Hydrogen Carriers from Industrial Biomass via Sub/supercritical water

A process modelling and technology evaluation study

Mohamed Magdeldin

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Abstract

Continued rise in global energy demand as well as concerns over the lasting impact of climate change call for revamping existing energy services and consumption models. Sub/supercritical water biorefineries are a technology platform that enable low carbon pathways for de-fossilizing existing infrastructure, in which electrification is limited. The complex physical nature of biomass feeds, especially industrial by-products, constitute the development of conversion technologies in which several valorization objectives are concurrently met. Sub/supercritical water reactor systems materialize various process intensification advantages for thermally efficient upgrading of biomass to hydrogen carriers.

The presented research is a process modelling study. The first pathway investigated is subcritical liquefaction for renewable fuels production for the transportation sector. The second pathway is the gasification of biomass into enriched synthetic methane and green hydrogen carriers for chemical and power generation sectors. The main contribution of this dissertation is considered to entail model development for satisfactory predictions of organic valorization in highly non-ideal conditions. The developed liquefaction and gasification models provide fundamental understanding on the driving forces for specific elemental, phase and product component yields at high temperature and pressure reactive processes. The constrained equilibria models extend knowledge on organic conversion inefficiencies in supercritical water to account for the role of inorganics in determining product gas composition and yields. In addition, the developed biorefinery flowsheets, case studies and assessment provides additional insights on the techno-economic opportunity and limitations present for future commercialization of the envisaged sub/supercritical water biorefineries.

It was found that a holistic and polygenerative nature of chemical and thermal products recovery is necessary for the examined biorefineries to offer improved technical and economic performance relative to other biomass based technologies. In considering the production of hydrogen carriers, power and heat, the thermal efficiency of liquefaction was found to be 41-87% and 67-84% for gasification. In terms of economics, they remain uncompetitive with fossil fuels, with non-catalytic liquefaction breaking even at a €150 price per oil barrel. The study did show that with a 30% reduction in reactor system capital costs and the availability of a solids biomaterial market, liquefaction is economically feasible under current carrier commercial prices.

The integration with pulp mills showed that gasification would improve existing thermal performance, as well as act as a capture and utilization technology for excess biogenic carbon present. The study showed that with increased integration of the gasification technology, the processing benefits lead to reduced minimum selling price of the mill specialty pulp product.

Keywords Biorefineries, Hydrothermal liquefaction, Supercritical water gasification, Renewable fuels, Hydrogen, Bio-SNG, Pulp mill integration

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Preface

This is, was and will always be about, and for your future ya Yasser.
I love you kiddo!

Helsinki, 4th of September, 2020.
Mohamed Magdeldin

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List of Publications

This doctoral dissertation is a summary based on the following publications, referred to in the text by their numerals. The papers are appended at the end of the thesis.

- I.Magdeldin, Mohamed;** Kohl, Thomas; Järvinen, Mika. 2017. Techno-economic assessment of the by-products contribution from non-catalytic hydrothermal liquefaction of lignocellulose residues. *Energy*, volume (137), 679-695. ISSN 0360-5442. <https://doi.org/10.1016/j.energy.2017.06.166>
- II.Magdeldin, Mohamed;** Kohl, Thomas; De Blasio, Cataldo; Järvinen, Mika; Won Park, Son; Giudici, Reinaldo. 2016. The BioSCWG Project: Understanding the Trade-Offs in the Process and Thermal Design of Hydrogen and Synthetic Natural Gas Production. *Energies*, volume (9), 838. ISSN: 1996-1073. <https://doi.org/10.3390/en9100838>.
- III.Magdeldin, Mohamed;** Kohl, Thomas; Järvinen, Mika. 2016. Process modeling, synthesis and thermodynamic evaluation of hydrogen production from hydrothermal processing of lipid-extracted algae integrated with a downstream reformer conceptual plant. *Biofuels*, volume (7), 97-116. ISSN 0360-5442. <https://doi.org/10.1080/17597269.2015.1118785>
- IV.Magdeldin, Mohamed;** Järvinen, Mika. 2020. Supercritical water gasification of Kraft black liquor: Process design, analysis, pulp mill integration and economic evaluation. *Applied Energy*, volume (262), 114558. ISSN 0306-2619. <https://doi.org/10.1016/j.apenergy.2020.114558>

Author's Contribution

Publication 1: *Techno-economic assessment of the by-products contribution from non-catalytic hydrothermal liquefaction of lignocellulose residues.*

The author was responsible for the design and execution of the study. The author performed the literature review, data collection, model development and validation, and conducted the subsequent analysis of the technical and economic findings. Thomas Kohl contributed with guidance on economic analysis. The author, with suggestions and feedback from the two co-authors, wrote the manuscript for the article.

Publication 2: *The BioSCWG Project: Understanding the Trade-Offs in the Process and Thermal Design of Hydrogen and Synthetic Natural Gas Production.*

and

Publication 3: *Process modeling, synthesis and thermodynamic evaluation of hydrogen production from hydrothermal processing of lipid-extracted algae integrated with a downstream reformer conceptual plant.*

The author, along with Thomas Kohl and Mika Järvinen were responsible for the design and execution of the study as part of the on-going BioSCWG project. The author performed the literature review, data collection, model development and validation. Thomas Kohl assisted the author on the heat integration study and following analysis. The author, with suggestions and feedback from the other co-authors, wrote the manuscript for both articles.

Publication 4: *Supercritical water gasification of Kraft black liquor: Process design, analysis, pulp mill integration and economic evaluation.*

The author was responsible for the design and execution of the study. The author performed the literature review, data collection, model development and validation, and conducted the subsequent analysis of the technical and economic findings. Mika Järvinen contributed with guidance and knowledge on the black liquor and recovery boiler modelling approach, and assisted with the analysis for the integration study with pulp mill operation.

1. Introduction

Since the industrial revolution, continued technological development and the ensued transition to digitalize our lives, have been driven by the availability of affordable and accessible energy supply chains. Fig. 1 illustrates how higher standards of human development, as defined by the United Nations (UN) development programme, correlate with higher national energy consumption per capita around the world.

Figure 1. The UN Human Development Index (HDI) plotted against primary energy consumption in GJ per capita for different countries as reported by the International Energy Agency (blue circles) [1]. The colored lines represent average values for the four HDI levels of classification (not scaled to the axis).

In recent years, the global community has come to realize the wider and negative environmental impact of continued reliance on old energy consumption models, specifically ones sourced from fossil fuels. In the context of combatting climate change, Fig. 1 does not represent a critique of human progress, but more an attempt to understand the material and subsequent energy costs associated with such progress and to underlie the supply challenge for maintaining such development paths.

This introductory chapter briefly explains the potential role of biomass as a source for renewable carbon and hydrogen carriers in matching near-term energy demand, while also mitigating global climate change. The chapter then lists some of the technical and commercial challenges facing biomass conversion practices, as well as drivers for further development.

1.1 The de-fossilizing vs. de-carbonizing debate: existing demand for bio-based carriers in mitigating climate change

The search for alternative energy sources, and feedstock to synthesize fuels and materials, has casted a wide net of natural resources such as hydropower, solar, wind, geothermal and biomass, among others. The latter, in particular residues from industrial biomass processing, the focus of this research, is a prime candidate to contribute to efforts in climate change mitigation. Biomass's physical characteristics enable it to act as an efficient transitional solution for de-fossilizing our lives [2]. The carbonaceous nature of biomass not only functions as a "natural" sink/store of recycled carbon, but also as a chemical binder for hydrogen, with its high-energy content, in a densified carrier form. The compatibility of biomass-derived fuels and materials with existing infrastructure, allows it to act as a cost and resource efficient pathway to displace the fossil carbon footprint of existing energy infrastructure in the near future [3].

