the reactor head. A gas sampling unit with high pressure valves was fitted on the reactor head. The maximum liquid loading did not exceed 15 ml to prevent pressure build up beyond the reactor specifications. The relationship between temperature, pressure and water loading has been studied (Onwudili and Williams, 2009). A schematic diagram of the 75 ml reactor is provided in Figure 3.1. The reactor consists of a two main parts; a reaction chamber and an upper part (reactor head) consisting of:

- A combined gas outlet/sampling valve which also doubled up as the inert gas inlet valve to purge the reactor.
- A safety rupture disc calibrated to 40 MPa. The reactor undergoes annual pressure safety tests by the manufacturer and the liquid loading during

experimentation did not exceed 15 ml to ensure excessive pressure is avoided in the sealed reactor.

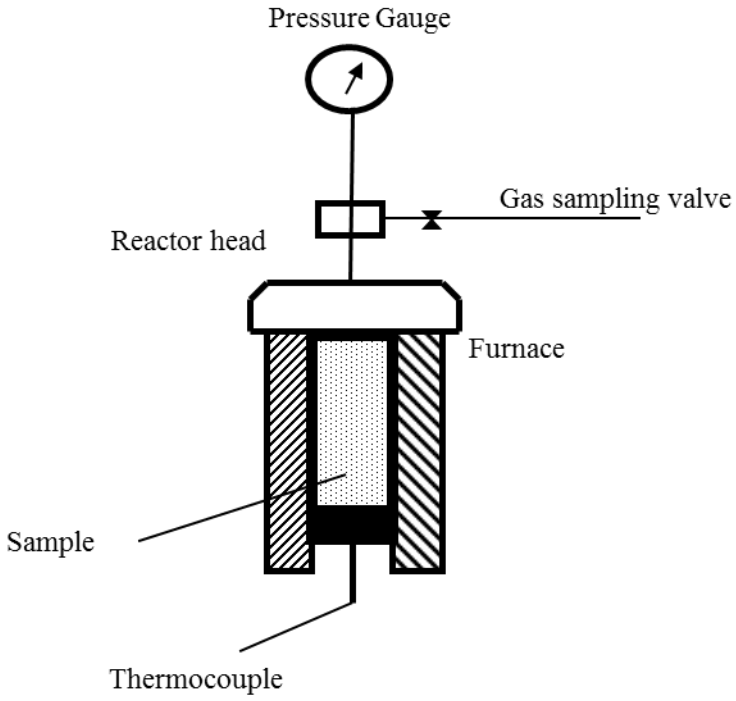


Figure 3.1 Schematic of 75 ml Parr reactor

3.3.2 SCWG Experimental procedure

Each experiment involved loading the reactor with a paste made from the dry macroalgae feed and an amount of deionised water required for the feed concentration under investigation. When required, the solid catalyst (ruthenium or nickel) was suspended at the top of the reactor in a stainless steel mesh gauze. For experiments using sodium hydroxide, the required mass of sodium hydroxide was added to the reactor to achieve the required concentration of sodium hydroxide. The reactor head was partially screwed on and the reactor purged with nitrogen. The

reactor was then sealed and the purging gas was allowed to fill the reactor to 0.5 MPa. The gas valve was then shut and the sampling attachment replaced. This acted as a pressure test for the reactor to ensure no leakage. The nitrogen was then released from the reactor returning it to ambient pressure. The reactor was heated at an average rate of 30 °C min^{-1} to the required experiment 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.

3.3.3 HTL Reactor

HTL experiments were performed in a 500 ml batch non-stirred reactor from Parr Instrument Co., Moline, Illinois, USA with a maximum operating temperature and pressure of 500 °C and 35 MPa respectively. The reactor's inner diameter is 63.5 mm and it has a wall thickness of 15.9 mm. The reactor was heated by a 3 kW ceramic knuckle heater and the reactor temperature was monitored by J-type thermocouple (accuracy ± 1 °C) inserted in a thermowell located on the reactor head extending into the interior of the reaction chamber. The operating pressure was measured with a pressure gauge with a calibrated range of 0 – 35 MPa (accuracy ± 0.05 MPa) mounted on the reactor head. A schematic diagram of the 500 ml reactor is provided in Figure 3.2. The reactor consists of a two main parts; a reaction chamber and an upper part (reactor head) consisting of:

- A gas inlet valve to introduce inert gas for purging.
- A gas outlet/sampling valve which also doubled up as the inert gas inlet valve to purge the reactor.

- A safety rupture disc calibrated to 25 MPa. The reactor undergoes annual pressure safety tests by the manufacturer and the liquid loading during experimentation did not exceed 100 ml to ensure excessive pressure are avoided in the sealed reactor.

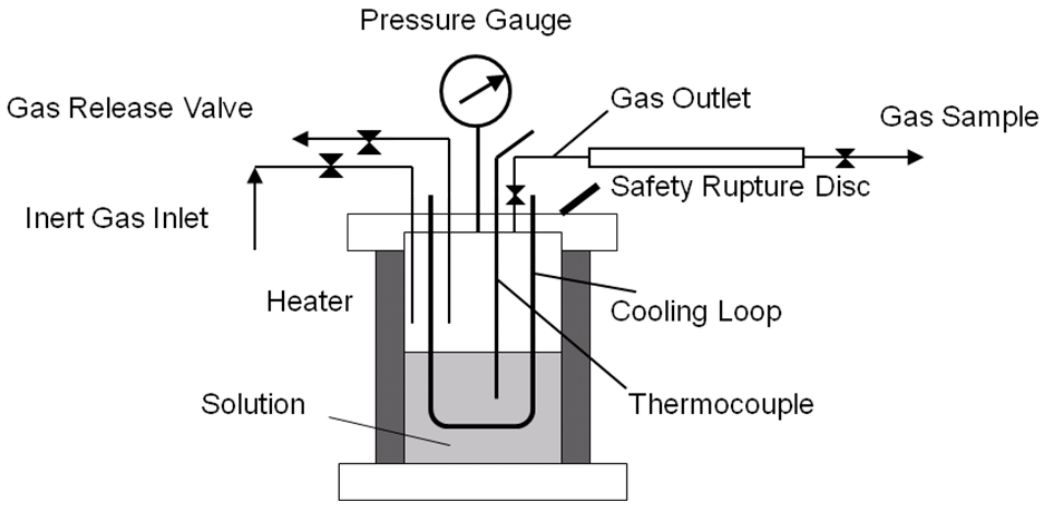


Figure 3.2 Schematic of 500 ml Parr reactor.

3.3.4 HTL Experimental procedure

Each HTL experiment involved loading the reactor with a paste made from the dry microalgae feed and an amount of deionised water required for the feed concentration under investigation. Following loading the reactor with the required reactants, the reactor head was secured and the reactor purged with nitrogen. The purging gas was allowed to fill the reactor to 0.5 MPa. The gas valve was then shut and the sampling attachment replaced. This acted as a pressure test for the reactor to ensure no leakage. The nitrogen was then released from the reactor returning it to ambient pressure. The reactor was heated at an average rate of 20 °C min^{-1} to the

required experiment 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.

3.3.5 Product separation and analysis

The schematic in Figure 3.3 illustrates the procedure for separation of products for both types of experiments (SCWG and HTL).

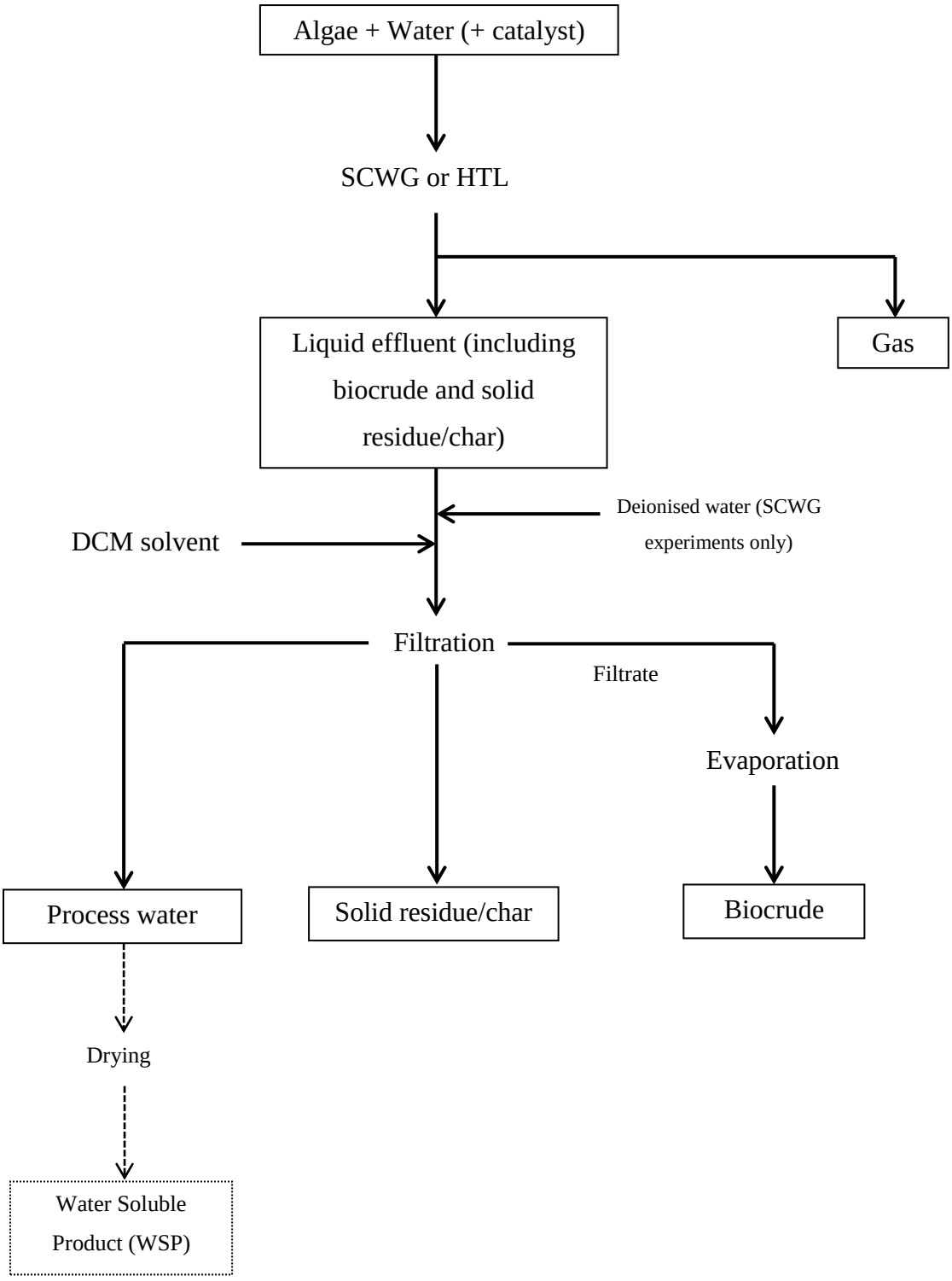


Figure 3.3 Schematic of experimental procedure and separation of products for SCWG and HTL experiments

3.3.5.1. Product gas analysis

The gas sampling valve was opened following reactor cooling to obtain two samples of the product gas. The samples were collected in gas-tight plastic syringes sealed with a gas-tight rubber stopper. The gas samples were analysed immediately using two gas chromatographs:

- Permanent gases – A Varian CP-3380 gas chromatograph with a thermal conductivity detector (GC/TCD) was used to detect hydrogen, oxygen, nitrogen and carbon monoxide. A Varian CP-3800 gas chromatograph was used to detect carbon dioxide. Both GC/TCDs were fitted with a 2 m long by 2 mm diameter, 60 - 80 mesh packed Hayesep molecular sieve column. Argon was used as the carrier gas and the column oven temperature was held at 40 °C and the injector temperature at 120 °C. The detector temperature was 120 °C with a filament temperature of 160 °C. The GC/TCD was regularly calibrated using standard gases obtained from Supelco, UK.
- Hydrocarbon gases – alkanes and alkenes from C_1 to C_4 were analysed using a Varian CP-3380 gas chromatograph fitted with a flame ionisation detector (GC/FID). The column was 2 m long by 2 mm diameter and packed with 80 - 100 mesh Hayesep. Nitrogen was used as the carrier gas and the injector temperature was held at 150 °C with the detector temperature at 200 °C. The oven temperature program was set to 60 °C for 3 min increasing to 100 °C for 3 min at a heating rate of 10 °C min^{-1} and finally increased to 120 °C for 9 min at a heating rate of 20 °C min^{-1}. The FID was regularly calibrated using standard gases obtained from Supelco, UK.

The standard gaseous mixtures of known vol % were injected into the GCs and the peak areas of each gas were used to calculate the response factor (RF) (μVolts per unit time per vol %) for each gas, Eq (17):

$$\text{Response Factor (RF)} = \frac{\text{peak area of standard gas}}{\text{\% vol of standard gas}} \quad (17)$$

Following injection of the experimental gas samples, the vol % of each gas species was calculated using Eq (18):

$$\text{Vol \% of analytical gas sample} = \frac{\text{peak area of gas species}}{\text{RF of standard gas}} \quad (18)$$

Several standard gas samples and experimental gas samples were injected into the GCs and the results showed good reproducibility with less than 1.2 % standard deviation (see 3.3.6).

The volume fraction of each gaseous species was used to calculate the mass of the gaseous products (in grams) using the Ideal Gas Law:

$$\text{mass of gaseous component (grams)} = \frac{P_T * \left(\frac{V_G}{100} * V_T\right) * MW}{R * T} \quad (19)$$

where P_T is the final pressure in atm of the cooled reactor, V_G is the vol % of the gaseous species obtained from Eq (18), V_T is the total volume of the reactor less the volume of the liquid phase, R is the gas constant (0.0821 L atm K^{-1} mol^{-1}) and T is the final temperature after cooling in K.

The mass of each gaseous component was used to calculate the calorific value of the product gas using Eq (3) described in section 2.6.

The gaseous yields were reported on a mol $kg^{-1}_{feedstock}$ basis using Eq (20):

$$\text{gas yield} = \frac{\text{mass of gaseous component}/_{Mw}}{\text{mass of feedstock}} * 1000 \qquad (\mathbf{20})$$

3.3.5.2. Liquid effluent

Following the experiment and gas analysis, the reactor was opened to collect the liquid effluent which is a mixture of solid residue, char and process water containing dissolved solids (water soluble products). The liquid effluent was poured into a clean reagent beaker and the volume noted. For SCWG reactions, the reactor was rinsed with deionised water several times until the rinsed liquid comes out clear. No additional deionised water was used in HTL experiments to prevent the dilution of the process water. 100 ml of dichloromethane was used as a solvent in rinsing the reactor to remove any biocrude and tars/chars adhering to the reactor walls. The liquid effluent was filtered through a pre-weighed Whatman filter paper (54 mm diameter) with a pore size of 22 μm under vacuum filtration to collect any solid residue/char. The collected residue was washed with DCM. The filtrate (process water plus solvent) was separated by gravity in a separating funnel. The solvent was evaporated and the mass of the biocrude fraction was determined. A sample of the separated process water was diluted using deionised water to a known volume and analysed by a total organic carbon analyser (HACH IL 550 TOC-TN) to determine the amount of total organic carbon in the process water. The inorganic carbon content (IC) was also noted as this represents the dissolved carbon dioxide in the water. TOC and IC measurements were repeated in duplicate and a mean value reported.

The mass of the total water soluble products (WSP) was determined by evaporating a known volume of the process water in a pre-weighed crucible over a water bath at 45 °C. The residue was dried at 105 °C then weighed to determine the mass of WSP and extrapolated to the full volume of process water. Measurements were repeated in duplicate and a mean value reported.

The main anions and cations were identified and quantified by ion chromatography (DX-100, Dionex, USA). Trace metal concentrations were measured by Optima 5300 DV inductively coupled plasma spectrometer (ICP) with optical emission spectrometry (Perkin Elmer, Cambridge, UK). Phenols, nitrate and total nitrogen levels were determined using colorimetry cuvettes (LCK345, LCK 340, LCK338, Hach-Lange, Germany). All measurements were repeated in duplicate and a mean value reported.

3.3.5.3. Biocrude from HTL of microalgae

The solvent was removed by evaporation to determine the mass of the biocrude. The biocrude yield is determined using Eq (21):

$$Yield = \frac{Biocrude\ mass}{Algae\ mass\ x\ (100-H_2O-Ash)/100} \quad (\mathbf{21})$$

The C, H, N, S contents of the biocrude from HTL and SCWG experiments and solid residue from SCWG experiments was measured using a CE Instruments Flash EA 1112 series elemental analyser. All measurements were repeated in duplicate and a mean value reported.

3.3.5.4. Catalyst weight and analysis by SEM/EDX

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 2%, indicating its hydrothermal stability. A high resolution scanning electron microscope (SEM, LEO 1530) coupled to an Energy Dispersive X-ray Spectrometer (EDXS) system was used to characterise and examine the surface of the catalyst.

3.3.5.5. 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 using Eq (3) (see section 2.6).