Global greenhouse gas emissions (GHG) from power generation have reduced significantly in recent years. The trend is expected to continue in the coming decades as intermittent renewable technologies mature and lower costs continue to be realized [3]. For example in the Nordics, in 2018, 90% of the electricity mix was already considered fossil free, and 69% coming from renewable sources¹ [4]. However, the per capita GHG emissions remain on par or higher than the EU28 average² [5]. This is primarily driven by the presence of energy-intensive industries, along with demand in residential and transportation services [3].

A recent policy report by the Intergovernmental Panel on Climate Change (IPCC) states that: [6]

Pathways limiting global warming to 1.5°C (compared to pre-industrial levels) with no or limited overshoot *would require rapid and far-reaching transitions in energy, land, urban and infrastructure (including transport and buildings), and industrial systems (high confidence)*. [Emphasis added]

The IPCC report findings reiterated the need for bio- energy systems coupled with carbon capture and storage (BECCS) to match the proposed target emission reductions. Biomass' contribution is proposed to be in the form of bio- electricity, hydrogen (H₂) and green carbon feeds for material and fuel substitutes. Carbon-neutrality is achieved by life cycle accounting, where anthropogenic carbon dioxide (CO₂) released is a result of (and offset by) sequestered carbon from the atmosphere, rather than sourced from fossil reservoirs. The driver for bio-fuels has been, and remains, the potential for short term GHG reductions [7].

---

¹ Renewable sources are defined here as non-nuclear sources, such as biomass, solar, wind and hydropower. Intermittency reflects the variable nature of the primary energy source based on climate.

² Exception Sweden (national per capita emissions), the Nordic context here refers to combined emissions from Norway, Denmark, Sweden, Finland and Iceland.

A recent study by de Jong et al. [8] showed that biomass derived fuels for the aviation sector (currently almost exclusively driven by petroleum distillates) would reduce GHG emissions per MJ of energy consumed more than 77% compared to the reference fossil case. Other studies have also shown a similar impact for the production of specialty chemicals from biomass [9]. This underlines the potential of sustainable biomass to balance carbon, even enable negative emissions when combined with carbon capture/utilization technologies. The target sectors would be where electrification is either technically constrained, or requires massive and costly infrastructure overhaul.

The global industrial sector, for example, is expected in 2020 to continue to account for around 50% of energy demand, with less than one third of that required in the form of power. Additionally, transportation will account for around 21% of demand with only around 5% electrified [10]. Under the four future scenarios investigated in the IPCC report [6], shown in Fig. 2, BECCS technologies alleviate the impact of controlled increases in global energy consumption, due to population growth and/or technology development. By the year 2050, the de-fossilizing impact by BECCS (and other utilization) systems could lead to 65-90% and 35-65% emission reductions in industry and transportation, respectively.

1.2 The future role of bio-based carriers and energy

Currently underway is the sustainably conscious transition from commercial 1st generation biofuels to 2nd generation and advanced technologies³. Historical arguments against the widespread expansion of bio-based energy and fuel technologies were mainly due to concerns around the sustainability of supply and carbon intensity of utilization. The first is addressed with sourcing advanced biofuels from aquatic biomass cultures such as algae or industrial side streams originating from lignocellulose utilization. Whereas for the latter, national management programs, as is the case in Finland, regulate consumption so that “farmed” forestry for material production maintains an annual net-growth of natural carbon-sink stocks [2]. Under such restrictions, farmed carbon is directed to holistic and more balanced utilization pathways. The primary production of bio-based materials is aggregated by residual (or waste) utilization in the form of carrier production. This is also of significant importance for market development. Sustainable procurement avoids reaching limits on supply chain capacity and retain economic viability. An illustrative example is Hydrogenated vegetable oils (HVOs), a commercially available substitute fuel at a scale of millions of tonnes per annum. However, potential growth globally remains constrained by access to sustainable supply of feedstock [11].

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³ Biofuels production technologies are traditionally classified based on the nature of feedstock utilized for production. Advanced biofuels include non-feed or energy crop feedstocks, and mainly originate as industrial processing byproducts or waste streams from material consumptions as the source for carbon.

Figure 2. Contribution of carbon emitting sectors to the global net- CO_2 emission under four proposed scenarios in the IPPC report. The scenarios are briefly described in the figure. The vertical axis represents baseline emissions to achieve 1.5°C global warming above pre-industrial levels. Abbreviations: AFOLU – removals in the Agriculture, Forestry and Other Land Use, BECCS – Bioenergy and Carbon Capture and Storage, and CDR – Carbon Dioxide Removal. Figure reproduced with permission from [6].

The carbon intensity concern for biofuels originates from the fact that combustion for combined heat and power (CHP) is the dominant application of today. Fig. 3 illustrates the national balance for the annual forest growth extracted in Finland in 2013 [2]. CHP production accounts for 42% of industrial wood consumption (almost exclusively all material side streams). Biomass have a higher capacity (or utilization) factor than other renewables and as a result, addresses the dispatchability concerns in power generation from e.g. wind or solar. However, this amounts to a missed technical, economic and environmental opportunity for the forestry industry in Finland. As an example, the current biofuels state of art provides a more cost efficient alternative to both electro fuels⁴ and battery electric vehicles (BEVs) for long distanced transportation (500 km) at both current battery costs of (\$250 - \$300 per kWh) or the set target price by the US department of energy (DOE) of \$125 per kWh in 2022 [11].

Figure 3. National industrial lignocellulose (wood) flows in Finland in 2013, figure reproduced with permission from [2].

Global biomass, considering wet and dry forestry, agricultural and waste amounts to 160 EJ annually. If energy crops (while maintaining food security) are included, a conservative supply estimate is 245 EJ [7]. Under an efficient utilization scenario (minimum 70% efficiency), biomass could theoretically cover anywhere between one-fifth (with waste valorization only) to one third of the 590 EJ of global primary energy demand in 2020⁵ [10]. As such, bio-carriers are not expected to become “the” single platform for energy and material supply, but would become a significant contributor to the transitioning economy.

⁴ Electrofuels are commonly referred to in literature as hydrocarbon fuels produced from: 1) captured CO₂ (from the atmosphere or industrial exhausts) and 2) H₂ originating from water electrolysis using renewable power sources only (Wind or PV).

⁵ for simplification 1 EJ (exa joule) = 24 Mtoe (Million tonne of oil equivalent)

1.3 The Green hydrogen economy

Hydrogen is expected to play an integral role in the future energy mix in several forms such as an energy vector and storage medium for CHP and the upgrading of chemicals and fuels in industrial applications. The green distinction commonly refers to hydrogen from renewable sources. The current green and commercial technology, being H_2 gas from water dissociation in electrolyzer systems, has only a 2% global market share. Conventional production such as steam reforming of natural gas (at 76%) and coal (23%) continue to dominate due to the significantly lower fuel and capital costs. As such, the carbon intensity of global production remains considerably high at 10 (for natural gas) and 19 (for coal) kg of CO_2 per kg of H_2 [12].

Another challenge facing the wider-development of a global hydrogen economy is supply chain restrictions. Compressed natural gas (CNG) and other fossil-liquids pipeline networks commonly have a high tolerance of direct H_2 gas blending. However, end-user restrictions vary significantly from 20 vol.% for some industrial boiler systems, to a threshold of less than 2% for grid connected gas engines [12]. Recently, a proliferation of alternative gaseous and liquid carriers has taken place to address such barriers. Methanol, synthetic hydrocarbons and other hydrogen carriers have experienced steady market growth [13].

1.4 Technology status of bio-based hydrogen carriers production

The sustainable supply of carbon and hydrogen is engineered by displacing CO_2 emissions from industrial side streams into a wider set of fuel and material co-products. Polygenerative biorefineries, analogous to existing fossil oil barrel infrastructures are possible platforms to perform that function [2]. Fig. 4 illustrates some of the near-to and commercial biomass conversion technologies.

Figure 4. Key liquid and gaseous bio-carrier production pathways (developing and commercial). Abbreviations (λ: air to fuel ratio, AtJ: alcohol-to-jet, BtL: biomass-to-liquid, DME: dimethyl ether, DSHC: direct sugar to hydrocarbons, FAME: fatty acid methyl ester, FT: Fischer-Tropsch, GTL: gas-to-liquid, HEFA: hydro-processed esters and fatty acids, HTL: hydrothermal liquefaction, HTG: hydrothermal gasification), Anaerobic Ferment.: anaerobic digestion. Figure reproduced with permission from [7].

Studies such as Refs. [8,9] show that when compared to other biological or biochemical conversion technologies, thermochemical processes offer the most positive contribution to lowering Global Warming Potential (GWP). This is attributed to reduced emissions from direct and indirect Land Use Change (LUC) and the absence of any biologically active components in the conversion mechanism [14]. Thermochemical processes under reductive conditions ($\lambda < 1$)⁶, red colored boxes in Fig. 4, allow for the valorization of solid biomass into intermediate liquid or gaseous bio-carriers to be further upgraded into renewable fuels. The bio-carrier can either be upgraded insitu in a biorefinery superstructure, or transported to centralized facilities (e.g. existing oil refinery) to act as a green drop-in feed or blend [7].

The ubiquitous nature of biomass, as well as several interlinked socio-economic structures continue to act as barriers to the wider deployment and market penetration of envisaged systems as discussed earlier [6]. However, some of the main challenges remain at heart of technical nature, such as resource and cost efficient processing, and integration within existing infrastructures and operations with minimum ecological disruptions.

The physical nature of biomass comprises a complex structure, when compared to fossil fuels. It contains high moisture content, higher oxygen to carbon and hydrogen ratios, recalcitrant organic polymers and high inorganic fractions [15]. These characteristics lead to an increase in the number of required processing stages and continue to hinder valorization from traditional thermochemical technologies, such as gasification for synthesis gas (Syngas) or pyrolysis for bio-oil production [16]. Some of the associated drawbacks are

- 1) Low thermal recovery due to the necessary pre-treatment drying step.
- 2) Low yields and product quality due to mass transfer limited kinetics,
- 3) Multitudinous downstream steps due to the presence of organic and inorganic impurities in the target products.

All of which, led to significant interest in the alternative hydrothermal technologies. This is primarily attributed to the latter's process intensification nature as reported in [17], [18] and [19]. Hydrothermal processes, examined in this research, utilize the unique thermo-physical properties of biomass' wet conditions around the critical point (CP) of the substrate moisture (or in some cases additional auxiliary water) at 22.1 MPa and 374 °C⁷.

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⁶ Reductive conditions ($\lambda < 1$) refers to the under-stoichiometric presence of O_2 (or other oxidizing agents). Combustion is a thermochemical process at higher than stoichiometric ratio of O_2 ($\lambda > 1$).

⁷ The "pseudo" critical point of a mixture is a function of relative water compositions to other constituents.

Kruse [17] in her review of the technology summarized operating in such higher temperature and pressure reaction regimes as: water rather than being a processing penalty, becomes a very functional and opportunistic working fluid

“in biomass conversion processes [...] water (in supercritical form) fulfills every possible role it is able to fulfill: It is solvent, catalyst or catalyst precursor, and reactant”.

1.5 Dissertation outline

This dissertation presents a summary of the research work performed by the author and the appended scientific publications produced. The following Chapter (2) presents a literature overview on the development in the hydrothermal technologies examined. The main gaps-of-knowledge are identified and the list of research objectives are presented in Chapter (3). The research methods and modelling approaches are described in Chapter (4). A summary of the main results and findings of the scientific publications are outlined in Chapter (5). The summary concludes with a discussion in Chapter (6) on the feasibility of the examined technologies and the techno-economic constraints facing commercial scale installations. Chapter (7) briefly concludes on the status of hydrothermal technologies and suggests future research questions.

“The motivation behind this research is to understand the existing bottlenecks for developing a holistic valorization technology, with integrated innovative conversion steps for biomass by-products that enable the optimal use of extracted natural resources, while minimizing material residuals and undesired socio-economic-environmental impacts.”

2. Research Background

Technical opportunity and challenges facing Sub/supercritical water reactor systems

Hydrothermal technologies, as commonly referred to in literature, are methods for aqueous treatment of organic feed streams at elevated pressures. Hereinafter known as Sub/supercritical water refining (SCWR), the distinction by the word “refining” is to accurately characterize the new chemistry which facilitates higher selectivity for target bio-chemicals and materials [16]. It is worth to note that, Sub/supercritical water (SCW) has long been, since the 1930s, the generally adapted technology for Rankine-cycle driven power generation. Advantages from process intensification by SCW in heat engine design are multifarious. Thermally, the absence of boiling (phase change) during heat addition leads to a lower heat rate⁸ and CO₂ reductions by as much as 15% compared to conventional plants [20]. The fuel savings, even when considering a cheap source as coal, along with reduced component sizing from the high pressures, offset additional capital costs associated with special fabrication materials [20]. More recently and with SCWR technologies in mind, special attention has extended towards the understanding and exploitation of SCW’s chemical and solvency properties as well.

This chapter presents the opportune thermo-physical and chemical properties of SCW as a processing medium to solid, liquid and gaseous biofuels. The chapter then outlines some of the techno-economic bottlenecks facing SCW based technologies and the research scope examined in this dissertation.

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⁸ The heat rate of a power plant cycle is defined as the amount of heat in kJ that is required to produce a unit power output kWh.

2.1 Sub/supercritical water thermo-physical properties

Supercritical water is often described in literature as a single homogenous phase [17]. This is in reference to the smooth (continuous) transition in measured macroscopic properties, such as density, viscosity and molecular diffusivity. The CP of water, at which the “new” phase computationally starts, lies at the end of the vapor-liquid equilibria (saturation or co-existence) line. As can be seen in Fig. 5, the vapor and liquid density of water at the CP point are found to reach a singular value known as the critical density (ρ), at 322 kg m⁻³ [21].

Figure 5. Illustrative S-L-V phase diagram of pure water on P-T scale. Figure reproduced with permission from [22].

The increased pressure weakens the distinctive hydrogen bonding found in liquid water. The structure of SCW as a working fluid is more dispersed and resembles that of a network of clustering molecules [23]. This leads to variation in the distinct and phase recognizable physical properties of water and a combination of vapor and liquid-like properties are observed. In the subcritical region (liquid like densities), the viscosity follows an Arrhenius behavior [23]. While at pressures higher than the critical, the impact of temperature change on viscosity is less perceptible. As shown in Fig. 6(a), viscosity increases with temperature but reaches only one tenth of that in liquid water at similar fluid like densities. As a result, supercritical water is a highly compressible and expandable fluid in comparison to liquid water, and viscosity typifies that of vapor [19]. The consequent transport coefficients in the supercritical region then become somewhat similar to those of high temperature conditions (vapor-like). As a result, the diffusivity of organic compounds in SCW drastically increases compared to ambient water. The diffusion coefficient of phenol, an organic model compound, increases from 1.025×10^{-5} at ambient conditions to 34.7×10^{-5} cm²/s at 400 °C and 25 MPa ($\rho = 352$ kg m⁻³) [24].