3.3.6 Experiment reproducibility

To test the reproducibility of the results, the product gas from the non-catalysed SCWG of *Laminaria hyperborea* was analysed by gas chromatography through injecting four samples to test the reproducibility of the gas analysis. The macroalga was gasified at 500 °C for 30 min at an algal concentration of 6.67%. Four samples of the product gas were analysed by gas chromatography. The results provided an accepted standard deviation of < 0.73%. The results are presented in Table 3.3. In addition, to test the reproducibility of the reactor, the SCWG of *Saccharina latissima* with and without catalyst was tested four times and the gas product was analysed by gas chromatography. The macroalga was gasified at similar conditions (500 °C, 30 min hold time and 6.67% algal concentration). The results provided an accepted standard deviation of < 1.2%. The results are summarised in Table 3.4.

Sample	H_2 (vol%)	CH_4 (vol%)	C_2-C_4 (vol%)	CO (vol%)	CO_2 (vol%)
Harvest Date: 18/07/2009					
L. hyperborea	26.1	11.4	6.79	0.84	54.9
L. hyperborea	26.6	11.8	7.47	0.82	53.3
L. hyperborea	26.1	11.5	7.18	0.82	54.4
L. hyperborea	26.2	11.3	6.92	0.86	54.7
Mean	26.3	11.5	7.09	0.84	54.3
Standard deviation	0.24	0.22	0.30	0.02	0.73

Table 3.3 Gas analysis from the SCWG of *L. hyperborea* at 500 °C, 30 min hold time and 6.67% algal concentration, to test reproducibility of gas chromatography – gas results presented in vol % with standard deviation < 0.73%.

Sample	H_2 (vol%)	CH_4 (vol%)	C_2-C_4 (vol%)	CO (vol%)	CO_2 (vol%)
Harvest Date: 15/07/2008					
S. latissima	26.3	12.6	6.69	1.55	52.9
S. latissima	25.4	14.4	7.93	1.51	50.8
S. latissima	26.7	12.3	7.24	2.12	51.7
S. latissima	25.1	13.3	8.30	1.23	52.0
Mean	25.9	13.2	7.5	1.6	51.9
Standard deviation	0.75	0.93	0.71	0.37	0.87
Harvest date: 15/07/2008					
S. latissima (1g Ru/Al_2O_3)	36.2	22.8	2.67	0.80	37.5
S. latissima (1g Ru/Al_2O_3)	34.6	23.4	2.73	0.63	38.6
S. latissima (1g Ru/Al_2O_3)	37.3	23.1	2.79	0.47	36.4
S. latissima (1g Ru/Al_2O_3)	36.9	21.7	2.62	0.45	38.3
Mean	36.3	22.8	2.7	0.59	37.7
Standard deviation	1.12	0.74	0.07	0.16	0.98

Table 3.4 Reproducibility test on SCWG of *Saccharina latissima* with and without catalyst (Ru/Al_2O_3) at 500 °C, 30 min hold time and 6.67% algal concentration – gas results presented in vol % with standard deviation < 1.2%.

4 SCWG of macroalgae combined with nutrient recycling for microalgae cultivation

4.1 Introduction

Following the main objective in studying the hydrothermal gasification of macroalgae under supercritical water conditions for the production of hydrogen and methane, a series of experiments were carried out with the following objectives:

- Investigate the product distribution and composition from the supercritical water gasification (SCWG) of macroalgae.
- Investigate the effect of ruthenium in catalysing the SCWG of macroalgae. Examine the effect on gaseous yields, gasification efficiency and catalyst poisoning.
- Investigate the influence of feedstock composition on gaseous yields. The composition of macroalgae has a seasonal variation and harvests across the season were hydrothermally gasified to analyse the effect of seasonal variation on gaseous yields and energy output.
- Assess the potential of recycling nutrients following hydrothermal gasification of macroalgae to cultivate microalgae. The process water from SCWG was used in cultivation trials of microalgae.

The composition of the gas product and process water from the SCWG of four macroalgae species were investigated (*Saccharina latissima*, *Laminaria digitata*, *Laminaria hyperborea,* and *Alaria esculenta*). In addition, summer harvests of the four macroalgae species were gasified with ruthenium catalyst (Ru/Al_2O_3).

The catalyst was chosen due to its successful application in catalysing hydrothermal gasification of biomass (see Table 2.17).

The potential for using the process water as a source of nutrients for microalgae cultivation was also assessed. Variation in the composition of macroalgae across the seasons has been reported (Adams et al., 2011), therefore, harvests of *Saccharina latissima* across the four seasons was gasified to assess the influence of biochemical content and ash on syngas composition. Following a series of dilutions, the process water from the non-catalysed and catalysed SCWG of *S. latissima* were used in cultivation trials of a microalga, *Chlorella vulgaris*, and compared to standard growth media, Bold's Basal Media (BBM).

4.2 Methodology

4.2.1 SCWG experiments

The SCWG experiments were performed in the 75 ml Parr reactor as described in Chapter 3. Each experiment involved loading the reactor with an algal paste made from 1.0 g of freeze dried macroalgae and 15 ml of deionised water. When required, 1.0 g of 5% Ru/Al_2O_3 catalyst was suspended at the top of the reactor in stainless steel mesh gauze. The reactor was purged with nitrogen and heated at an average rate of 30 °C min^{-1} to 500 °C and held at this temperature for a designated reaction time of 0, 30 or 60 min.

4.2.2 Cultivation trials

The setup for the cultivation trials involved seven bioreactors and a cultivation period of 14 days. Each bioreactor consisted of a 500 ml conical flask with a constant supply of air to provide a source of carbon dioxide and provide agitation of

the culture. The setup was illuminated for 12 hours a day using fluorescent lamps which were placed 40 cm above the bioreactors. Cultivation trials were conducted with the process waters from catalysed SCWG of *S. latissima*. The process waters were sterilized and diluted, using dilution factors; 50, 200 and 400x in 500 ml conical flasks ready for inoculation with 20 ml of *C. vulgaris*. BBM was used as the control experiment. The growth rate in the bio-reactors was monitored through daily measurements of turbidity and pH of the media. 10 ml samples were collected and measured for pH using a calibrated pH meter and for turbidity using a HACH-DR 890 Colorimeter. At the end of the cultivation period, the cultures were harvested by centrifugation, dried and weighed to obtain the mass of biomass produced after cultivation.

4.3 SCWG of macroalgae

The main gaseous products from the non-catalytic SCWG of the four macroalgae species were hydrogen, methane and carbon dioxide; however their concentrations in the product gas varied depending on the hold time. Taking *S. latissima* as an example (Figure 4.1), at 0 min hold time, a relatively high vol % of carbon monoxide (~ 20%) was present in the product gas. The decrease in vol % of carbon monoxide as the hold time increased to 30 and 60 min hold times suggests consumption of carbon monoxide through the water-gas shift reaction and methanation reaction. Studies have suggested that the water-gas shift reaction rate in SCWG is improved due to the presence of inorganic metal salts and by variation of the physical properties of water at supercritical conditions (Kruse et al., 2008; Sınağ et al., 2003). Adams et al., (2011) report high concentrations of inorganic metals in macroalgae in studying the chemical composition of macroalgae as a bioenergy feedstock. SCWG at longer hold times (30 and 60 min) results in high amounts of hydrogen and carbon

dioxide in the product gas, 4.23 and 6.26 mol H_2 $kg^{-1}_{macroalgae}$ respectively. Similar high amounts of H_2 and CO_2 from the hydrothermal gasification of macroalgae have been reported (Schumacher et al., 2011).

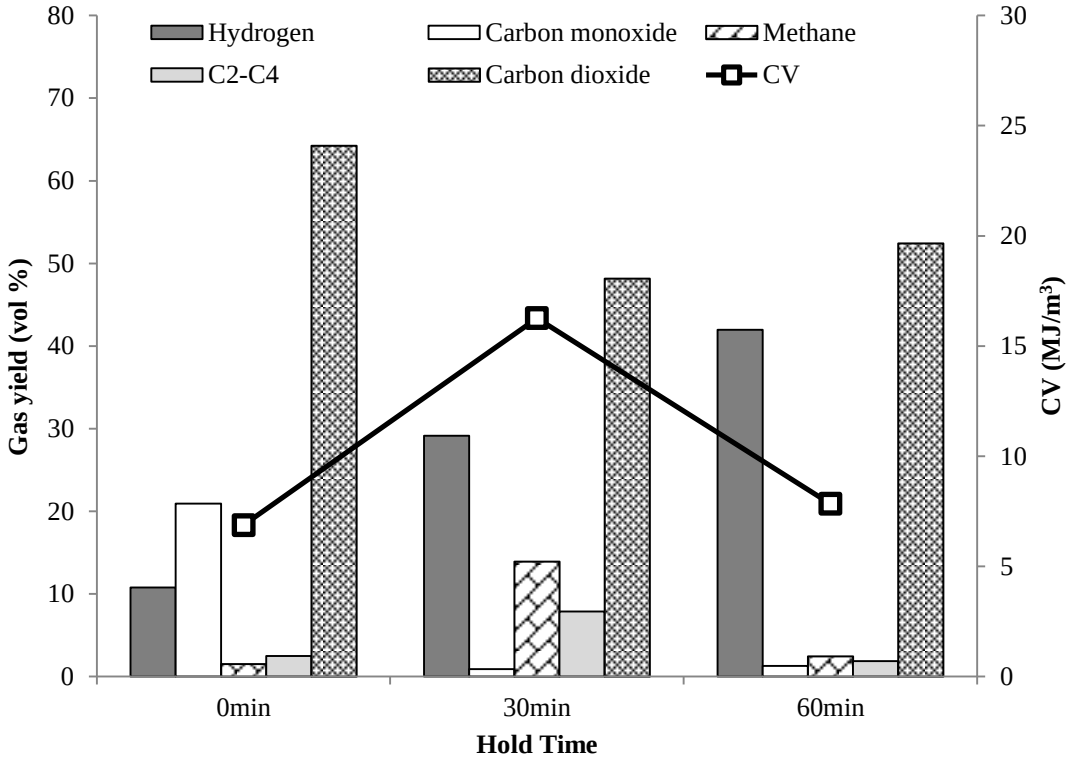


Figure 4.1 Gas composition from the supercritical gasification of *S. latissima* at hold times of 0, 30, and 60 minutes. T_{end} = 500 °C, P_{end} = 23.6 - 28.1 MPa, algal concentration = 6.67 wt.%. Calorific values using second y-axis.

The calorific value of the product gas from the SCWG of *S. latissima* varied based on the gas composition with the highest calorific value (16.3 MJ m^{-3}) obtained at a hold time of 30 min due to the higher percentage of CH_4 and C_2 – C_4 gases compared to the product gas at 0 and 60 min hold time.

Table 4.1 summarises the gas yields from SCWG of the four macroalgae species at a hold time of 30 min and compares them to gas yields from the SCWG of lignocellulosic biomass and microalgae at similar conditions (Yanik et al. (2007) and Yoshida et al. (2003)). SCWG of macroalgae resulted in hydrogen yields of 3.3 - 4.2 mol H_2 $kg^{-1}_{macroalgae}$ and methane yields of 1.6 - 3.3 mol $kg^{-1}_{macroalgae}$ which compares favourably to lignocellulosic biomass and microalgae.

Sample	Temp (°C)	Feed conc. (wt. %)	Hold time (min)	H_2 (mol kg^{-1})	CH_4 (mol kg^{-1})	C_2-C_4 (mol kg^{-1})	CO (mol kg^{-1})	CO_2 (mol kg^{-1})	Reference
S. latissima	500	6.7	30	4.2	2.0	1.8	0.25	7.9	
L. digitata				3.6	1.9	1.7	0.14	8.2	
A. esculenta				3.3	3.3	2.3	0.16	7.8	
L. hyperboria				3.7	1.6	1.5	0.13	7.3	
Spirulina platensis	500	6.7	30	5.0	5.25	3.5	1.0	9.0	(Onwudili et al., 2013)
Chlorella vulgaris				4.0	3.9	3.25	1.0	10.0	
Lignocellulosic biomass (cellulose, lignin, hemicellulose mixtures)	500	5.9	60	2 – 4.5	1 – 5			4 - 10	(Yanik et al., 2007)
Lignocellulosic biomass (cellulose, xylan, lignin mixture (with Ni catalyst)	400	25 MPa†	20	1.7 – 5.3	0.9–1.1	0.1 – 0.3		6.6 – 9.5	(Yoshida et al., 2003)

† 0.1 g of feedstock used and water added to the reactor establish a pressure of 25 MPa

Table 4.1 Gas yields (mol kg^{-1}) from SCWG of macroalgae compared to microalgae and lignocellulosic biomass.

4.4 Catalytic SCWG of macroalgae

The four macroalgal species were gasified in the presence of 5% Ru/Al_2O_3 catalyst with a catalyst ratio of 1:1. The effect of the catalyst on gas yields is presented in Table 4.2. On average, catalytic SCWG with a 1:1 ratio of catalyst to algae resulted in a doubling of the hydrogen yield and a trebling of the methane yield compared to non-catalytic SCWG. *S. latissima* was further experimented with 2:1 catalyst to algae ratio. Increasing the catalyst to algae ratio to 2:1 resulted in a 22% increase in methane yield coupled with a 22% decrease in hydrogen yield. This can be explained by the promotion of the methanation reaction by the Ru catalyst which results in the consumption of hydrogen to produce methane and water.

Sample	Catalyst ($g_{catalyst}$:g_{algae})	H_2 (mol kg^{-1})	CH_4 (mol kg^{-1})	C_2-C_4 (mol kg^{-1})	CO (mol kg^{-1})	CO_2 (mol kg^{-1})
S. latissima	-	4.23	2.01	1.82	0.25	7.86
	1:1	10.2	6.38	1.00	0.18	10.5
	2:1	7.92	7.81	0.02	0.07	11.5
L. digitata	-	3.57	1.85	1.69	0.14	8.23
	1:1	7.85	6.05	0.93	0.12	10.2
A. esculenta	-	3.30	3.29	2.34	0.16	7.80
	1:1	7.75	5.94	0.55	0.05	10.8
L. hyperboria	-	3.70	1.56	1.48	0.13	7.34
	1:1	8.50	4.67	1.05	0.10	10.9

Table 4.2 Experimental conditions and results for the hydrothermal gasification of macroalgae samples, T_{end} = 500 °C, P_{end} = 23.6 – 28.1 MPa, holding time = 30 min, algal concentration = 6.67 wt.%, 5% Ru/Al_2O_3 catalyst

The results for the carbon balances (over 90%) in Table 4.3 suggest good accountability for the products. The carbon gasification efficiency increased to over 90% in the presence of fresh catalyst compared to non-catalysed SCWG of

S. latissima. This can be explained by examining the gas yields in Table 4.2 which show a doubling in the yield of methane for catalysed SCWG of *S. latissima* compared to non-catalysed SCWG. High gas production with high levels of methane has been reported by Osada et al. (2006) in ruthenium catalysed biomass gasification experiments. In this study, catalysed SCWG of *S. latissima* with a 1:1 and 2:1 catalyst to algae ratio resulted in methane yields of 6.38 and 7.81 mol $kg^{-1}_{macroalgae}$ respectively.

Experiment Run	Gas (%)	Solid Residue (%)	IC (%)	TOC (%)	Carbon Balance (%)	CGE (%)
Non-catalysed	51.63	11.84	6.15	22.23	91.9	57.78
Standard deviation	0.87		2.39	3.55	4.36	
Fresh Catalyst	75.60	7.48	16.09	15.12	114.2	91.69
Standard deviation	0.98		0.72	0.35	1.26	
Regenerated catalyst	66.08	5.54	8.46	18.53	98.6	74.54
Standard deviation	0.98		0.39	0.03	1.06	
Regenerated catalyst (2x)	68.64	10.77	7.03	15.48	101.9	75.67
Standard deviation	0.98		0.26	0.01	1.01	
Regenerated catalyst (3x)	63.48	12.81	7.64	25.75	109.7	71.12
Standard deviation	0.98		0.04	0.03	0.98	

Table 4.3 Carbon balance and gasification efficiency from supercritical gasification of macroalgae, T_{end} = 500 °C, P_{end} = 23.6 - 28.1 MPa, holding time = 30 min, algal concentration = 6.67 wt.%, 5% Ru/Al_2O_3 catalyst. IC = inorganic carbon, TOC = total organic carbon, CGE = Carbon Gasification efficiency.

Experiment Run	H_2 (mol kg^{-1})	CH_4 (mol kg^{-1})	C_2-C_4 (mol kg^{-1})	CO (mol kg^{-1})	CO_2 (mol kg^{-1})
Non-catalysed	4.23	2.01	1.82	0.251	7.86
Fresh Catalyst	10.2	6.38	1.00	0.175	10.5
Regenerated catalyst	7.30	3.62	1.58	0.185	11.0
Regenerated catalyst (2x)	6.75	2.75	1.45	0.096	10.6
Regenerated catalyst (3x)	6.20	2.74	1.60	0.127	9.80

Table 4.4 Gas composition and yields from supercritical gasification of *S. latissima* T_{end} = 500 °C, P_{end} = 23.6 - 28.1 MPa, holding time = 30 min, algal concentration = 6.67 wt.%, 5% Ru/Al_2O_3 catalyst

The yield of combustible gases (H_2, C_1-C_4) of the gas product increased by 30% in the presence of ruthenium catalyst (Table 4.2) for all 4 species of macroalgae. For *S. latissima*, the hydrogen yield increased from 4.23 mol kg^{-1} to 10.2 mol kg^{-1} in the presence of catalyst. Table 4.2 and Table 4.4 summarise the catalysed runs in this study showing an increase of over 100% in hydrogen yield and over 200% in methane yield of the gas composition as the catalyst promotes the formation of methane. *S. latissima* and *L. digitata* showed the largest increase in yields of combustible gas through catalysed SCWG.