Figure 6. The viscosity – η (a) and the dielectric constant – ϵ (b) for water at temperatures up to 1000 °C and density up to 1 g cm⁻³. Figure reproduced with permission from [23].

In addition, the dielectric constant (ϵ) or relative permittivity of water, which controls solvent behavior and the dissociation of ions, varies distinctively with change in temperature and density, as shown in Fig. 6(b). The impact of elevated pressures is noticeable, where at low temperatures in the subcritical region (~ 200 °C), ϵ remains around 80, similar to liquid water. While, transitioning closer to the critical density of water, the ϵ drops to the range of 10–25 [18]. The latter of which are similar to the polarity of common organic solvents. This allows water near to and beyond the CP to be an excellent dissolver of depolymerized organic monomers and oligomers [16]. The ability of supercritical fluids to replicate performances of common organic solvents have often lead to it being described as a green solvent in industrial chemistry applications. Ogiwara et al. [25] corroborated via visual observations that at lowered SCW densities, the dissolution of cellulose increases. That, along with water's reactivity causes the cellulose-crystalline structure to swell, followed by a collapse into a wide set of fractionation products [16].

The lower densities in the supercritical region also reduce the ability of water to ionize electrolytes ($\epsilon = 6$ at the CP). Inorganic salts, common in biomass processing, do not dissolve anymore and get separated in the form of a brine or solid precipitate [26]. The low ionic product (K_w) around the CP, which describes the auto-dissociation of water, and is defined as the product of water's acid and base forms $[H_3O^+][OH^-]$, has wide implications on biomass chemistry and kinetics [14]. At ambient conditions, K_w is around 10^{-14} and increases with temperature at liquid like densities to a peak of 10^{-11} around 350 °C, followed by a gradual reduction reaching five orders of magnitude less around 500 °C [14].

In the supercritical region, the low K_w favors free-radical mechanisms and a gasification regime is observed [16]. The higher temperatures along with the observed fast kinetics in SCW lead to water molecules participating actively in gas reforming reactions [22]. Following Le Chatelier's equilibria principle, the endothermic conversion into a H_2 enriched product gas becomes dominant near to 600 °C [19]. While at higher densities and lower temperatures, the exothermic methane (CH_4) formation mechanisms are more favored [17].

In the subcritical region, the high K_w is of great importance for biomass fractionation. In contrast to current practice, hydrolytic mechanisms⁹ are catalyzed without reliance on strong acids, and their negative environmental impact [16]. In addition, the high magnitude of variation in K_w under subcritical conditions allows for the presence of both competing radical and ionic-based reaction mechanisms, with the latter slightly favored [27]. This often leads to a wide range of (and competing) de-polymerization routes for present organic substrates in the treated biomass slurry. The list of subcritical products are traditionally divided by the three distinctive phase yields: a homogenous water-insoluble oily phase known as biocrude, water-soluble depolymerized organics and finally, an undissolved pyrolytic char, known as hydrochar [14,16].

It is important to note here, the low temperature (150 – 280 °C) subcritical conditions favor the production of the lignite-like hydrochar, with the process commonly known as the Hydrothermal Carbonization (HTC). Hydrochar is an interesting SCW product for many target end-use applications such as a: super capacitor component, fuel source, binding material, organic catalyst, soil amendment, wastewater adsorbent, and fertilizer [15]. However, in this dissertation, the focus is on the high temperature process (between 270 and 400 °C), where liquid biocrude production is favored, and hydrochar is a secondary co-product.

In summary, the advantages of operating at SCW conditions for biomass treatment include,

1. Dissipative thermal losses associated with biomass drying are avoided, extending the list of possible biomass or waste feedstock applicable for thermo-chemical valorization.
2. The use of water as a working fluid reduces the environmental impact associated with refining complex organic structures: replacing fossil-based solvents, metal-based catalysts and acting as a sterilized medium to remove possible toxins or pathogens found in biomass.
3. Process intensification enables efficient utilization of energy consumed upstream, and as a result, more thermally efficient densification to the chemical products downstream.
4. The higher densities than vapor and lower viscosities than liquid, enable SCW to access the biomass solid matrix like gases and dissolve its fragments like a liquid.
5. The versatility from the changing thermo-physical properties below, at and above the CP, allow for the fine-tuning and engineering of SCW as a platform technology to serve multiple processing objectives for a variety of possible bio-products within a refinery superstructure.

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⁹ Hydrolysis reactions are referred to the cleavage of chemical bonds by the addition of water.

2.2 Thermal and process design advantages of sub/supercritical water systems over conventional thermochemical pathways

For thermal gasification and fast pyrolysis¹⁰, the operating temperatures needed for the target hydrogen bio-carriers are relatively higher than their respective SCWR conditions. This is of great importance as the highest temperature within a reactor system plays an integral role in dictating the hot utility demand in most plant layouts, and subsequently, the overall thermal efficiency of any proposed production route [28]. Thermal gasification temperatures between 600-900 °C depending on the gasifying agent are needed for syngas production, compared to 500-700 °C for non-catalytic supercritical water gasification (SCWG) process [17]. While, catalytic SCWG conversion have demonstrated in lab-scale runs the ability to recover almost all carbon in the syngas at temperatures below 450 °C [19].

Similarly, for liquid carriers, the fast pyrolysis process is referred to in some literature as indirect liquefaction. The conversion step includes the condensing of organic pyrolysis vapors into a liquid phase product known as bio-oil [2]. Pyrolysis reactions take place in the absence of air ($\lambda = 0$) and with reactor temperatures between 400 and 550 °C at ambient pressures [14]. Other indirect thermochemical liquefaction pathways are the downstream reforming (for e.g. with FT or Methanol synthesis) of syngas from the high-temperature upstream gasifiers [2]. In contrast, subcritical or hydrothermal liquefaction (HTL), referred to historically as direct liquefaction, operates at pressures higher than that of vapor saturation to maintain liquid processing. The reportedly optimum temperature conditions for lignocellulose feedstock are around 320 - 350 °C only [18].

Aside from thermal utility design advantages, the target product thermo-physical quality (properties) is another perspective to consider when evaluating the opportunity from SCWR technologies. Experimentally, pyrolysis based bio-oil yields are reported to be around 60-75%. This is relatively higher than that reported for HTL biocrude from woody biomass, between 20 to 50% for non-catalytic runs [15]. However, the latter, being a product of partial oxidation has a higher degree of removal for unwanted heteroatoms [29]. The subcritical water processing leads to the rearrangement of hydrophilic organic fragments via condensation, cyclisation, and polymerization producing new larger, hydrophobic and de-oxygenated macromolecules [18].

The HTL biocrude as a result is a more viscous but a less dense liquid than bio-oil [30]. HTL biocrude has both lower moisture and oxygen levels, leading to improved higher heating value (HHV) of 25-35 MJ/kg compared to pyrolysis bio-oils at 14-20 MJ/kg [14]. Recent reports by Lykeskog et al. [30] showed that HTL biocrude is also more thermally stable, and better suited for transportation and long-term storage purposes. This was attributed primarily to the reduced presence of both: organic reactive components such as carboxylic acids/aldehydes and residual catalytic minerals originating from the biomass feed [31].

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¹⁰ Pyrolysis applications are classified based on reactor residence time and the subsequent emphasized product. Fast pyrolysis (in order of seconds) targets bio-oil production, while Slow pyrolysis (minutes to hours) targets charcoal production.

The general processing objective behind thermochemical treatment of biomass epitomizes in two distinct functions: physical transformation into a densified transportable form and the de-oxygenation of feedstock to increase the stored heating (chemical) value. The production of H_2 , with a HHV of 142 MJ/kg and 13 MJ/Nm³, in its pure gaseous form or bound to a carbon carrier (CH_4 , Methanol or other hydrocarbons), has been the target application for gasification systems since their conceptual inception.

The motivation continues as part of an envisaged zero or low carbon Hydrogen economy. Syngas from thermal gasification has a molar H_2 content between 10-60% depending on the feedstock, gasifying agent and operating conditions. The syngas balance consists mostly of reduced carbon, with the majority in the form of carbon monoxide (CO). The design of thermal gasification plants as a result typically includes reforming the CO fraction, via water gas-shift (WGS) reaction. This is performed either to boost the hydrogen purity or to adjust the H_2 /CO ratio depending on the downstream kinetic or equilibria requirements for conversion to the target carrier [32].

In SCWG, the presence of an aqueous medium combines the two processing steps, and the balance syngas is found in the oxidized carbon form of CO_2 (hence the partial oxidation description in some literature) [14]. The present process water even contributes to the hydrogen carrier (or gas) formation either as a reactant via dissociation in subcritical conditions and reforming agent in the supercritical regime [19]. The reported hydrogen gasification efficiencies in experimental work exceed 100% in reference to the biomass content [15].

Kruse [17] stated that part of the motivation for high pressure processing in SCWG is to minimize water vapor losses during gasification in the form of steam, instead directing it to become part of the product. However, aside from the description of the observed mechanisms, there has been scarcity in the reporting on impact and quantification of “reactive” water in the literature. This is primarily attributed to the dehydrated nature of product recovery in experimental procedures for analytical purposes. The knowledge-gap is addressed with modelling studies as represented in this dissertation.

Nonetheless, given that hydrogen content in virgin biomass, does not exceed that of water, a theoretical optimum for H_2 production would be, the energy consuming, endothermic electrolysis (water dissociation) process. As such, to ensure techno-economic viability, proposed design constraints for SCWG reactor systems have been either set to match pumpability limits for biomass based residue slurries (to perform the waste valorization function), and/or maintain thermally self-sufficiency (or auto-thermal) performance (to minimize the auxiliary energy consumption) [19].

2.3 Techno-economic bottlenecks facing sub/supercritical water technologies addressed in this dissertation

Despite the advantageous nature and listed opportunities from SCWR technologies, many engineering bottlenecks remain to be addressed before widespread commerciality can be achieved. A number of reviews have been published in literature recently. Recommended reading on technology specific analysis of HTL could be found in [14,18,33] and in [17,19,22,34] for SCWG. Other recent reviews have examined in detail both SCW biomass chemistry [15,16] and the fluid's thermo-physical properties [23,26]. This section reviews the SCW reactor systems from this dissertation's perspective, in which, the specific gaps of knowledge addressed are listed and the research scope examined is highlighted.

#1: Unfavorable economics compared to reference technologies

SCWR as a technology is considered in pilot/demo scale development [33], or in other words, at TRL(s) between five and seven¹¹ [29]. Operational data for continuous pilot-plant operations are available for HTL units, but to a lesser extent for SCWG, with near-commercial (or demonstration) data for SCWR systems absent, for obvious confidentiality reasons [29]. It is important to note that many research efforts are currently directed to the liquefaction pathway, more so than the gasification. A quick search in the Scopus database (as of October 2019) shows that the average annual publications with “Hydrothermal liquefaction” as a keyword is 186, compared to 107 for “Supercritical water gasification” during the previous four years [35]. This is driven historically by economic interest in substitute liquid fuel production, and are commonly linked to the barrel of oil market price. Castello et al. [29] published Fig. 7 to represent the underlying motivational context. In addition, the low natural gas prices in recent years, leading to the low hydrogen production costs, has also been a deterrent to renewable gas technologies, such as SCWG [12].

Figure 7. Historical oil price trends plotted for context with respect to global HTL research and development leading to pilot-scale operations. Figure reproduced with permission from [29].

¹¹ Technology Readiness Level (TRL) is a tool adapted by major funding instruments to evaluate technology maturity on a scale of 1-9, as a guide on research activities' timeline relative to commercialization.

Research frontier on the HTL platform is tasked with process design optimization for higher carbon recovery in the primary liquid products. Whereas, depending on the feedstock nature and solids loading, reactor operating condition, and catalytic effects, anywhere between 30-70% of carbon feed ends up as part of the by-product non-crude phases [14,15,18,29,33,36]. Holistically, and when considering the most examined renewable fuel production pathway, a HTL reactor system (upstream), followed by biocrude hydrotreatment (downstream), the carbon recovery reaches a reported maxima of 66% for lignocellulose and 84% for algal feeds [29]. This leads to eventual high production costs. As such, the minimization or valorization of residual streams becomes evidently an opportunity for cost reductions. A techno-economic sensitivity analysis by Zhu et al. [37] in 2014 describing development efforts at Pacific Northwest National Laboratory (PNNL) showed that with a set research target of 20% improvement in reducing organic partitioning into residue streams from the catalytic HTL process, the minimum selling price (MSP) of renewable liquid fuels would reduce by 43%. However, the MSP would remain 1.5 times higher than the highest price point of fossil-based gasoline between 2007 and 2012.

#2: The need for a more holistic valorization platform to address process residual streams

In addition to economic considerations, the significant phase partitioning of organics under SCWR systems raises environmental concerns regarding disposal measures for residual streams. In the liquefaction platform; the aqueous yield is characterized by the presence of high total organic carbon (TOC) content [33]. While, the solids hydrochars, is defined by the existing aromatic structure and significant mineral content [36]. **Publication I** in this dissertation examines and attempts to quantify the thermal and economic gains from alternative co-product upgrading technologies, and end-user scenarios for non-catalytic processing in the HTL reactor system. The term “non-catalytic” throughout this dissertation refers to the absence of heterogeneous catalysts addition to the reactor system. The presence of enclosed catalytic effect from process water, chemical components of industrial streams or SCWR reactor material is considered part of the non-catalytic system.

The primary product carriers from the HTL biorefinery examined are renewable gasoline and diesel, compatible with existing transportation infrastructure. Catalytic HTL research, both within macro-reactor and plant system levels, has received extensive attention in literature [29]. In this research, an alternative biorefinery design objective is investigated, where organic partitioning from non-catalytic HTL is utilized as an opportunity to extend a single product platform (renewable liquid fuels) into a potential biorefinery with valorized co-products: solid biomaterials and gaseous hydrogen (energy) carriers.

SCWG of the HTL aqueous byproduct for insitu H_2 production is one of the alternative scenarios considered in **Publication I**. In addition to the treatment of the water-soluble organics present, this pathway addresses sustainability concerns for H_2 gas procurement for the downstream biocrude hydrotreating

step. A limitation shared with other commercial 2nd generation biofuel pathways, which continue to rely on steam reforming of fossil hydrocarbons as a hydrogen source [8].

Publication II reports the findings from a heat integration study for a SCWG based biorefinery targeting the production of a carbonaceous hydrogen carrier, Bio-SNG. An earlier parametric study by the author [38] showed that the design of reactor conditions for a high purity gas product is constrained by equilibria yields. Fig. 8 shows the dry molar composition of the SCWG product from two model compounds of biomass intermediates. Glucose represents the hydrolysis of cellulose and phenol for the de-polymerization of lignin. Under equilibrium assumption, where mass and heat transfer limited kinetics are not considered, the CH₄ purity plateaus between 42-48 mol.% for glucose and 53 to 57 mol.% for phenol at lower reactor temperatures and higher solids loading. Similar observation could be made when considering the targeted production of Green hydrogen. The molar fractions of H₂ gas from SCWG reach 44 and 55 mol.% for phenol and glucose respectively at 600 °C and a low solids loading.