4.5 Catalyst poisoning and spent catalyst re-use

Several gasification experiments were performed in order to regenerate the catalyst and test the effect of poisoning from sulphur and calcium (present in the ash). Osada et al. (2007b) studied the effect of sulphur on supercritical catalytic gasification of lignin where they concluded that sulphur poisoned the active sites for carbon-carbon bond breaking and methanation reaction but did not block sites for the water-gas shift reaction. The shift in the selectivity of the gas products to hydrogen during catalyst re-use, may be related to catalyst deactivation due to sulphur poisoning. In a recent study, Guan et al. (2012b) demonstrated the

deactivation of Ru/C catalyst during the SCWG of the microalga *Nannochloropsis*. They found that subsequent re-use of the catalyst resulted in poorer gas yields due to loss of catalytic activity and traced the problem to the sulphur content of the microalga. Additionally, Onwudili and Williams (2013) recently showed that hydrogen yields increased while methane yields decrease during hydrothermal gasification of glucose using spent Ru/Al_2O_3 catalyst, which agreed with the observations of Osada et al. Results in this study (Table 4.4) show a decrease in molar yield of CH_4 by 40% and an increase of CO_2 by 32% through re-using the catalyst. Likewise, the gasification efficiency drops from 92% to 71%. Waldner et al. (2007) report catalyst deactivation due to the formation of stable ruthenium sulphate complexes in syngas production from gasification of biomass. Figure 4.2 shows images of the surface of fresh and regenerated catalyst using SEM-EDXS. Results highlight the sulphur and calcium build-up on the catalyst surface.

(a)

(b)

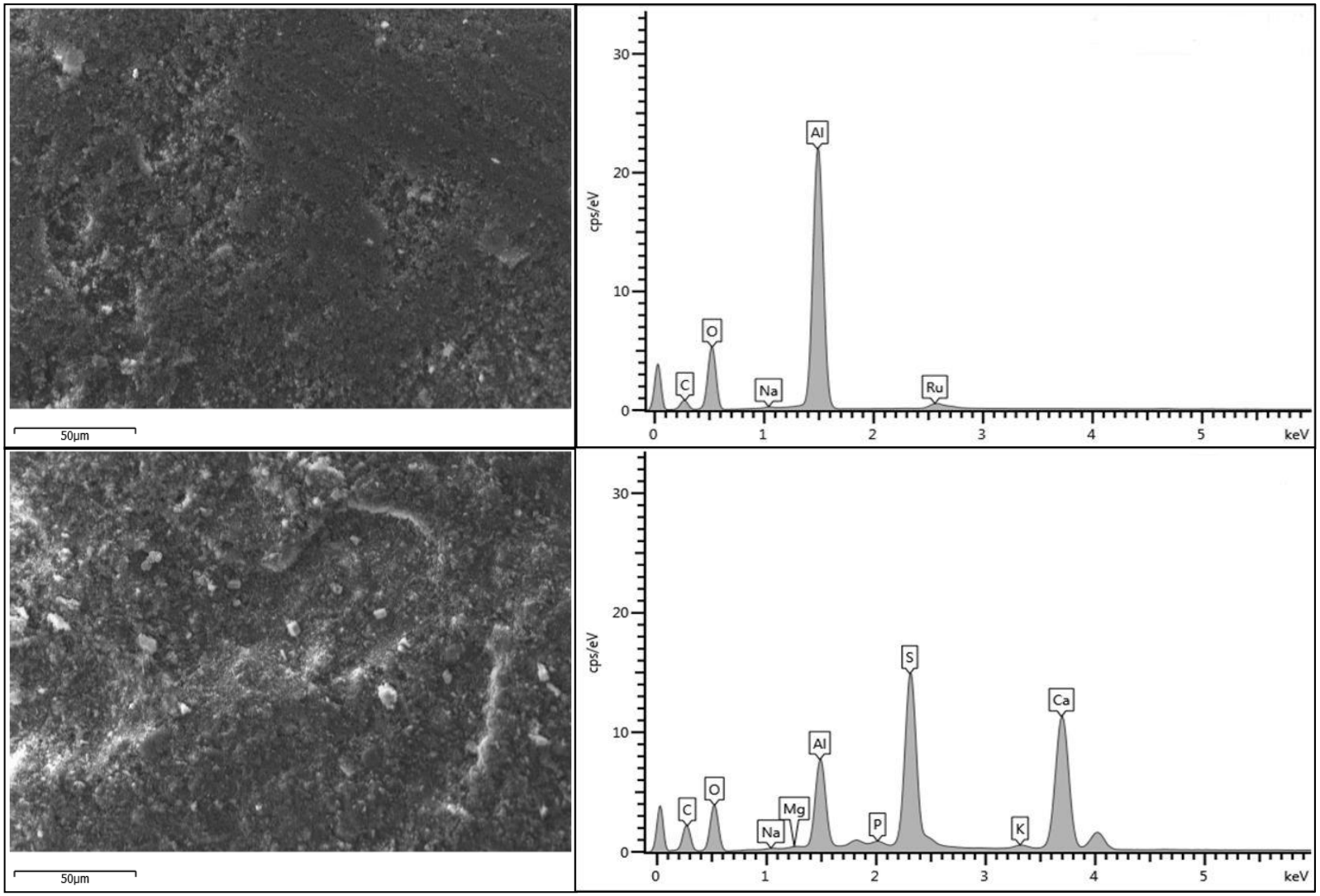


Figure 4.2 SEM-EDXS of (a) fresh and (b) used Ru/Al_2O_3 catalyst surface at 1200x magnification (cps/eV: counts per second/electonvolt).

4.6 Hydrogen yields

The hydrogen yields for the four macroalgae species are higher than those reported for microalgae in literature; *Chlorella vulgaris* (Chakinala et al., 2010; Minowa and Sawayama, 1999), *Spirulina platensis* (Stucki et al., 2009a), *Nannochloropsis* sp. (Brown et al., 2010). At a temperature of 500 °C, hold time of 60 min, and 5% algal concentration Schumacher et al. (2011) produced 6.0 mol and 6.5 mol H_2 $kg^{-1}_{seaweed}$ from *L. digitata* and *A. esculenta* respectively. In this study, non-catalysed gasification of *S. latissima* at 500 °C, 60 min hold time and 6.67 wt.% algal concentration produced 6 mol H_2 $kg^{-1}_{macroalgae}$. Non-catalysed gasification of summer samples of both *L. digitata* and *A. esculenta* at 500 °C, 30 min hold time and 6.67 wt.% algal concentration, produced 4 mol of H_2 $kg^{-1}_{macroalgae}$ with the catalysed experiments producing 8.0 mol H_2 $kg^{-1}_{A.\ esculenta}$ and 8.5 mol H_2 $kg^{-1}_{L.\ digitata}$.

4.7 Effect of seasonal variation on SCWG of *Saccharina latissima*

Non-catalysed SCWG of *S. latissima* harvested across the four seasons at 500 °C, 30 min hold time and 6.67 wt.% algal concentration resulted in a hydrogen yield of 4.3 mol kg^{-1} that did not vary significantly across the samples. The seasonal variation in biochemical and ash composition of seaweed is reflected in the calorific value of the product gas from SCWG (Figure 4.3); 16.3 MJ m^{-3} for the summer (July) harvest and 14.0 MJ m^{-3} for the winter (Jan) harvest of *S. latissima*. The hydrocarbon (C_1-C_4) yield varied between summer (July) and winter (Jan) harvests; 3.63 mol kg^{-1} and 3.03 mol kg^{-1} respectively. The higher hydrocarbon yield from the summer harvest can be explained by the higher carbohydrate and lower ash content

compared to winter harvest (Figure 4.4). The ash content of the summer harvest was 23.4% compared to the winter harvest of 44.0%.

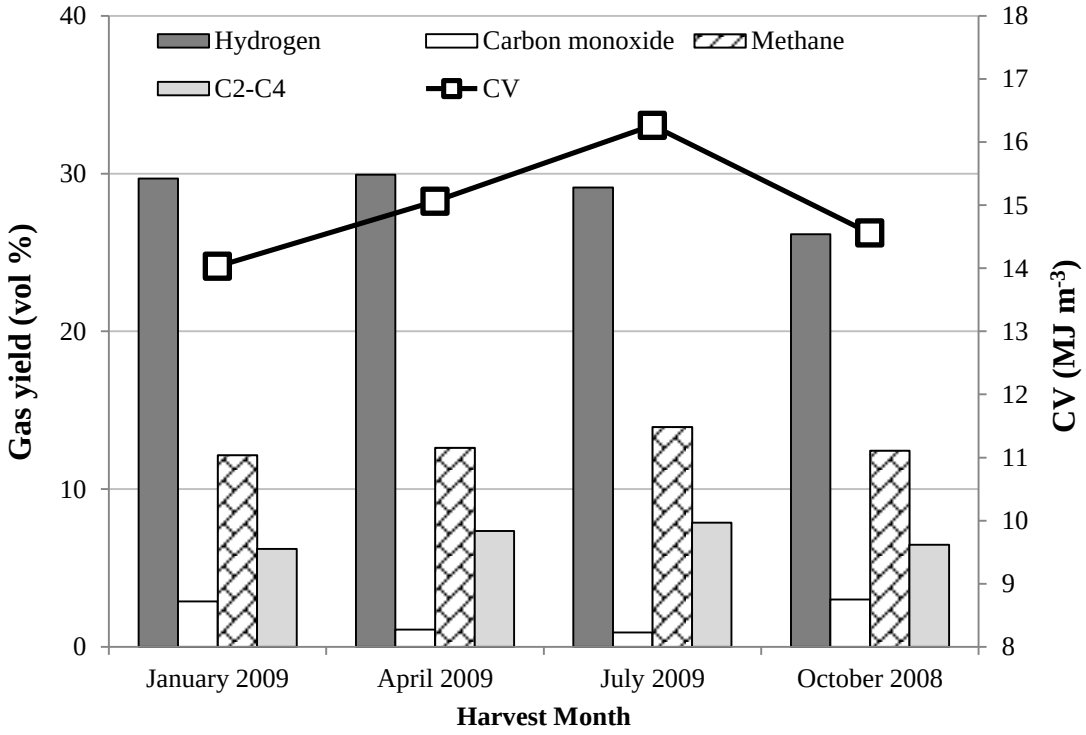


Figure 4.3 Gas composition from the SCWG of *S. latissima* at four harvest points across the year at 500 °C, 30 min hold time and 6.67 wt.% algal concentration. Calorific values using second y-axis.

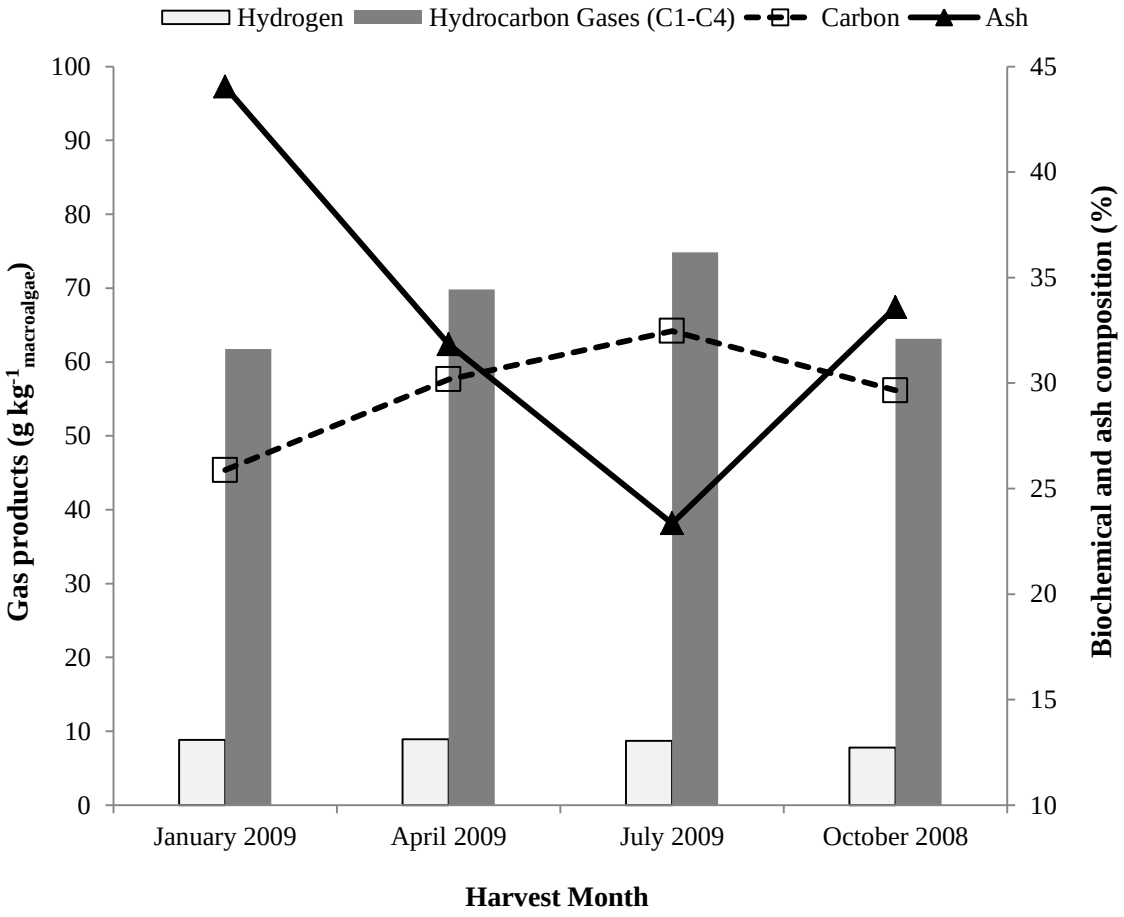


Figure 4.4 Hydrogen and hydrocarbon gas yields from the SCWG of *S. latissima* at 500 °C, 30 min hold time and 6.67 wt.% algal concentration at four harvest points across the year. Carbon and ash content using second y-axis.

4.8 Process water and cultivation trials of *Chlorella vulgaris*

Nutrients and important metals from the process waters of catalysed and non-catalysed SCWG of *S. Latissima* are presented in Table 4.5. They both compare favourably with the standard growth medium, BBM, due to high concentrations of nitrogen and potassium which in addition to carbon and phosphorus are essential for algal growth (Grobbelaar, 2004). Compared to non-catalysed process water, the catalysed process water contains a lower concentration of phenols which are known growth inhibitors. Phenols are toxic compounds to microalgae and alter the structure

and function of membranes due to hydrophobic interactions causing partitioning of lipophilic compounds into the membrane (Leonard and Lindley, 1999). Studies by Nakai et al. (2001) and Scragg (2006) have demonstrated the inhibitory effects of phenols on algal growth (Jena et al., 2011b). In testing the effect of phenol on the growth of *C. vulgaris*, Scragg reports the microalga was inhibited by phenol concentrations of 100 - 400 ppm. In this study, there is a reduced growth rate in the non-catalysed process water corresponding to an increased phenol content compared with the catalytic process water suggesting some inhibitory effect. This is clearer in the cultivation trial using 50x dilution (Figure 4.5).

ppm	**Non-catalysed *S. latissima***	**Catalysed *S. latissima***	**BBM**
TOC	4,313	3,291	-
Total N	908	1,274	41
NH_4^+	696	1,180	-
PO_4^{3-}	-	23	153
K	5,715	4,657	84
Acetate	1,467	1,230	-
NO_3^-	165	478	182
Phenols	405	151	-

Table 4.5 Nutrients and important metals in ppm from the process water of SCWG of *S. latissima* T_{end} = 500 °C, P_{end} = 23.6 – 28.1 MPa, compared to standard growth medium BBM.