Figure 8. The SCWG equilibria dry molar composition and product gas yields at different different feed solid content, for model biomass substrates: Glucose (G) and Phenol (P). Top figure is at 600 °C reactor operating temperature (T) and 250 bar pressure (P), and bottom figure is at 450 °C. The calculation is performed with Gibbs minimization reactor module in AspenPlus® and the Soave-Redlich-Kwong equation of state (SRK EOS).

The objective from **Publication II** is to assess the different utilization scenarios for the SCWG gas balance (off-gases): primarily CO₂ along with a smaller fraction of H₂ (or CH₄), and minor yields of CO and light hydrocarbons. The main design objective is to aggregate Bio-SNG (or Green hydrogen) production via downstream methanation (or steam reforming) of the process off-gas. The

proposed biorefinery designs are compared to the off-gases utilization for excess CHP production, adapted in earlier literature [28]. The study along with **Publication III** extends the SCWR biorefinery analysis to reactor conditions of 600 °C for Green hydrogen as a target product.

#3: Complex interacting chemistry coupled with the non-ideal thermodynamic conditions lead to convoluted characterizations of the mechanisms taking place

The analysis of SCWR biorefinery superstructures attempts to aggregate both thermal and chemical processing opportunities. In order to carry out factual mass and heat integration studies, accurate and reliable quantification is needed for the encompassed thermal properties and chemical conversion steps. This is considered exceptionally challenging for SCWR reaction regimes. The presence of non-ideal thermodynamic conditions requires reliance on sophisticated computational methods [21]. In addition, unlike conventional fuels, SCWR products contain a wide range of chemical moieties [16]. Modelling SCWR includes representing largely unknown intermediates, interactive multi-phase reaction pathways, and kinetic rates, as part of complex chemistry present in real biomass feeds [17].

It is important to note that SCWR reactions are logically kinetic driven, similar to other organics' chemistry [17]. Many attempts to construct and characterize generalized SCWR kinetics are available in literature [15-17,19]. They remain limited to biomass' substrates or model compounds and directed toward the optimization of macroscale reactor conditions, such as reaction temperatures, residence times, and choice of catalyst [34]. The developed mechanistic models have greatly contributed to the fundamental understanding of organic chemistry involved in SCWR regimes, especially that of biomass fractionation and hydrolysis [16]. However, they are limited to the specific conditions in which the kinetic-fitting data is extracted, and require rigorous computation to be extrapolated for a real reactor system with complex feed mixtures.

Figure 9 recently published by [27], shows a set of parallel mechanisms compiled to describe the liquefaction of a blackcurrant pomace feed. The proposed kinetic pathways in the study are based on the group's own experimental runs of a wide range of model compounds, under catalytic (NaOH) and non-catalytic conditions, and are complimented with reported data from similar studies in literature.

The authors concluded that:

The comparison of the hydrothermal liquefaction results of blackcurrant pomace and two model mixtures shows that the real case can be qualitatively represented by using model mixtures, especially when model polymers are used to represent the fiber content of biomass (cellulose and lignin). GC-MS¹² analysis of the products showed that real systems were however more complex than model mixtures.

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¹² GC-MS: Gas chromatography–mass spectrometry analysis is an analytical tool to measure the presence of chemical components and compounds within a given experimental test sample.

As such, the adapted thermodynamic modelling approach in this research is owed to the data requirements compared to kinetic modelling, which are less, in terms of quantity, and easier to measure [39]. A more practical approach when considering the complexity of industrial bio- waste or residue streams examined in this dissertation, such as forest residues (**Publication I**), lipid extracted algal (LEA)¹³ (**Publication II and III**) and weak black liquor (WBL)¹⁴ in (**Publication IV**).

#4: The diluted processing nature requires an efficient heat recovery system in order to realize thermal efficiency improvements

Another of the SCWR systems challenges is the energy intensive nature. By virtue of elevated thermal conditions, heat integration becomes essential. As can be seen from Fig. 10, the combined enthalpy difference needed to pressurize liquid water to 250 and 300 bar and preheat from 25 to 500 °C is 3084 and 3007 kJ/kg respectively. Which is a considerable higher thermal demand when compared to the evaporation load of 2580 kJ/kg at atmospheric pressure. The dilution of solids in the aqueous feed lead to the SCWR systems faltering from a thermal perspective in the absence of efficient mass and heat recycling. This was illustrated by an early life-cycle assessment study by Gasafi et al. [40] in 2003. The study showed that the SCWG process could possibly lead to worse GWP performance compared to other thermochemical or wastewater treatment (WWT) technologies for a wet bio-sludge feed. The main source of emissions, given the absence of energy optimization, was auxiliary natural gas burned to preheat the system.

Figure 10. Enthalpy change needed for liquid water at 25 °C to reach SCW conditions at 250 and 300 bar, compared to water vaporization (Evap.) into saturated vapor. Enthalpy values are based on the IAPWS formulations 1995 [21]. The calculation was performed with heater module in AspenPlus®. The electrolyte non-random two-liquid (ELECNRTL) activity coefficient module was used to account for the water dissociation reaction.

¹³ LEA are by-products from currently under-development algae to biodiesel synthesis plants, in which, the 50-60 wt.% lipid fractions (fatty acid), undergo transesterification to produce long chain alkyl-esters.

¹⁴ WBL refers to the residual liquid from the digestive pulping unit in Kraft mills, where 90 to 95% of the lignin, other organics (polysaccharides, aliphatic acids and extractives) and the spent inorganic cooking chemicals are washed from the cellulose fibers (pulp product) with water or other mill condensates.

The thermal efficiency advantage from aqueous treatment is only realized when the removal of evaporative (drying) load is complimented by efficient recovery of heat from the process aqueous streams. A more recent study by Gassner et al. [28] showed that through process (and heat) integration, polygenerative SCWG biorefinery superstructures match the performance of thermal gasification systems for the production of Bio-synthetic natural gas (Bio-SNG). The SCWG biorefinery, with a reactor system operating temperature as high as 480 °C and a feed moisture content of 50%, had a thermal efficiency of around 61% on Lower heating value (LHV) basis. Gassner et al. [28] along with other similar system-level evaluations [15,17,34], showed that with feedstock of higher moisture levels, heat integrated SCWG based Biorefineries would possibly exceed the thermal efficiency of gasification systems.

#5: The fate of biomass inorganics under SCWR processing

Another biorefinery design objective from operating into the supercritical region is the recovery of inorganic salts around the pseudo-critical conditions [15]. The reduced solubility limits, presented in Fig. 11, are primarily attributed to the higher melting temperatures of salts, which exceed the CP of water. Precipitation takes place during experimental procedures as salt's liquid – solid (L - S) equilibria lines cross the liquid – gas (L - G) critical line of the more-volatile water [23]. Continued operational plugging and clogging of reactors remains a challenge in many of the reported SCWG experimental setups [34].

Several reactor designs adapted from the more technologically mature supercritical water oxidation (SCWO) process¹⁵, such as centrifuge reactors, hydrocyclones and the reverse flow MODAR reactor have been proposed to address the operational issues in SCWG [26,34]. The Vogel et al. team at the Paul Scherrer Institute (PSI) devised a three-stage SCW reactor system to valorize separated inorganics as an enriched by-product brine [41]. The experimental setup includes an intermediate step (independent from the catalytic reaction regime in their case) around the pseudo critical conditions of the aqueous mixture [42-45]. The PSI separator unit, similar to the MODAR reactor, utilizes the variation in water solvency to extract solids via gravity-induced precipitation in the more-dense subcritical phase. The reverse flow is induced in a vertical tubular vessel, in which enriched brine is extracted from the unit bottom. A recent collaboration with the group of Boukis et al. at Karlsruhe Institute of Technology (KIT) applied the separator concept to the 100 kg/h (maximum) capacity SCWG Verena pilot plant [46].

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¹⁵ SCWO is the treatment of waste in the presence of oxygen ($\lambda > 1$) at water's supercritical conditions with a target to destruct via oxidation all hazardous organic and inorganic material present in the feed.

Figure 11 Solubility limits for inorganic salts reported in literature as a function of water density to account for variation in experimental temperature and pressure conditions. Figure reproduced with permission from [26].

The role of inorganics' solubility and their interaction with organic substrates in SCWR systems is modelled in (**Publication IV**) as part of a wider process integration study for a commercial Kraft pulp mill (KM) case. The high process induced inorganic to organic ratio, compared to conventional biomass, is a characteristic of many industrial residual streams. The choice of Kraft (or sulfate) mill as a case study is due to the high throughput of lignocellulose materials. The pulping industry is the largest consumer of forestry biomass, and are well positioned to function as future platform Biorefineries [2]. The pulping process residual, WBL, includes around 50% of the organic structural matrix of the wood feed, and is almost exclusively combusted as a low value fuel for in-situ CHP, as well as for recycling the inorganics to the process [2]. WBL is an aqueous base mixture. The alkali present originating from both the cooking chemicals, sodium (Na) and extracted potassium (K) from the wood species results in a high pH (~13). The positive catalytic effect of alkali on biomass fractionation in subcritical water has been well documented, referred to in literature as base depolymerization mechanisms [14-16,27]. Also in supercritical conditions, alkali promotes H_2 gas yield through both neutralizing carboxylic acids and through WGS mechanisms [15,17,19,34].

Alkalis are considered a homogenous catalyst due to their solubility in water during preheating. They are favored to heterogeneous catalysts, as the latter reportedly suffer from sintering, dissolution, poisoning, internal diffusion limitation, and inactivation in hydrothermal regimes [14,19,36]. In addition, the continued presence of noble and transition metals (originating from the catalyst) in the product from the harsh reactor conditions directly impedes the design and viability of downstream upgrading stages [29]. In **Publication IV**, the mass balance closure is calculated for organics, Na, K, sulfur (S) and chlorine (Cl) around the SCWR system. The inclusion of S and Cl is primarily due to their importance as part of inorganic recycling within the KM operations. However, knowledge on the partitioning of each is also of extreme importance from a SCWR operational perspective. The reduced form, hydrogen sulfides (H_2S), in gaseous phase, along with the formation of sticky salts by the oxidized sulfates (SO_4), contribute to many of the sulfur catalyst deactivation reports in literature [14,15,34,45]. While, the presence of chlorine at a hydrolytic equilibrium rate in orders of magnitude higher than normal conditions leads to the presence of the highly corrosive alkali halides [23].

Peterson et al. [14] reported that enough experimental evidence in literature support the notion that protective layers of commercial reactors (manufactured mostly from nickel and chromium) are oxidized and dissolved by SCW. Although, fresh reduced metal surfaces contribute catalytically to the process [17], the continuous mass loss is unsustainable and hazardous for industrial scale operation [34]. As such, developments efforts in material sciences for SCW corrosion resistant alloys remain integral for industrial-scale SCWR systems [26,34]. However, they are out of research scope here. **Publication IV** offers a better understanding of the phase partitioning for some of the contributing ions, which could possibly offer guidance in the design of corrosion mitigation strategies.

#6: The integration of SCWR systems in existing industrial infrastructure

The separation of inorganics from SCWR not only serves as an operational necessity, but also improves the qualitative yield of the technology as other co-products serve other processing requirements in an industrial site. The potential from other biomass-sourced inorganics has also been examined in literature [22,47-49]. Haiduc et al. [41] showed as part of their SunChem design that nutrient demand for algal cultivation mediums could be partially fulfilled by recycled nitrogen compounds. While, Boukis et al. [46], during their bio-sludge experiments in the VERENA pilot plant illustrated the recovery of phosphorus by up to 80%, a limited resource without a fast natural cycle. For the industrial case study in **Publication IV**, the mass and energy balance implications from recycling inorganics under SCWR are compared to the traditional KM chemical recovery cycle. The material site integration is combined with economic considerations to account for commercial feasibility constraints. This, along with the stand-alone HTL biorefinery considerations in **Publication I**, enable mapping the economic constraints for SCWR systems in reference to commercial technologies for hydrogen carriers, as well as integration within existing synergetic industrial infrastructure.

3. Research Objectives

“Many industrial studies have compared the monies spent on process design and construction projects to the fraction of the costs committed as the project progress. Typical results indicate that, a company will have spent 15 to 20% of the total funds devoted. However, the decisions the preliminary design team makes fix about 80% of the subsequent costs.” Biegler et al. [50]

The research presented in this dissertation is aimed to evaluate and identify favourable SCWR biorefinery configurations for the primary production of commercial liquid (from HTL) and gaseous (from SCWG) hydrogen bio-carriers.

The study focuses on the development of modelling tools for the upstream SCWR reactor systems and relies on available literature for the more matured downstream technologies within the system-level techno-economic evaluations.

The main questions attempted to be answered in this research are:

1. What is the quantifiable contribution of water as a reactive component in SCWR systems in reducing the carbon intensity of hydrogen bio-carrier production?
2. What is the role of biomass' inorganic-organic substrate interactions on the SCWR reactor conversion?
3. Could the augmentation of carbon and hydrogen in the non-catalytic SCWR by-products, lead to reducing process residuals, while matching the technical specifications and economic gains of reference technologies?
4. What are the commercial feasibility drivers and constraints for potential co-products in the developed non-catalytic SCWR biorefinery concepts?
5. What are possible material recycle synergies and added-value from the SCWR system site integration with existing industrial biomass processing plants?

4. Research Methods

The modelling framework applied in this dissertation combines four levels of scrutiny:

1. Rigorous thermodynamic modelling of the SCWR reactor systems.
2. Process flowsheeting for the biorefinery case studies examined.
3. Process (heat and site) integration.
4. Economic analysis.

Figure 12 illustrates the boundary conditions applied at each level for the biorefinery cases examined. To guide the reader: the term (SCWR) is used during generalized discussions on both the liquefaction and gasification reactor systems, while the terms (HTL) and (SCWG) are used to describe the reactor systems within the context for technology specific case studies.

The findings from the modelling framework attempt to extend available *preliminary designs* in the literature to a *detailed-estimate design* level of understanding for the possible SCWR biorefinery configurations [51]. The detailed-estimate quantifies processing flow rates, complete material and energy balances and consequent integration opportunities, offsite raw material demands and knowledge on target commercial specification and quality, process units' conversion yields, reaction rates and operational cycles.

The first level of modelling includes developing quantitatively descriptive models on the AspenPlus® process simulation tool [52] for the core biorefinery technology, the SCWR reactor system. The reactor model development includes and accounts for:

1. Screening and validating predictive correlations and properties databases for high-pressure thermodynamic calculation routines and the experienced multi-phase physical properties.
2. Deviation from equilibria in organic conversion within reactor systems.
3. Solubility of inorganics in SCW and subsequent impact on organic valorization.
4. The distinctive heat of reaction and phase properties for the different stages within the SCWR reactor system.

Figure 12. The different modelling scrutiny levels and boundary conditions applied in this research. Publ.: Publication, B.O.P.: Balance of plant, AspenPlus®: Commercial process simulation software by Aspentech [52].