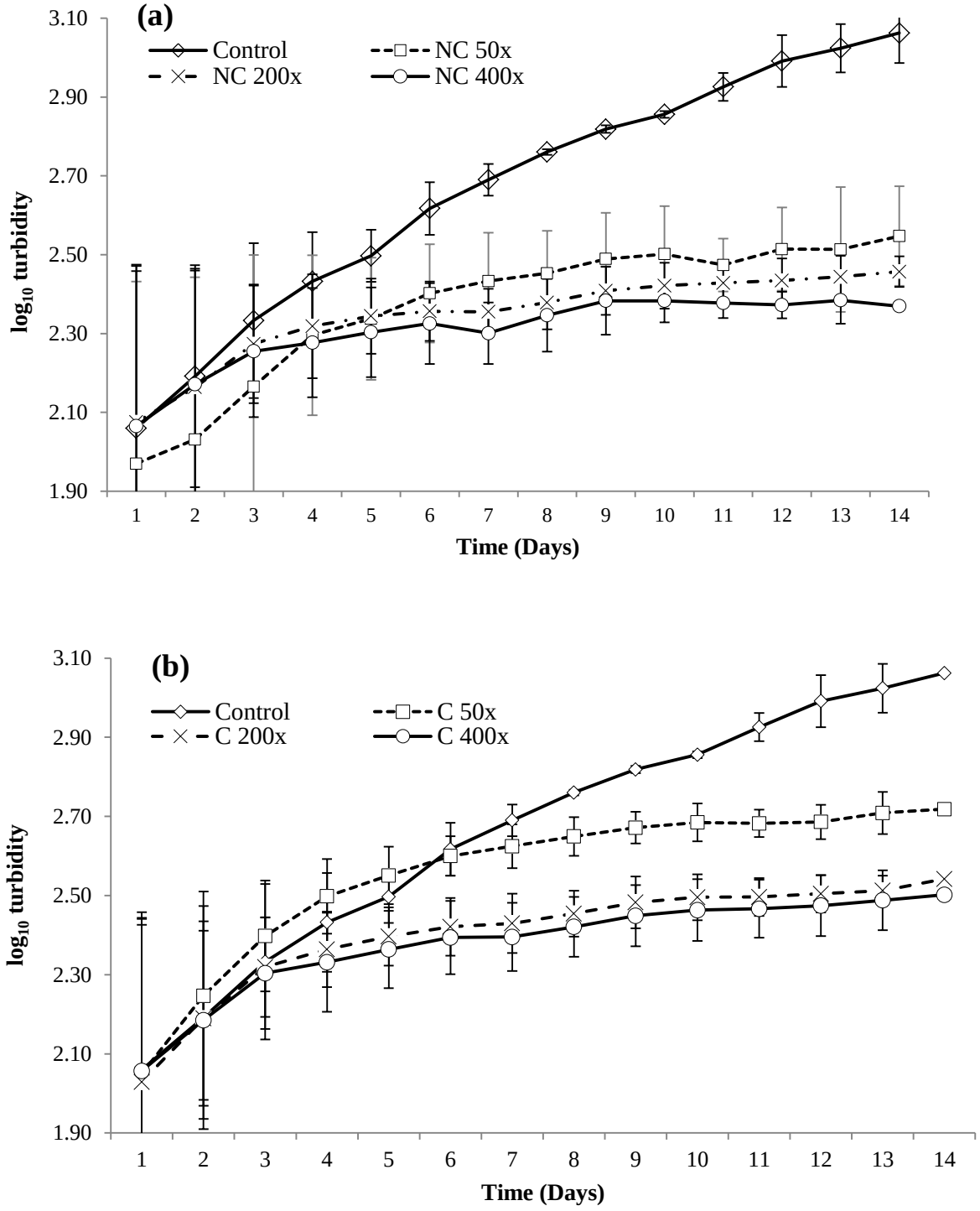


Figure 4.5 Growth of *C. vulgaris* across the 14 day cultivation period as a function of log turbidity measurements. Process water and dilutions from SCWG of *S. latissima* (a) without catalyst (NC); (b) with catalyst (C).

High concentration of acetate in the process water may be beneficial due to mixotrophic growth, thus increasing biomass productivity (Bhatnagar et al., 2011). However, nickel concentrations as low as 0.85 ppb have an inhibitory effect on the growth of microalgae (*C. vulgaris* for example (Spencer and Nichols, 1983). In testing the effect of nickel on algae growth, Haiduc et al. (2009) report adverse effects at nickel concentrations of 1, 5 and 10 ppm with complete inhibition of cell division at 25 ppm. The process water from catalysed SCWG contained nickel at concentrations less than 4 ppm and following dilution for cultivation trials this resulted in concentrations of less than 1.2 ppm.

The growth of microalgae reduces as the process water is diluted suggesting insufficient nutrient availability. This is illustrated by a higher growth rate with the 50x dilution compared to the 200 and 400x dilution (Figure 4.5). This is also confirmed by measuring the total biomass following the 14 day trials shown in Figure 4.6. The cultivation trials are compared to the growth using a standard medium (BBM). In terms of biomass concentration (Figure 4.6) *C. vulgaris* grew best in the catalysed process water at 50x dilution with a final yield of 400 mg L^{-1}.

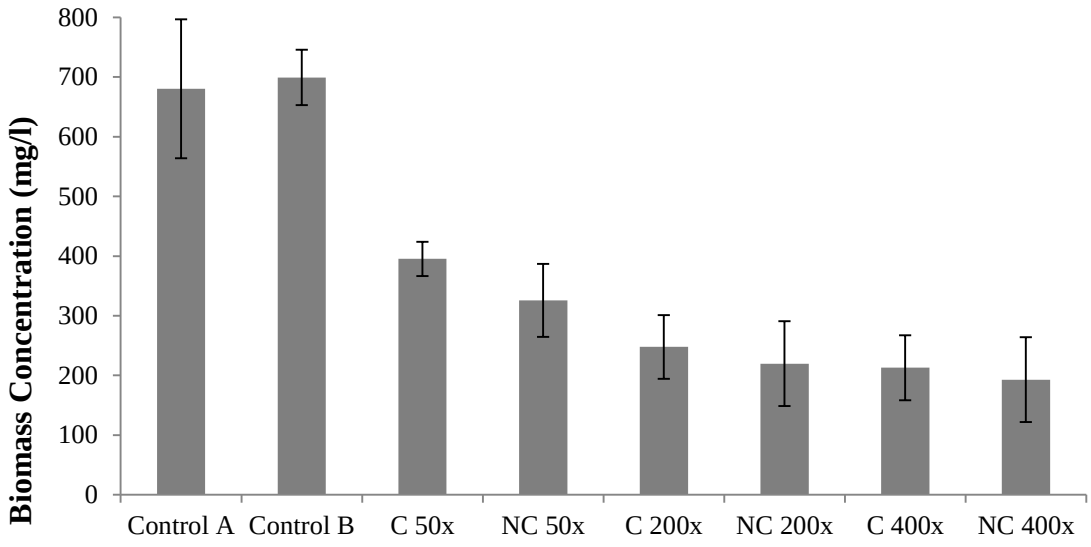


Figure 4.6 *C. vulgaris* concentration (mg L^{-1}) following 14 day cultivation in bioreactors. Process water and dilutions from SCWG of *S. latissima*; without catalyst (NC); with catalyst (C).

4.9 Conclusions

The results indicate that the four macroalgae species (*Saccharina latissima*, *Laminaria digitata*, *Laminaria hyperborea* and *Alaria esculenta*) can be successfully gasified in supercritical water to produce a product gas rich in hydrogen and methane. Non-catalysed SCWG of macroalgae resulted in hydrogen yields of 3.3 - 4.2 mol H_2 kg^{-1} and methane yields of 1.6 - 3.3 mol $kg^{-1}_{macroalgae}$ which compared favourably to lignocellulosic biomass and microalgae. Catalytic SCWG using ruthenium resulted in yields of 7.8 - 10.2 mol H_2 kg^{-1} and methane yields of 4.7 - 6.4 mol $kg^{-1}_{macroalgae}$.

High gasification efficiencies (> 90%) were obtained in the presence of ruthenium catalyst with the yield of combustible gases of the product gas increasing by 30%. The adverse effect of sulphur was demonstrated through a decrease in the yield of methane following poisoning of the catalyst surface.

The summer harvest of *S. latissima* yielded a higher calorific value product gas due to its higher carbohydrate and lower ash content compared to harvests from other seasons. The calorific value of the product gas from SCWG of *S. latissima* was 16.3 MJ m^{-3} for the summer (July) harvest and 14.0 MJ m^{-3} for the winter (Jan) harvest.

The process waters from SCWG of *S. latissima* compared favourably with standard growth media (BBM). Process waters from catalytic SCWG of *S. latissima* showed significant growth of *C. vulgaris* suggesting suitability of nutrient recycling from SCWG of macroalgae.

5 Parametric study on SCWG of *Laminaria hyperborea*

5.1 Introduction

This chapter investigates the SCWG of *Laminaria hyperborea*. It explores the potential of SCWG of the macroalgae for hydrogen and methane production. Selectivity towards hydrogen and/or methane production from macroalgal SCWG was assessed as to whether it can be controlled by the combination of catalysts and varying reaction conditions. A series of experiments were carried out with the following objectives:

- Investigate the product distribution and composition from the supercritical water gasification (SCWG) of *Laminaria hyperborea*.
- Analyse the influence of catalysts on the gaseous yield and gasification efficiency from the SCWG of macroalgae. The chosen catalysts (ruthenium, nickel, alkali reagents such as sodium hydroxide) have a proven track record in successfully catalysing hydrothermal gasification reactions – particularly using biomass and biomass model compounds.
- Study the effect of varying reaction parameters on the gaseous yield, gasification efficiency and energy recovery. Reaction parameters include:
    - SCWG temperature
    - Reaction hold time
    - Feed concentration (macroalgae concentration)
    - Catalyst loading

5.2 Methodology

The SCWG experiments were performed in the 75 ml Parr reactor as described in Chapter 3. The reactor was purged with nitrogen and heated at a rate of 30 °C min^{-1} to the required temperature for each experiment for the designated reaction time. The conditions for each experiment are summarised below:

- Effect of catalyst – ruthenium, nickel and sodium hydroxide were used as catalysts under conditions of 500 °C, 30 min hold time, 6.67% feed concentration (1.0 g of algae in 15 ml deionised water). The mass and loading of each catalyst used was as follows: 1.0 g 5% Ru/Al_2O_3, 1.0 g 5% Ni/Al_2O_3 and 1.5 M NaOH.
- Effect of catalyst loading – ruthenium and sodium hydroxide were used at catalysts under conditions of 500 °C, 30 min hold time, 6.67% algal concentration (1.0 g of algae in 15 ml deionised water). The mass of Ru/Al_2O_3 catalyst was fixed at 1.0 g and the metal loading on the support was varied (5%, 10% and 20%). The concentrations of sodium hydroxide tested were 0.5, 1.5 and 3.0 M.
- Effect of feed concentration – algal concentration was varied at 500 °C, 30 min hold time using 20% Ru/Al_2O_3 and 1.5 M NaOH as catalysts. The algal concentrations used were 3.33%, 6.67% and 13.33%.
- 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 6.67%.
- Effect of temperature – the effect of temperature (400, 450, 500, 550 °C) was studied at a feed concentration of 6.67% and a total reaction time of 32 min, using 20% Ru/Al_2O_3.

5.3 Catalytic SCWG of macroalgae: *Laminaria hyperborea*

Figure 5.1 shows the gas yields, carbon gasification efficiency and energy recovery from the use of ruthenium, nickel and sodium hydroxide catalysts compared to a non-catalysed experiment and Table 5.1 shows the mass balances.

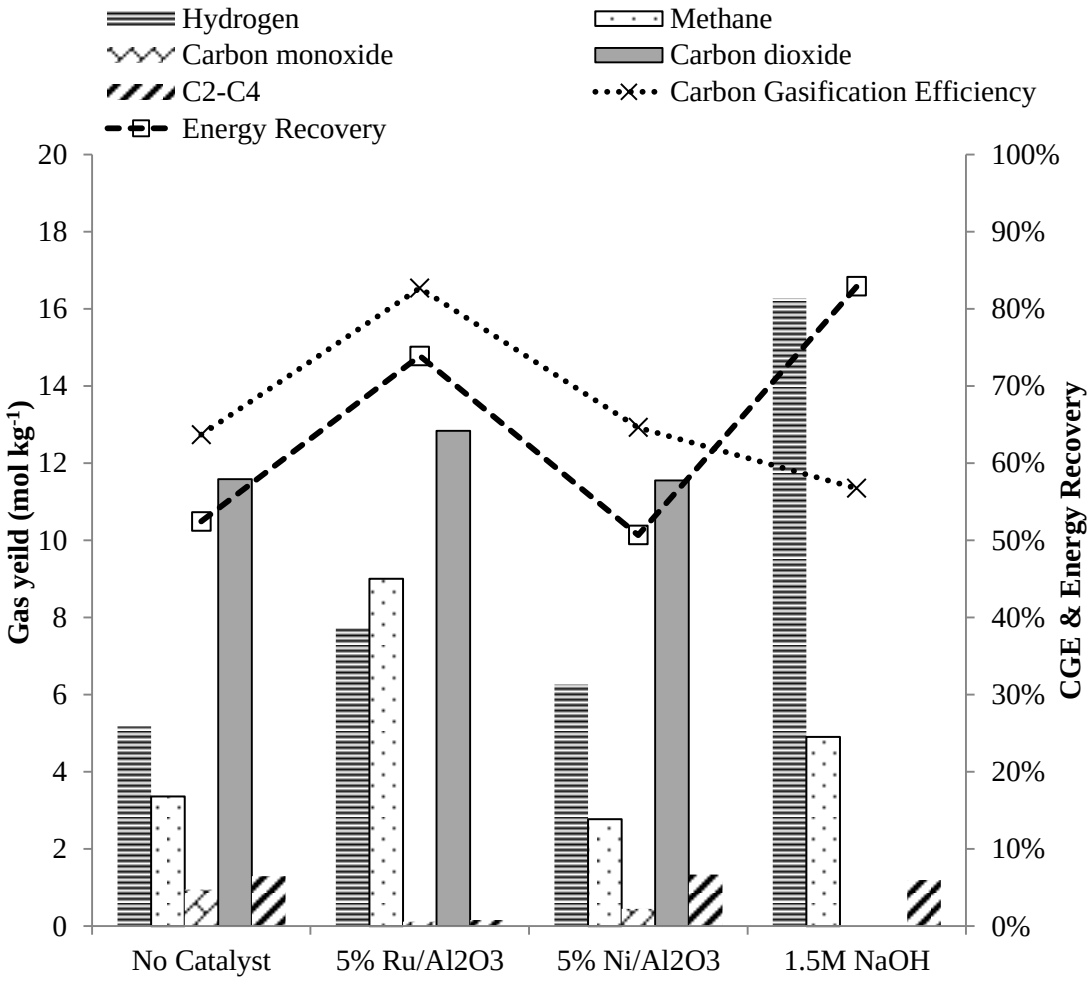


Figure 5.1 Gas yield, carbon gasification efficiency and energy recovery from the SCWG of *L. hyperborea* at 500 °C, 30 min hold time, 6.67% algal concentration, with and without catalysts.

	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 5.1 Mass balances from the SCWG of *L hyperborea* at 500 °C, 30 min hold time, 6.67% algal concentration, with and without catalysts.

The mass balance for each experiment was >97%. Hydrogen, methane and carbon dioxide were the main three constituents of the gas product from the non-catalysed SCWG of *L. hyperborea*. Small amounts of carbon monoxide and C_2 - C_4 hydrocarbons were also produced. The energy recovery (an expression of how much chemical energy of the feedstock is recovered in the gas product) was 52.4% for the non-catalysed SCWG and the carbon gasification efficiency was 63.7%. Catalytic SCWG using nickel showed no significant variation in gas yields, carbon gasification or energy recovery compared to the non-catalysed experiment. Higher hydrogen and methane yields were observed using ruthenium and sodium hydroxide catalysts which resulted in an increase in energy recovery.

The yield of hydrogen was approximately three times higher when using sodium hydroxide (16.3 mol H_2 $kg^{-1}_{macroalgae}$) compared to non-catalysed SCWG of *L. hyperborea* (5.18 mol H_2 $kg^{-1}_{macroalgae}$). 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 (Figure 5.1). 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).

5.4 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 6.67%. The mass of Ru/Al_2O_3 catalyst was fixed at 1.0 g. Figure 5.2 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 0.5 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.

5.5 Effect of feed concentration

The solid concentration in the feedstock has an important effect on the gasification efficiency in supercritical water with experimental data indicating a decline in gasification efficiency when the feed concentration exceeds 2% (Basu, 2010; Mettanant et al., 2009; Schmieder et al., 2000). However, very low feed concentrations require high pumping costs and effluent disposal/recovery thus impeding commercialisation of supercritical water gasification technology.

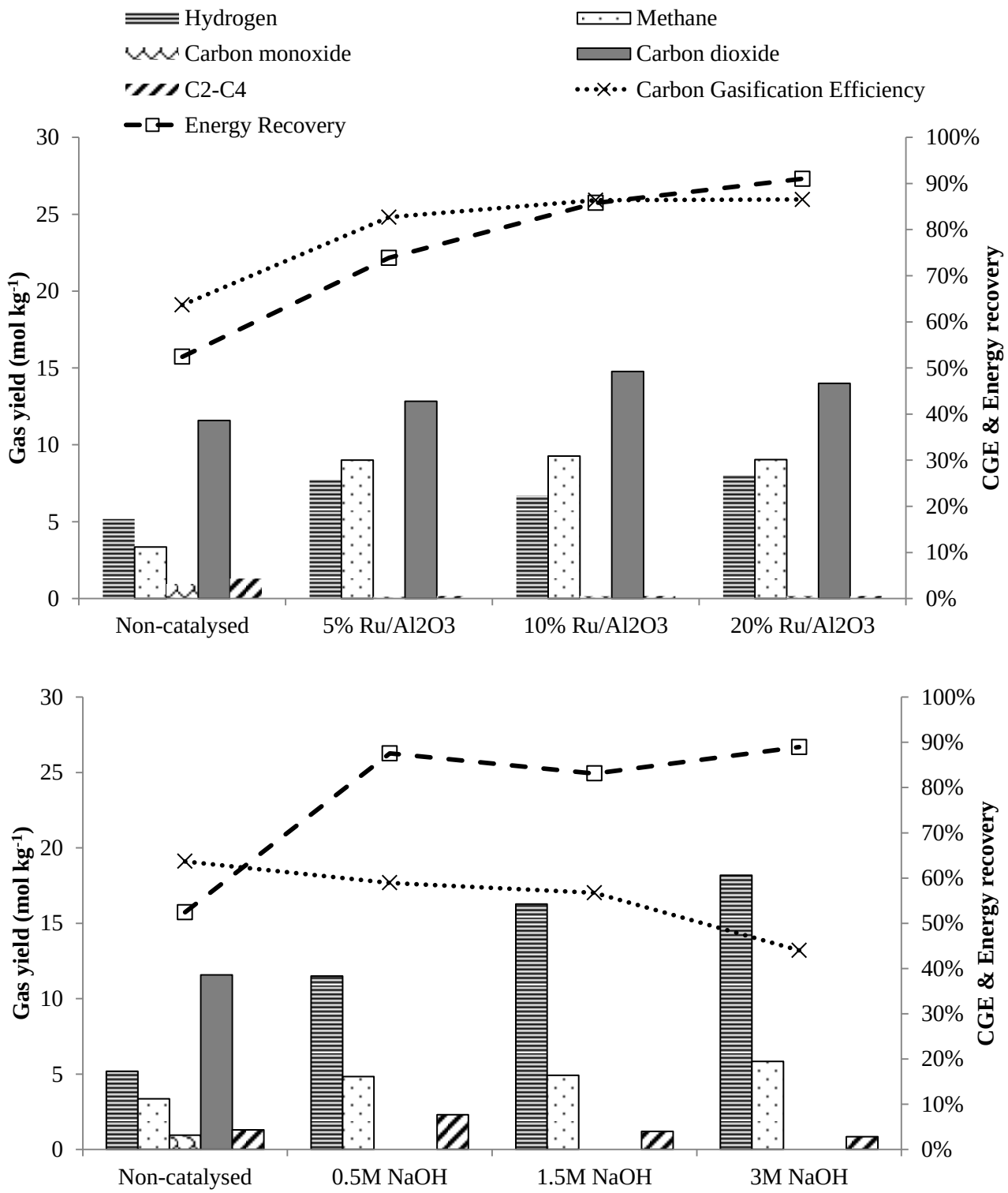


Figure 5.2 Effect of catalyst loading on SCWG of *L. hyperborea* at 500 °C, 30 min hold time, 6.67% feed concentration.

Figure 5.3 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 1.5 M NaOH catalysts. Methane yields from the ruthenium catalysed experiments showed no significant difference with varying feed concentrations of 3.33, 6.67 and 13.3%. However, the 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 6.67% 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 $kg^{-1}_{L.\ hyperborea}$ and 6.21 mol CH_4 $kg^{-1}_{L.hyperborea}$ resulting in an energy recovery of 111%. 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 6.67 and 13.3% resulted in a larger decrease in energy recovery to 82.9 and 50.4% respectively.

5.6 Effect of hold time

The effect of varying hold times (0, 30, 60 and 120 min) on the SCWG of *L. hyperborea* was studied at 500 °C and a feed concentration of 6.67%. Figure 5.4 shows the results from non-catalysed experiments and experiments using 5% Ru/Al_2O_3 and 1.5 M 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 $kg^{-1}_{L.\ hyperborea}$ respectively. The highest hydrogen yield obtained using

sodium hydroxide was 16.3 mol $kg^{-1}_{L.\ hyperborea}$ 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.

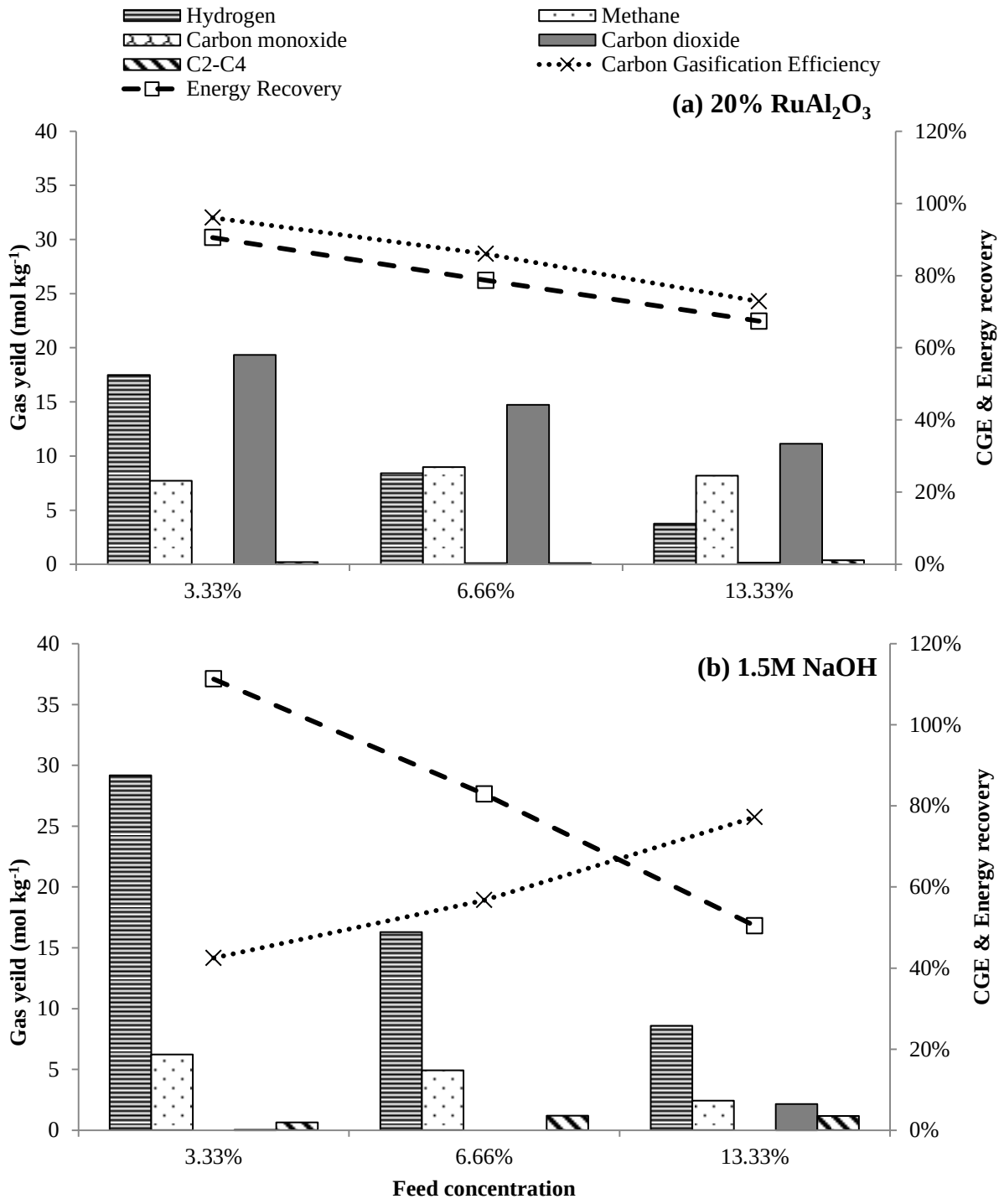


Figure 5.3 Effect of feed concentration on SCWG of *L. hyperborea* at 500 °C, 30 min hold time with catalysts: (a) 20% Ru/Al_2O_3 (b) 1.5 M NaOH.

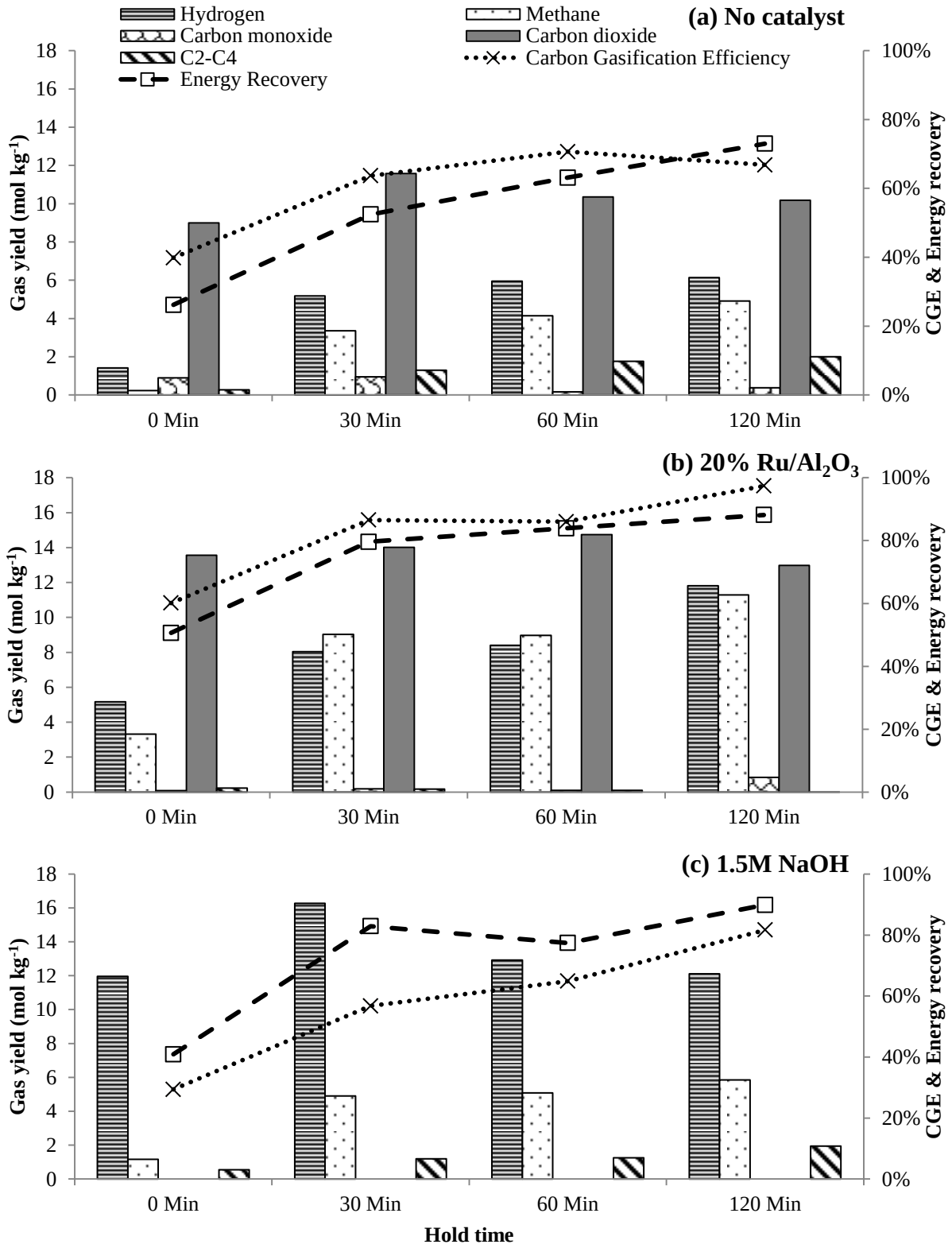


Figure 5.4 Effect of hold time on SCWG of *L. hyperborea* at 500 °C, 6.67% feed concentration (a) non-catalysed (b) 20% Ru/Al_2O_3 (c) 1.5 M NaOH.

5.7 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 5.5 shows the effect of increasing temperature (400, 450, 500 and 550 °C) on the SCWG of *L. hyperborea* at a feed concentration of 6.67% 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 $kg^{-1}_{L.\ hyperborea}$) compared to non-catalysed SCWG.

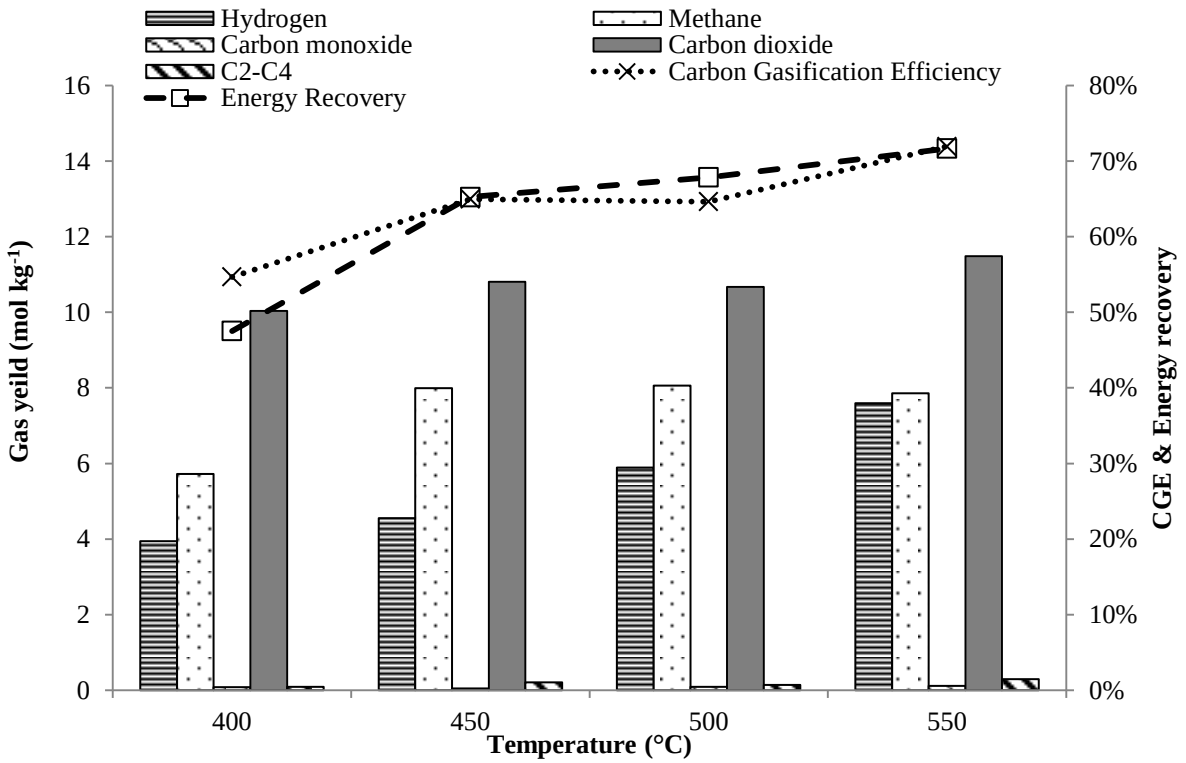


Figure 5.5 Effect of temperature on SCWG of *L. hyperborea*. 32 min total reaction time and 6.67% feed concentration with 20% Ru/Al_2O_3 as a catalyst

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Improvements in gasification efficiencies or yields of 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 °C against the net gain in energy recovered. To do this, the energy required to heat the macroalgae up to the reaction temperature (E_{SG} or Energy Input) was calculated by using Eq (22) (adapted from (Xu et al., 2011)),

$$E_{SG} = w_{H_2O} \times (\Delta H_{H_2O}^{T_1} - \Delta H_{H_2O}^{T_0}) + w_{cell\times} C_{ps} (T_2 - T_0) \qquad (22)$$

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), $\Delta H_{H_2O}^{T}$ is the enthalpy of water at a given 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 °C).

The energy of the product gas (E_{PG}), which represents the energy output from SCWG was simply estimated from the sum of the mass of each component (M_n) multiplied by its calorific value (CV_n), Eq (23):

$$E_{PG} = \sum (M_1 * CV_1, M_2 * CV_2, \ .... \ M_n * CV_n) \qquad (23)$$

Table 5.2 shows the E_{SG} and the E_{PG} obtained from the SCWG at the two different temperatures. The calculations indicated 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 the 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 importance in a complete process.

Energy parameters	400 °C	550°C	ΔE (kJ)
$\Delta H(H_2O)$ (kJ kg^{-1})	2816.8	3291.9	–
Energy Input (kJ)	5.9	8.1	2.2
Energy Output (kJ)	6.14	11.2	5.06

Table 5.2 Energy balance for SCWG of *L. hyperborea* at 400 and 500 °C.

5.8 Conclusions

Out of the three catalysts used in the study (nickel, ruthenium and sodium hydroxide), both ruthenium and sodium hydroxide increased the gaseous yields, gasification efficiency and energy recovery from the SCWG of *L. hyperborea*.

The methane yield increased 2.5 times using 5% Ru/Al_2O_3 compared to non-catalysed SCWG. An increase in catalyst loading had no significant effect on the methane yield. Longer hold times and increased reaction temperature favoured methane production when using ruthenium.

The hydrogen yield increased three fold using 1.5 M sodium hydroxide compared to non-catalysed SCWG. Higher hydrogen yields were obtained through using higher concentration of sodium hydroxide, lower algal feed concentration and shorter hold times (~30 min). Increasing reaction times (> 30min) with a base catalyst decreases the hydrogen yield.

Overall energy recovery was highest at the lowest feed concentrations; 90.5% using ruthenium and 111% using sodium hydroxide.

Increasing the reaction temperature from 400 °C to 550 °C resulted in a 37% increase in energy requirement but resulted in 82% increase in energy output reflected in the energy of the product gas. On the basis of energy alone, it was beneficial to carry out SCWG at higher temperatures however consideration must be given to the mechanical requirements of the reactor.

6 Hydrogen production from the catalytic SCWG of microalgal HTL process water

6.1 Introduction

With the majority of research into hydrothermal processing of algae focused on biocrude production from microalgae, the process water has been identified as a rich source of organic carbon that requires treatment to reduce the chemical oxygen demand. The process water also contains significant amount of nutrients that can be recycled for algal cultivation benefiting process economics. Previous research has focused on the subcritical HTG of the process water to produce a biogas along with nutrient recycling (Jones et al. 2014) (see Figure 6.1).

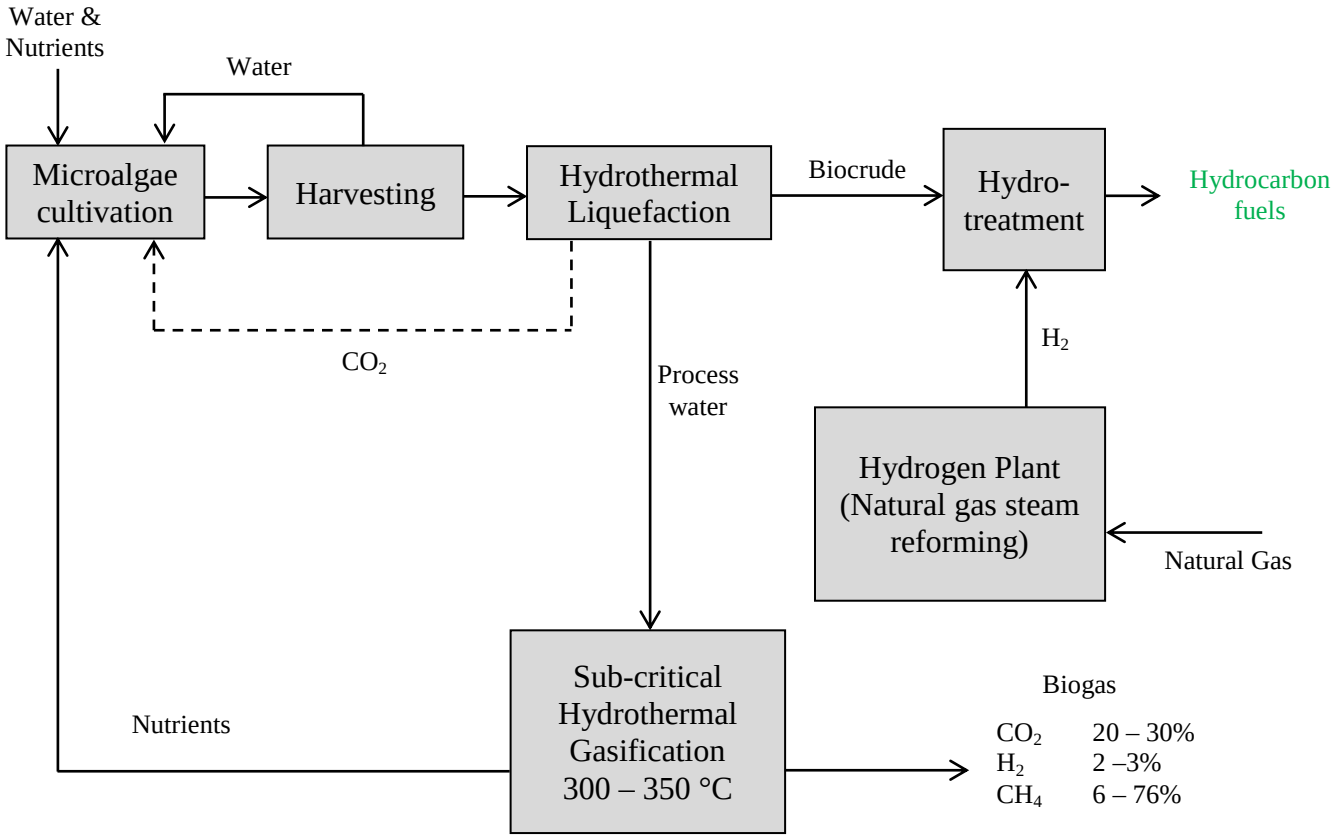

Figure 6.1 Schematic layout of HTL of microalgae with subcritical HTG of the process water for biogas production.

This study has investigated the use of supercritical water gasification technology to upgrade the process water from microalgal HTL to maximise hydrogen production for biocrude hydrotreating. The nutrient content of the process water from SCWG is analysed to determine suitability of nutrient recovery for algal growth. A series of experiments were carried out with the following objectives:

- Investigate the product distribution from the HTL of microalgae with different biochemical compositions and determine the organic carbon content of the process water.
- Investigate the influence of HTL reaction hold time on the distribution and composition of products.
- Investigate the effect of biocrude recovery (solvent extraction vs. gravity separation) on the quality of the biocrude and organic carbon content of the process water.
- Assess the upgrading of the process water through SCWG to maximise hydrogen production with the use of catalysts.
- Determine the process conditions required to generate sufficient mass of hydrogen for hydrotreating the biocrude.
- Determine the maximum hydrogen yield obtained through SCWG of the process water from microalgae HTL under the reaction conditions examined.

The microalgae strains include *Chlorella vulgaris*, *Pseudochoricystis ellipsoidea* (a high lipid strain), and the cyanobacteria *Spirulina platensis*. The process water from HTL was upgraded through catalytic HTG using sodium hydroxide under supercritical water conditions to maximise hydrogen production for biocrude

hydrotreating. The amount of hydrogen produced was compared to the amounts needed for complete hydrotreating of the biocrude (~5 g H_2 $g^{-1}_{biocrude}$ - see Table 2.12). The nutrient content of the process water following SCWG was analysed to determine suitability of nutrient recovery for algal growth.

6.2 Methodology

HTL experiments were performed in the 500 ml reactor described in Chapter 3. Each experiment involved loading the reactor with 6.0 g microalgae and 60 ml deionised water. The reactor was purged with nitrogen and heated at an average rate of 10 °C min^{-1} to 350 °C and held for the designated reaction time (0, 30 or 60 min). Following liquefaction, the gas fraction was sampled and analysed offline through gas chromatography. 100 ml of dichloromethane was added to the reaction mixture and the contents separated without the addition of any water (to avoid diluting the process water). The solvent was removed by evaporation to determine the mass of the biocrude. The HTL experiment at 0 min hold time was repeated and the biocrude separated by gravity separation in a separating funnel without the addition of any solvent. This was done to test the effect of solvent use on the organic content of the process water and the quality of the biocrude.

The SCWG experiments were performed in the 75 ml Parr reactor as described in Chapter 3. Each experiment involved loading the reactor with the process water from the HTL experiment at the required concentration. When required, 1.0 g of ruthenium catalyst was suspended at the top of the reactor in stainless steel mesh gauze; or the required mass of sodium hydroxide was added to the reactor to achieve the required concentration of sodium hydroxide. The reactor was purged with nitrogen and heated at a rate of 30 °C min^{-1} to 500 °C and held at this temperature

for 30 min. The product gas was analysed by gas chromatography and the post gasification aqueous fraction was transferred from the reactor and analysed for organic carbon and nutrient content by ion chromatography.

6.3 Hydrothermal liquefaction (HTL) of *Chlorella* at varying hold times

The distribution of products from the HTL of *Chlorella*, at 350 °C for 0, 30 and 60 min is shown in Figure 6.2. The biocrude yield following HTL was 27%, 28% and 31% for the three holding times respectively. A slight increase in biocrude yield was observed as the holding time increased. The increase in biocrude yield was very small; 1% from 0 to 30 min and 3% from 30 to 60 min. More pronounced variations in biocrude yield is observed when varying the holding time at much lower HTL temperatures of around 175 - 275 °C (Garcia Alba et al., 2012). There was a significant increase (~55%) in TOC when the holding time was increased from 0 to 30 min with only small increases in TOC content of the process water when increasing the holding time to 60 min.

HTL of *Chlorella* at 0 min holding time was repeated and the oil extracted without the use of a solvent to study the effects on the organic carbon content of the process water and the quality of the biocrude. A breakdown of the products of HTL of *Chlorella* at 0 min without the use of solvent was not presented due to the difficulty in extracting all the biocrude on the reactor walls without the use of a solvent. The TOC content of the process water using no solvent (13,000 mg L^{-1}) was approximately double that of the process water when solvent was used (7,000 mg L^{-1}) to extract the biocrude, suggesting that the solvent extracts a large amount of organic carbon dissolved in the process water. If the process water has a

higher organic concentration then it would be a more suitable feedstock for SCWG in terms of maximising H_2 production. A continuous flow reactor for microalgal HTL combined with gravity separation for the biocrude product has been demonstrated by Elliott et al. (2013a) in a process development study.

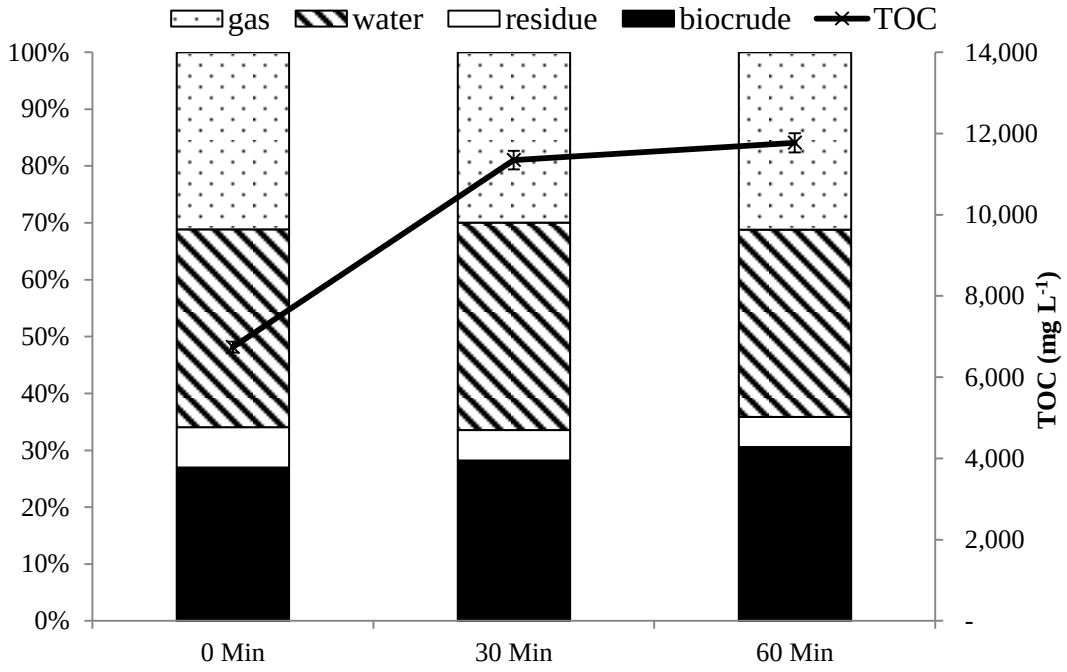

Figure 6.2 Product distribution from the HTL of *Chlorella* at 350 °C at varying hold time.

The ultimate analysis of the biocrude is presented in Table 6.1. The main difference between the quality of the biocrude extracted with a solvent is the nitrogen content (6.1%) compared to the biocrude separated without solvent (5.3%). Similar results have been reported in terms of lower nitrogen content in the biocrude separated without solvent extraction and explained by the higher content of cyclic N-containing compounds in the biocrude extracted with a solvent (Xu and Savage, 2014).

Comparing the biocrude extracted with a solvent at varying hold times, the carbon content of the biocrude increased and the nitrogen and oxygen content decreased with increasing holding time. In addition, an increase in hold time from 0 to 30 min resulted in a decrease in the TOC content of the process water by 17%. This indicates that increasing the hold time promotes oil forming reactions converting water soluble products into oil – an observation also noted by Garcia Alba et al. in studying the effect of hold time and temperature on the HTL of microalgae (Garcia Alba et al., 2012). In addition, oil deoxygenation and denitrogenation were achieved as the hold time increased.

Hold time	**C (%)**	**H (%)**	**N (%)**	**S (%)**	**O (%)**
0 min (no solvent)	73.2	8.5	5.3	0.7	12.3
0 min	73.2	9.0	6.1	0.5	11.2
30 min	75.1	9.0	5.2	0.6	10.1
60 min	76.7	9.2	5.0	0.8	8.3

Table 6.1 Influence of hold time on the biocrude composition from the HTL of *Chlorella* at 350 °C (extracted with dichloromethane and separated by gravity for 0 min experiment with no solvent)

A breakdown of the gas products from the HTL of *Chlorella* at varying hold times is presented in Table 3. The major constituent of the gas phase is CO_2, approximately 90%. Hydrogen and methane concentrations increased three fold and two fold respectively as the holding times increased from 0 to 60 min. The increase in the yields of hydrogen and methane with longer holding times maybe due to water gas shift and methanation reactions although the concentrations of these gases are still very low.

Hold time	H_2 (mol kg^{-1})	CH_4 (mol kg^{-1})	CO (mol kg^{-1})	CO_2 (mol kg^{-1})	C_2-C_4 (mol kg^{-1})
0 min	0.03	0.04	0.31	5.38	0.31
30 min	0.06	0.05	0.72	5.20	0.35
60 min	0.10	0.08	0.00	5.54	0.35

Table 6.2 Influence of hold time on the gas composition from the HTL of *Chlorella* at 350 °C.

6.4 SCWG of the process water from HTL of *Chlorella*

Samples of the process water from the HTL of *Chlorella* at 30 min were gasified under supercritical conditions at varying concentrations. Table 6.3 presents the gas yields from the supercritical water gasification (SCWG) of the undiluted process water (11,000 mg TOC L^{-1}) and a diluted concentration (2,000 mg TOC L^{-1}) both with and without a catalyst (NaOH). The gas yields presented are those considering the total process water from the HTL of *Chlorella* at 30 min was gasified at a similar concentration. The results indicate that a lower organic concentration results in a higher gasification efficiency and a higher hydrogen concentration. Lu et al., (2006) reported similar results in studying the effects of solution concentration in the production of hydrogen from biomass gasification in supercritical water. A decrease in the TOC contents from 11,000 mg L^{-1} to 2,000 mg L^{-1} saw the yield of hydrogen increase seven fold from 0.021 g H_2 $g^{-1}_{biocrude}$ to 0.153 g H_2 $g^{-1}_{biocrude}$. The addition of 1.5 M NaOH to the reaction resulted in a doubling of the hydrogen yield at the same organic concentration. This can be attributed to the role of sodium hydroxide in capturing the CO_2 and catalysing the water-gas shift reaction and increasing hydrogen production (Onwudili and Williams, 2009). The resulting hydrogen yield

using 1.5 M NaOH and an organic concentration of 2,000 mg L^{-1} in the process water was 0.292 g H_2 $g^{-1}_{biocrude}$.

The GE increased to 94.2% when the organic concentration was reduced to 2000 mg L^{-1} from 11,000 mg L^{-1} and a further increase in GE to 98.7% was observed with the addition of 1.5 M NaOH.

Concentration	**Gas Composition (mol kg^{-1})**						**Gasification efficiency**
(mg L^{-1})	**H_2**	**CH_4**	**CO**	**CO_2**	**C_2-C_4**	**g H_2 $g^{-1}_{biocrude}$**	**(%)**
11,000	3.31	1.79	0.25	2.66	0.79	0.021	51.9
11,000 (+1.5 M NaOH)	7.45	2.45	0.00	0.02	0.56	0.048	78.5
2,000	23.65	1.65	1.79	11.77	4.64	0.153	94.2
2,000 (+1.5 M NaOH)	45.28	1.88	0.00	0.00	5.67	0.292	98.7

Table 6.3 Gas yields (mol kg^{-1} *Chlorella* processed) and gasification efficiency from the SCWG of the process water from HTL of *Chlorella*.

The mass of hydrogen required for hydrotreating the biocrude averages 0.04 - 0.05 g H_2 $g^{-1}_{biocrude}$ based on the studies reported in Chapter 2 (see Table 2.12). The mass of hydrogen produced from the SCWG of the process water is compared with the mass of biocrude produced from HTL of *Chlorella* at 30 min hold time (g H_2 $g^{-1}_{biocrude}$ column in Table 6.3). Without diluting the process water to avoid an energy penalty of gasifying more water, sodium hydroxide must be used during SCWG to produce a sufficient mass of hydrogen to consider hydrotreating the biocrude. The hydrogen yield following catalytic SCWG of the undiluted process water of HTL of *Chlorella* was 0.048 g H_2 $g^{-1}_{biocrude}$. This equates to the amount of hydrogen required for hydrotreating the biocrude. SCWG following dilution of the process water to 2000 mg L^{-1} results in 23.7 mol H_2 $kg^{-1}_{Chlorella}$ increasing to

45.3 mol H_2 $kg^{-1}_{Chlorella}$ with the addition of 1.5 M NaOH. This equates to 0.15 and 0.29 g H_2 $g^{-1}_{biocrude}$ respectively; yields of hydrogen in excess of the requirement for complete hydrotreating of the biocrude.

The experiments described in this study are performed in a batch reactor. In a continuous system, operating parameters would differ due to faster heating and cooling rates and shorter hold times, however, the results of these batch experiments demonstrate the potential for providing sufficient hydrogen for upgrading the biocrude using the organic carbon dissolved in the process water.

6.5 Composition of the process water

Table 6.4 lists the main components identified in the process water from HTL of *Chlorella* at varying hold times and in the process water following SCWG of the HTL process water at the two organic concentrations (2,000 mg L^{-1} and 11,000 g L^{-1}). Comparing the two experiments at 0 min holding time, the dissolved organic material remains in the process water when no solvent is used for biocrude extraction resulting in higher concentrations of acetate and TOC. In addition, the concentration of phosphate is twofold higher when no solvent is used. This may be due to the presence of organophosphates such as phospholipids which are extracted into the solvent during solvent extraction of the biocrude.

A reduction in the concentration of acetate and TOC is observed following SCWG of the HTL process water. However, no significant change is observed in the concentrations of ammonium, potassium and nitrate following SCWG. The results indicate that the post-SCWG process waters are still rich in nutrients that can be recycled for algal cultivation. The results are compared to the standard growth medium - BBM. In the HTL process water, concentrations of phosphate and

potassium are orders of magnitude higher than those found in the standard growth medium. These nutrients are important for algal growth and recycling helps ease the economic constraint in algal cultivation. Acetate can act as a substrate for mixotrophic growth, increasing productivity and recycling carbon (Bhatnagar et al., 2011).

	HTL process water				SCWG process water				
(ppm)	**0min (no solvent)**	**0 min**	**30 min**	**60 min**	**11,000 mg L^{-1}**	**11,000 mg L^{-1} (+1.5 M NaOH)**	**2,000 mg L^{-1}**	**2,000 mg L^{-1} (+1.5 M NaOH)**	**BBM**
pH	8.2	8.4	8.0	8.6	9.3	12.6	9.34	13.0	
TOC	13,091	6,996	10,843	11,771	5,219	2,327	104	24	
Acetate	9,454	6,546	8,600	8,733	4,290	2,866	1,269	1,335	
Nitrate	18.2	17.6	18.0	18.6	18.4	17.4			182
Phosphate	8,022	3,954	3,877	4,235	3,230	969	1,715	155	153
Sulphate	560	131	424	392	453	604	32	226	
Ammonium	11,931	10,767	12,339	13,620	10,336	9,918	1,593		
Potassium	573	438	511	573	491	531	85	308	84
Calcium	27	25	16	13	16	9	12	7	
Magnesium	18.2	16.2	17.2	21	9.6	7.6	2.4	4.4	

Table 6.4 Nutrients and important metals in ppm from the process waters following HTL *Chlorella* at varying hold time and SCWG of the HTL process water at 30 min at different organic concentration.

6.6 Combined HTL and SCWG of *Chlorella, Pseudochoricystis, and Spirulina*

Pseudochoricystis, and *Spirulina* were hydrothermally liquefied at 350 °C for 30 min to compare the study on *Chlorella* with microalgal strains with different biochemical compositions. The distribution of products is shown in Figure 6.3. HTL of *Pseudochoricystis* resulted in a higher biocrude yield (35%) and a higher organic carbon concentration of the process water (17,000 mg/l) due to its higher lipid and carbohydrate content compared to *Chlorella* and *Spirulina*.

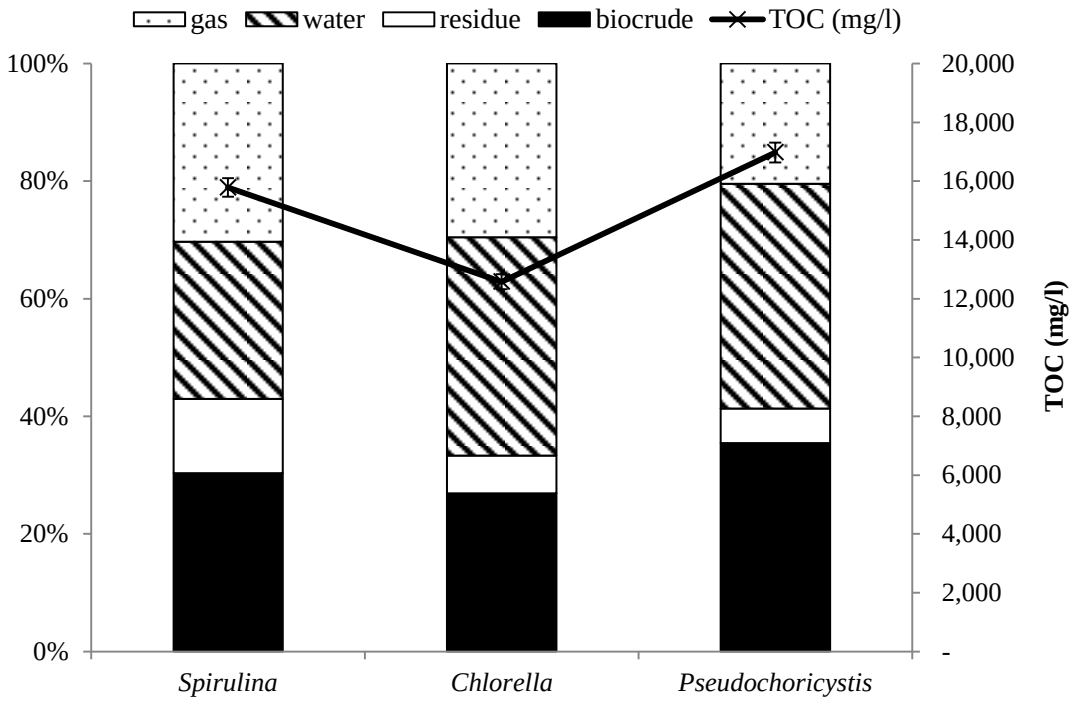

Figure 6.3 Product distribution from the HTL of *Chlorella, Spirulina and Pseudochoricystis* at 350 °C and 30min hold time.

	Gas Composition (mol kg^{-1})						Gasification efficiency (%)
	H_2	CH_4	CO	CO_2	C_2-C_4	g H_2 $g^{-1}_{biocrude}$	
Chlorella	45.3	1.88	0.00	0.00	5.67	0.29	98.7
Pseudochoricystis	31.4	8.03	0.00	0.00	1.15	0.18	98.1
Spirulina	29.9	5.57	0.00	0.00	0.35	0.20	98.7

Table 6.5 Gas yields (mol kg^{-1} algae), hydrogen yield per gram of biocrude, and gasification efficiency from the SCWG of the process water from HTL of *Chlorella*, *Pseudochoricystis* and *Spirulina*.

A sample of the process water was diluted six fold and hydrothermally gasified under supercritical conditions with the addition of 1.5 M NaOH. Considering all the process water was gasified at similar conditions, the gas yields are presented in Table 6.5. High yields of hydrogen were produced (0.18 – 0.29 g H_2 $g^{-1}_{biocrude}$) with near complete gasification of the organics (~98%). Following upgrading through SCWG (at 500 °C and 30 min hold time), the process water from the HTL of all three species produced excess hydrogen for biocrude hydrotreating.

6.7 Conclusions

6.7.1 HTL of microalgae

The effect of holding time (0, 30 and 60 min) on the HTL of *Chlorella* at 350 °C had no significant effect on the biocrude yield, however, the TOC content of the process water increased by 55% to 10,800 mg L^{-1} when the holding time increased from 0 to 30 min. Doubling the hold time from 30 to 60 min increased the TOC content of the process water by a further 8% to 11,700 mg L^{-1}.

Separation of the main products (biocrude from the process water) with the use of a solvent resulted in extraction of half the organic content of the process water. The TOC content of the process water using gravity separation following HTL of *Chlorella* was 13,000 mg L^{-1}compared to 7,000 mg L^{-1} when a solvent was used to extract the biocrude. In addition, the nitrogen content of the biocrude collected by gravity separation was 5.3% compared to biocrude extracted with a solvent 6.1%.

Based on the higher quality of the biocrude and the higher TOC content of the process water when no solvent is used to separate the biocrude, a continuous process based on gravity separation of the biocrude would be preferable. The resulting high TOC content in the process water would be a better feedstock for subsequent SCWG to maximise hydrogen production.

6.7.2 SCWG of the process water from microalgae HTL

SCWG of the process water from the HTL of *Chlorella* resulted in high hydrogen yields and high gasification efficiencies when the organic concentration was low (i.e. the process water was diluted) and a catalyst (NaOH) was used:

- The gasification efficiency increased to 94.2% when the organic concentration was reduced to 2000 mg $L^{-1}$from 11,000 mg L-1 and a further increase in GE to 98.7% was observed with the addition of 1.5 M NaOH.
- The hydrogen yield increased to 0.153 g H_2 $g^{-1}_{biocrude}$ when the organic concentration was reduced to 2,000 mg L^{-1} and a further increase in H_2 yield to 0.292 g H_2 $g^{-1}_{biocrude}$ was observed with the addition of 1.5 M NaOH.
- Without diluting the process water to avoid an energy penalty of gasifying more water, sodium hydroxide must be used during SCWG to produce a sufficient mass of hydrogen to consider hydrotreating the biocrude. The H_2 yield following catalytic SCWG of the undiluted process water of HTL of *Chlorella* was 0.048 g H_2 $g^{-1}_{biocrude}$. This equates to the amount of hydrogen required for hydrotreating the biocrude.
- SCWG following dilution of the process water to 2000 mg L^{-1} results in 23.7 mol H_2 $kg^{-1}_{Chlorella}$ processed and 45.3 mol H_2 $kg^{-1}_{Chlorella}$ processed with the addition of 1.5 M NaOH. This equates to 0.15 and 0.29 g H_2 $g^{-1}_{biocrude}$ respectively; yields of hydrogen in excess of the requirement for complete hydrotreating of the biocrude.

The nutrient content of the process water post SCWG shows high concentrations of phosphate and potassium which are important nutrients for algal growth. The concentration of phosphate and potassium are orders of magnitude higher compared to standard growth medium, BBM. In addition, acetate is also present in the process water which can act as a substrate for mixotrophic growth. The results indicate that post-SCWG process waters are still rich in nutrients that can be recycled for algal cultivation.

The process waters from the HTL of *Chlorella*, *Pseudochoricystis*, and *Spirulina* were all gasified under SCW conditions to maximise H_2 production. The results indicate that excess hydrogen (0.18 – 0.29 g H_2 $g^{-1}_{biocrude}$) can be produced from SCWG of the process water of HTL along with near complete gasification of the organics (~98%). As such, the process water can be upgraded through SCWG to produce hydrogen to hydrotreat the biocrude.

7 Conclusions

7.1 Introduction

The introduction to the thesis identifies the need to diversify our energy supplies, especially in the transport and electricity generation sectors where a significant increase in renewable energy is required to meet decarbonisation targets. Algae have been identified as suitable alternative feedstocks for third generation biofuels due to their fast growth rates and non-competitiveness with land for food crops. Hydrothermal processing of algae is an appropriate conversion route as it allows the processing of the wet feedstock and removes the energy penalty of drying.

The main focus of the published work has been on hydrothermal liquefaction of microalgae with limited work on the hydrothermal processing of macroalgae. The use of supercritical water gasification for the hydrothermal processing of macroalgae has several advantages based on the nature of the process and the composition of the feedstock. The objective of this research was to study the supercritical water gasification of macroalgae to produce hydrogen and methane in the view of the growing interest of a future algal biorefinery concept.

In addition, with the majority of research into hydrothermal processing of algae focused on biocrude production from microalgae, the process water from the process has been identified as a rich source of organic carbon that requires treatment to reduce the chemical oxygen demand. The process water also contains significant amount of nutrients that can be recycled for algal cultivation benefiting process economics. Research has focused on the subcritical hydrothermal gasification of the process water to produce a biogas along with nutrient recycling. This research has

investigated the use of supercritical water gasification to upgrade the process water from hydrothermal liquefaction of microalgae to maximise hydrogen production for biocrude hydrotreating.

7.2 Supercritical water gasification of macroalgae

7.2.1 Non-catalytic SCWG of macroalgae

The supercritical water gasification (SCWG) of the four macroalgae species investigated (*Saccharina latissima*, *Laminaria digitata*, *Laminaria hyperborea*, and *Alaria esculenta*) produced a gas that mainly consisted of hydrogen, methane and carbon dioxide. Non-catalytic SCWG resulted in hydrogen yields of 3.3 - 4.2 mol $kg^{-1}_{macroalgae}$ and methane yields of 1.6 – 3.3 mol $kg^{-1}_{macroalgae}$.

The SCWG of *S. Latissima* at a hold time of 30 min produced the highest calorific gas (16.3 MJ m^{-3}) compared to the gas produced at 0 and 30 min hold times. The composition of the gas was as follows: hydrogen (29%), methane (14%), carbon dioxide (48%), C_2 - C_4 gases (8%) and carbon monoxide (1%).

7.2.2 Catalytic SCWG of macroalgae using ruthenium

Catalytic SCWG (using 5% Ru/Al_2O_3) resulted in hydrogen yields of 7.8 - 10.2 mol $kg^{-1}_{macroalgae}$ and methane yields of 4.7 - 6.4 mol $kg^{-1}_{macroalgae}$. High gasification efficiencies (> 90%) were obtained in the presence of ruthenium catalyst with the yield of combustible gases of the product gas increasing by 30%. Re-using the catalyst resulted in a decrease in molar yield of CH_4 by 40% and an increase of CO_2 by 32%. In addition, the gasification efficiency decreased from 92% to 71%. Examination of the catalyst surface identified sulphur and calcium deposits which caused catalyst deactivation.

7.2.3 Seasonal variation in macroalgae and influence on gas yields

The summer harvest of *S. latissima* yielded a higher calorific value product gas due to its higher carbohydrate and lower ash content compared to harvests from other seasons. The calorific value of the product gas from SCWG of *S. latissima* was 16.3 MJ m^{-3} for summer (July) harvest and 14.0 MJ m^{-3} for winter (Jan) harvest.

7.2.4 Nutrient recycling from macroalgae for microalgae cultivation

The process waters from SCWG of macroalgae compared favourably with standard growth media (BBM) in terms of nutrients. Process waters contained high concentrations of nitrogen, potassium and acetate. Process waters from catalysed SCWG of *S. latissima* showed significant growth of *C. vulgaris* suggesting suitability of nutrient recycling from SCWG of macroalgae. *C. vulgaris* showed the highest growth (in terms of biomass concentration) with a 50x dilution of the process waters from SCWG of *S. latissima*. Further dilution (200 and 400x) resulted in significantly less growth due to insufficient nutrient availability.

7.2.5 Catalytic SCWG of macroalgae using ruthenium, nickel and sodium hydroxide

The yield of hydrogen was approximately three times higher when using sodium hydroxide (16.3 mol H_2 $kg^{-1}_{macroalgae}$) compared to non-catalysed SCWG of *L. hyperborea* (5.18 mol H_2 $kg^{-1}_{macroalgae}$). 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 83% compared to 52% for the non-catalysed SCWG of *L. hyperborea*.

The yield of methane was approximately 2.5 times higher (9.0 mol CH_4 $kg^{-1}_{macroalgae}$) when using ruthenium catalyst compared to the non-catalysed experiment (3.36 CH_4 $kg^{-1}_{macroalgae}$) and the energy recovery increased by 22% to 74%.

7.2.6 Influence of catalyst loading

Increasing the ruthenium loading from 5% to 20% resulted in 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 maximum energy recovery achieved was 92% using 20% Ru/Al_2O_3 during SCWG of *L. hyperborea*.

An increase in sodium hydroxide concentration from 0.5 M to 3 M resulted in a near doubling of hydrogen yield to 18.2 mol H_2 $kg^{-1}_{macroalgae}$ and a threefold decrease in the amount of $C_2 - C_4$ hydrocarbons present in the product gas. The maximum energy recovery achieved was 89% using 3 M NaOH during SCWG of *L. hyperborea*.

7.2.7 Influence of algal concentration (feed concentration)

Methane yields from the ruthenium catalysed experiments showed no significant difference with varying feed concentrations of 3.33, 6.67 and 13.3%. However, the 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 6.67% 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 $kg^{-1}_{L.hyperborea}$ and 6.21 mol CH_4 $kg^{-1}_{L.hyperborea}$ resulting in an energy recovery of 111%. The overage in energy recovery was due to the participation of the water medium as a reactant for hydrogen gas production. Increasing the feed concentration to 6.67 and 13.3% resulted in a decrease in energy recovery to 82.9 and 50.4% respectively.

The highest energy recoveries were achieved at the lowest algal feed concentration tested (3.33%); 90.5% using ruthenium and 111% using sodium hydroxide.

7.2.8 Effect of hold time

Generally, longer hold times allow for better yields and this was 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 to 60 min using 20% ruthenium catalyst, however, doubling the hold time to 120 min resulted in a 30% increase in hydrogen and methane yields to 10.4 and 11.2 mol $kg^{-1}_{L.hyperborea}$ respectively.

The highest hydrogen yield obtained using 1.5 M NaOH was 16.3 mol $kg^{-1}_{L.hyperborea}$ 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.

7.2.9 Effect of temperature

The effect of temperature was studied on the catalytic SCWG of *L. hyperborea* using 20% ruthenium. It was observed that an increase in temperature to 550 °C caused a doubling in the yield of H_2 compared to 400 °C. The carbon gasification

efficiency and energy recovery increased to 71% at 500 °C compared to 65% at 400 °C.

An evaluation of the energy balance in terms of energy requirements for the SCWG process at 400 and 550 °C against the net gain in energy recovered was conducted. Results indicated a 37% increase in the energy requirement to conduct the SCWG at 550 °C compared to the process at 400 °C. However, an 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.

7.3 SCWG of the process water from hydrothermal liquefaction of microalgae

7.3.1 HTL of *Chlorella* and the separation of biocrude

The effect of holding time (0, 30 and 60 min) on the HTL of *Chlorella* at 350 °C had no significant effect on the biocrude yield, however, the TOC content of the process water increased by 55% to 11,000 mg L^{-1} when the holding time increased from 0 to 30 min. Doubling the hold time from 30 to 60 min increased the TOC content of the process water by a further 8% to 11,700 mg L^{-1}.

Separation of the main products (biocrude from the process water) with the use of a solvent resulted in extraction of half the organic content of the process water. The TOC content of the process water using gravity separation following HTL of Chlorella was 13,000 mg L^{-1} compared to 7,000 mg L^{-1} when a solvent was used to extract the biocrude. In addition, the nitrogen content of the biocrude collected by gravity separation was 5.3% compared to biocrude extracted with a solvent 6.1%.

Based on the higher quality of the biocrude and the higher TOC content of the process water when no solvent is used to separate the biocrude, a continuous process based on gravity separation of the biocrude would be preferable. The resulting high TOC content in the process water would be a better feedstock for subsequent SCWG to maximise hydrogen production.

7.3.2 SCWG of the process water from HTL of *Chlorella*

SCWG of the process water from the HTL of Chlorella (organic carbon concentration of 11,000 mg L^{-1}) resulted in a hydrogen yield of 3.31 mol H_2 $kg^{-1}_{Chlorella}$ with a gasification efficiency of 51.9%. The hydrogen yield equated to 0.021 g H_2 $g^{-1}_{biocrude}$. Without diluting the process water to avoid an energy penalty of gasifying more water, sodium hydroxide must be used during SCWG to produce a sufficient mass of hydrogen to consider hydrotreating the biocrude. The hydrogen yield following catalytic SCWG of the undiluted process water was 0.048 g H_2 $g^{-1}_{biocrude}$. This equates to the amount of hydrogen required for hydrotreating the biocrude.

SCWG of the process water from the HTL of *Chlorella* resulted in higher hydrogen yields and higher gasification efficiencies when the organic concentration was low (i.e. the process water was diluted) and a catalyst (NaOH) was used:

- The gasification efficiency increased to 94.2% when the organic concentration was reduced to 2000 from 11,000 mg L^{-1} and a further increase in gasification efficiency to 98.7% was observed with the addition of 1.5 M NaOH.
- SCWG following dilution of the process water to 2000 mg L^{-1} results in 23.7 mol H_2 $kg^{-1}_{Chlorella}$ and 45.3 mol H_2 $kg^{-1}_{Chlorella}$ with the addition of

1.5 M NaOH. This equates to 0.15 and 0.29 g H_2 $g^{-1}_{biocrude}$ respectively; yields of hydrogen in excess of the requirement for complete hydrotreating of the biocrude.

7.3.3 Nutrient content of the process water post SCWG

The nutrient content of the process water post SCWG shows high concentrations of phosphate and potassium which are important nutrients for algal growth. The concentration of phosphate and potassium are orders of magnitude higher compared to standard growth medium, BBM. In addition, acetate is also present in the process water which can act as a substrate for mixotrophic growth. The results indicate that post-SCWG process waters are still rich in nutrients that can be recycled for algal cultivation.

7.3.4 HTL and SCWG of *Chlorella, Pseudochoricystis, and Spirulina*

The process waters from the HTL of *Chlorella*, *Pseudochoricystis*, and *Spirulina* were all gasified under SCW conditions to maximise hydrogen production. The results indicate that excess hydrogen (0.18 – 0.29 g H_2 $g^{-1}_{biocrude}$) can be produced from SCWG of the process water of HTL along with near complete gasification of the organics (~98%). As such, the process water can be upgraded through SCWG to produce hydrogen to hydrotreat the biocrude as illustrated in the schematic layout in Figure 7.1, thus removing the need for a hydrogen plant to generate the required hydrogen.

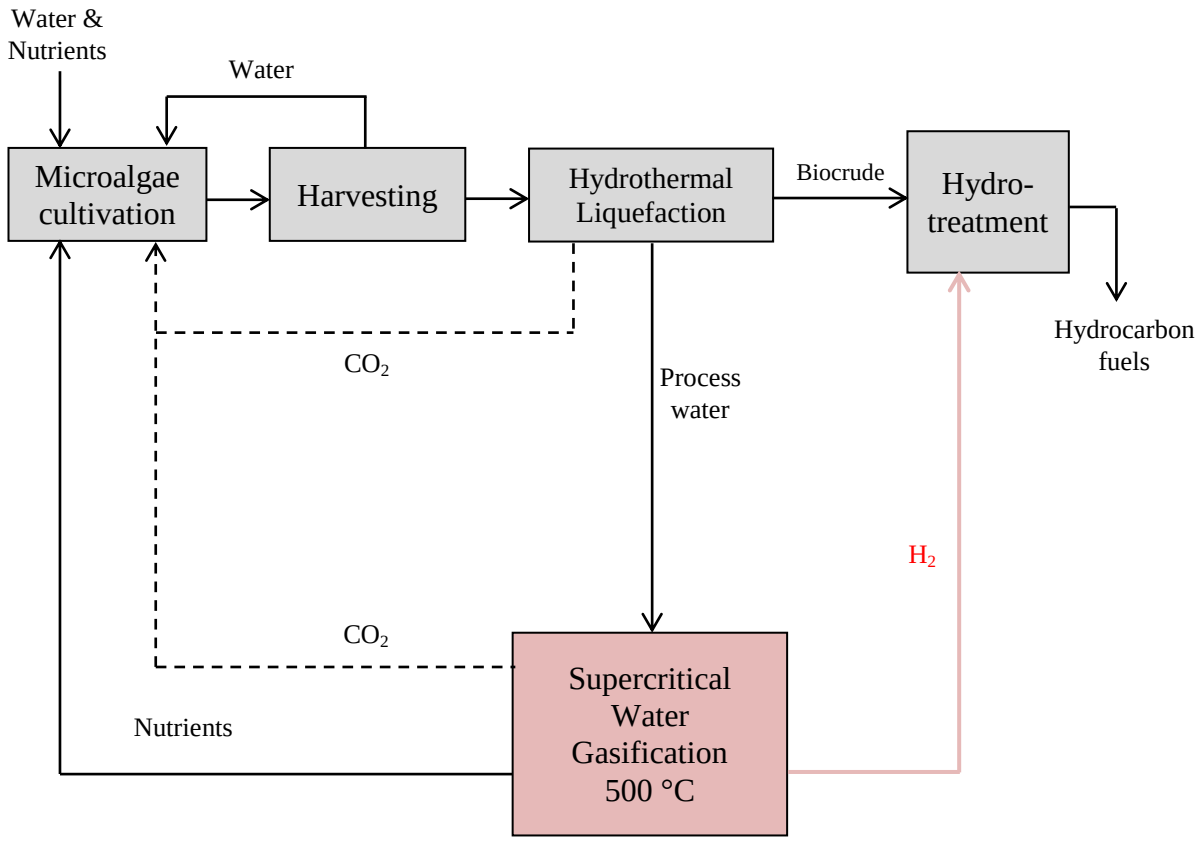

Figure 7.1 Schematic layout of HTL of microalgae with SCWG of the process water for hydrogen production

8 Future work

Extending the results from this thesis (obtained in 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, reaction hold times as well as reactor feedstock considerations (allowable concentrations and particle size). These issues are discussed in the context of future research in the following sections.

8.1 SCWG challenges of scaling up batch to continuous reactors – feedstock and catalyst considerations

In a batch reactor, higher concentrations of an insoluble solid feedstock can be gasified as opposed to a continuous reactor due to reactor plugging issues in a continuous system. In a comparative study of the SCWG of glycerol in the presence of water-soluble alkaline catalysts, Wu et al., (2011) found that hold 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 hold 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 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. A salt precipitator can be fitted prior to either a batch or a continuous SCWG reactor (Zöhrer et al., 2014). This has been demonstrated in the case of SCWO (Huang et al., 1992) and proposed for the SCWG

of microalgae in terms of process efficiency and preventing catalyst deactivation (see Figure 2.15) (Stucki et al., 2009a)

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 and heated with the feedstock in batch experiments. On the contrary, in continuous operations, the catalysts are held in a fixed bed over which the feed solution is passed. 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 supercritical conditions would be needed for the design of a continuous supercritical gasification process for macroalgae.

The composition of macroalgae differs from that of lignocellulosic biomass in that macroalgae require flexible fronds to withstand stormy marine conditions and as such they do not contain high levels of lignocelluloses. Rigid terrestrial feedstocks are rich in cellulose (grasses and straws) and lignin (woody biomass). However, processing macroalgae to form a pumpable feedstock may still present a challenge and further work to test continuous feeding of macroalgae in the operation of a SCWG plant is required. Matsumura et al. (2005) investigated the hydrothermal pretreatment at 150 – 200 °C and 30 min for feeding cabbage. The hydrothermal

pretreatment resulted in dissolving of the hemicellulose and the cell structure of the biomass was destroyed. Further investigation into the hydrothermal pretreatment of macroalgae prior to SCWG can be investigated in order to improve the pumping of the macroalgal slurry into the reactor. This can be done through two main routes:

- Hydrothermal pretreatment at low temperatures (100 – 200 °C)
- Microwave pretreatment at a range of powers (300 – 600 W)

Microwave processing as a pretreatment method has the advantages of energy efficiency and better control of reaction conditions compared to hydrothermal processing. If the feedstock is stirred, microwave processing provides a uniform method of heating due to the rotation of dipolar molecules and vibration of ions in solution in an electromagnetic fields (Tsubaki et al., 2012). This method of heating can reduce reaction hold times, increase reaction rates and provide greater accuracy and control in the pretreatment process. The advantages of microwave processing can be summarised as follows:

- application of non-contact heating (conventional heating first applies heat to the part of the material in direct contact with container),
- the transfer of microwave energy instead of heat (better energy efficiency),
- rapid and material selective heating (different components of the material respond differently to energy absorption),
- high safety and automation levels and volumetric heating of the material

Furthermore, the addition of salts can improve hydrolysis during microwave processing as demonstrated by Tsubaki et al. (2012). As such, macroalgae (a feedstock high in salts) could be a promising feedstock for microwave processing.

Microwave processing can be used to facilitate extraction of valuable compounds such as polysaccharides or protein (Budarin et al., 2012). Table 8.1 illustrates the commercial market for macroalgae. The extraction of value-added compounds prior to hydrothermal processing of algae is essential to improve the economics of producing renewable fuel from algae.

Industry	Market Value† ($)	Quantity (tonnes)
Food (human)	6 bn	6.4m
Agar	255.6 m	55,650*
Alginate	158.4 m	126,500*
Carrageenan	288 m	33,000*
Feed (Animal)	6 m	50,000
Fertiliser	6 m	10,000

† adjusted to market value (2011). * dry basis

Table 8.1 Commercial market for macroalgae products - adapted from Budarin et al., (2011)

Designing a pretreatment process that can selectively extract such high-value compounds and prepare macroalgae for further hydrothermal processing requires further investigation. Seeing as the integration of macroalgae into a biorefinery remains a challenge due to high levels of halogenated compounds, alkali earth metals and heavy metals, the pretreatment process can also help address these issues by producing a pumpable feedstock that can be easily integrated into a hydrothermal system (see Figure 8.1). Research into hydrothermal microwave processing as a pre-treatment and extraction technique has been demonstrated for microalgae (Biller et al., 2013).

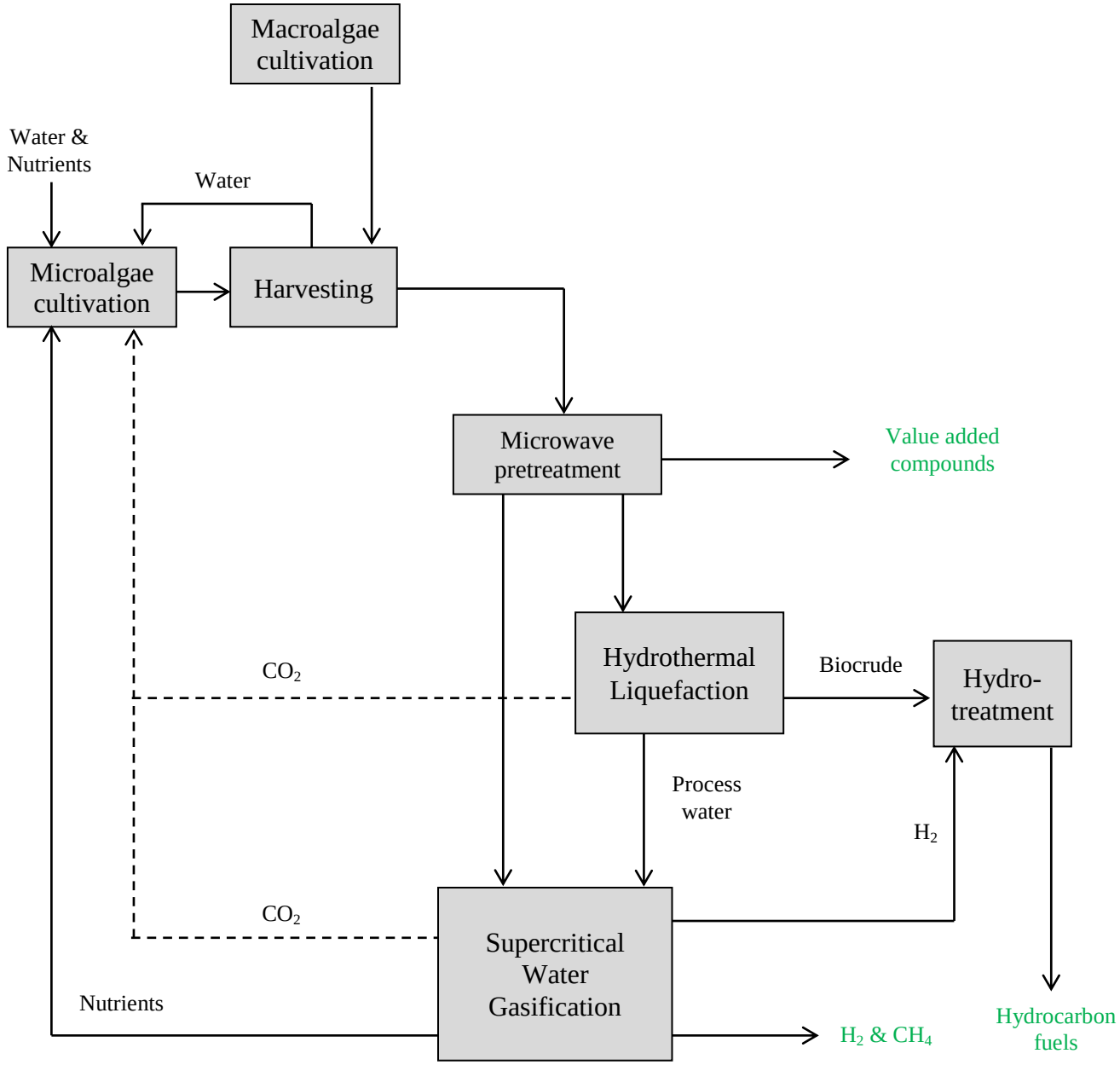

Figure 8.1 Schematic of an algal biorefinery with microwave processing for pretreatment and extraction of value added compounds

8.2 Integration of HTL and SCWG for macroalgae

This thesis demonstrated the production of excess hydrogen for hydrotreating microalgal biocrude through SCWG of the process water from HTL. Studies have demonstrated the HTL of macroalgae to produce a biocrude and process water rich in organics (Anastasakis and Ross, 2011; Bach et al., 2014; Yang et al., 2014; Zhou et al., 2010). HTL work was carried out on a macroalga, *Enteromorpha prolifera*, by Zhou et al. (2010) with the use of Na_2CO_3. The biocrude yield was 23% at 300 °C, 30 min hold time, and 5% Na_2CO_3. The biocrude had a HHV of 30 MJ kg^{-1} and was analysed and reported as a complex mixture of ketones, aldehydes, phenols, alkenes, fatty acids, esters, aromatics, and nitrogen containing heterocyclic compounds. Acetic acid was the main component of the water-soluble products in the process water. Yang et al. (2014) studied the HTL of the same macroalga at varying conditions and reported the biocrude be a mixture of fatty acids, ketones, alkenes and 5-methyl furfural. The main components of water soluble organics in the process water were pyridines, carboxylic acids and glycerol.

Anastasakis and Ross (2011) investigated the HTL of *Saccharina latisima* and reported a 19.3% yield of biocrude at 350 °C, 10% algal concentration and 15 min hold time. The biocrude had an HHV of 36.5 MJ kg^{-1}. Several experimental conditions were tested to study the effect of operation conditions on the quality of the biocrude. The biocrude was analysed to determine its elemental composition and the ranges reported were: C (74 – 84%), H (7 - 10%), N (3 - 6%), O (5 - 12%). The produced macroalgal biocrude has a high heteroatom content and requires hydrotreatment. Further research into the SCWG of the process water from macroalgae HTL can assess the potential to produce hydrogen for hydrotreating the biocrude.

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