The validated mass and energy yields from the first level are used as the fundamental basis for the subsequent system-level studies. Synthesized process flowsheeting on AspenPlus® is performed for the balance of plant (BOP) components in **Publication I, II and III**. In the context of this thesis, the BOP refers to all process units excluding the SCWR reactor system. The reactor system product is upgraded insitu to commercial product specifications. The process flowsheeting (Level 2a in Fig. 12) relies on reported unit conversion for commercial technologies to calculate relevant mass and energy formulations. Table 1 lists the case studies examined, including the different modelling levels and target hydrogen carriers evaluated.

For **Publication IV**, the bio-carrier is utilized insitu (without upgrading) as part of the KM site integration or sold to be upgraded offsite. The mass and energy flow exchanged between the SCWR reactor system and the industrial site is calculated in a spreadsheet according to the reported performance of a reference KM in the literature [53] (Level 2b in Fig. 12). The only exception is the recovery boiler (RB). The impact of co-firing the SCWG reactor yield on the chemical balance of the RB is examined in detail in an AspenPlus® sub-model.

Level three considers process integration from both a material and heat perspective. The IEA defined process integration as [54]:

“Systematic and general methods for designing integrated production systems ranging from individual processes to total sites, with special emphasis on the efficient use of energy and reducing environmental effects”

Several methods for process integration studies exist. They include (but not limited to) the integration of heat exchanger networks (HEN), process material flows, water utility networks, site facilities and sectoral coupling. For **Publication I, II and III**, level 3a considers heat integration within the proposed biorefinery boundaries. This includes the exchange of process heat between the material streams of the SCWR system and the downstream upgrading units. In addition to the presence of a common utilities network, where off-gases and other residue streams of thermal value are fired in centralized units.

For level 3b in **Publication IV**, the SCWR reactor system is considered as a stand-alone unit located within the KM boundary conditions. The internal heat transfer within the reactor system streams and the consequent auxiliary boiler, are independent from the KM. The site integration considers the “drop-in” effect of the SCWR products within the KM operation. The design constraint for the integration study is to maintain minimal disturbances to existing power, steam, cooling and water utilities infrastructure. The impact on the KM power and steam production is accounted for in the level 2b balance formulations.

The feedstock procurement is one of the distinctions between the case studies examined. **Publication I, II and III** examine a stand-alone biorefinery, in which the feedstock LEA and Forrest residue, albeit being industrial by-products, are considered to be purchased offsite of the biorefinery. **Publication IV** considers the site localization affect, and as such, the WBL procurement is examined within the KM economic boundaries of level four.

The hydrogen carrier co-products for all case studies are considered to be sold “over the counter”, and as such transportation and distribution costs to end-users, as well as, energy and fuel market analysis, are not accounted for in detail within the research.

Table 1. Case studies presented in this dissertation for the SCWR biorefinery configurations.

SCWR Case*	Biorefinery design Downstream tech.	Primary product	Bio co-products	Process integration Heat recovery	industrial site	Econ.	Publ.
HTL1 (15% slds, 330 °C & 210 bar)	(B) Hydrotreatment	Ren. liq.	Hydrochar	Biorefinery level	No	Yes	
HTL2 (15% slds, 330 °C & 210 bar)	(B) Hydrotreatment (G) Steam reform (S) CHP	Ren. liq.	Hydrogen	Biorefinery level	No	Yes	
HTL3 (15% slds, 330 °C & 210 bar)	(B) Hydrotreatment (G) Steam reform (Aq.) SCWG (S) CHP	Ren. liq.	Hydrogen	Biorefinery level	No	Yes	I
HTL4 (15% slds, 330 °C & 210 bar)	(B) Hydrotreatment (G) Steam reform (Aq.) SCWG	Ren. liq.	Hydrogen Hydrochar	Biorefinery level	No	Yes	
SCWG1A (18% slds, 450 °C & 250 bar)	Methanation	Bio-SNG	- Heat	Biorefinery level	No	No	
SCWG1B (18% slds, 600 °C & 250 bar)	Methanation	Bio-SNG	Power Heat	Biorefinery level	No	No	II
SCWG2A (18% slds, 600 °C & 250 bar)	Steam reform	Green H ₂	Power	Biorefinery level	No	No	
SCWG2B (5% slds, 600 °C & 250 bar)	Steam reform	Green H ₂	Power	Biorefinery level	No	No	II and III
SCWG2C (5% slds, 600 °C & 250 bar)	-	Green H ₂	Power	Biorefinery level	No	No	
SCWG3A (18% slds, 600 °C & 250 bar)	-	H ₂ -rich gas	Pulp Power CTO Heat	Stand-alone SCWG	Yes	Yes	
SCWG3B (18% slds, 450 °C & 250 bar)	-	CH ₄ -rich gas	Pulp Power CTO Heat	Stand-alone SCWG	Yes	Yes	IV

* The SCWR reactor conditions for each case study is listed inside (): solid content of feed in wt.%, reactor target temperature in °C and pressure in bar.

Acronyms: slds: solids content, Econ.: Economic analysis, B: HTL Biocrude, G: HTL Gas, Aq.: HTL Aqueous yield, S: HTL solid yield, Ren. Liq.: Renewable gasoline and diesel, CTO: Crude tall oil.

4.1 Hydrogen carriers' production case studies

The set SCWR reactor system conditions (temperature, pressure, and solid content), along with primary bio-carrier nature differentiate the case studies examined. The HTL biorefinery in **Publication I** aims to model renewable liquid fuel production, compatible as a low-carbon or green-blend for the transportation sector. The downstream upgrading technologies for HTL biocrude are synonymous to existing oil refining stages such as hydrotreating and hydrocracking [37]. Nonetheless, a higher concentration of oxygenated and reactive functional groups in HTL biocrude, necessitate special attention to the gaps of knowledge remaining on the “drop-in” impact of biocrude in existing oil refinery units [18]. As such, the proposed biorefinery design is a stand-alone concept, in which primary products share similar chemical functionalities and physical properties to fossil-based fuels. The proposed point of supply chain integration is offsite, at end-user distribution facilities. Similar approaches have been most common for the commercialization of 2nd generation fuels [7].

Publication II and III aim to model the production of compatible gaseous H₂ carriers for industrial and power generation sectors. Green hydrogen with a purity up to 99.99% is intended to be used in CHP generation, liquefied storage, fuel hydrogenation, and water chemistry industrial applications. **Publication II** also examines the production of Bio-SNG compatible with Finnish grid-quality standards as an alternative carrier to gaseous H₂ production. It is important to note here that thermochemical pathways for Bio-SNG production continue to retain the largest share of newly installed “green” commercial projects [12]. This is primarily driven by both technology maturity, as well as existing synergies with fossil methane supply chains

Publication IV, similar to **Publication II and III**, examines the SCWG platform for both hydrogen or methane rich gas production. **Publication IV** differs in the absence of insitu SCWG product gas upgrading or enrichment. The product Syngas is either directly fired within the mill boundaries or sold to offsite or co-located facilities for further upgrading, similar to existing KM supply chains for biofuel production [2].

4.1.1 Liquid carriers: renewable fuels production

Figure 13 illustrates the different process blocks within the HTL biorefinery case studies investigated for renewable liquid fuels production. The examined HTL reactor system is for non-catalytic operations. The addition of homogenous alkali or heterogeneous catalysts as part of the SCWR reaction regime in general and organic capping agents for the liquefaction platform specifically reduce solids yield [36]. However, the latter come with their own separation and recovery challenges in subcritical operations [33]. The main feed to bio-product conversion route is common for all case studies. This includes the direct liquefaction of wet feedstock, followed by a hydrotreatment system, similar to proposed pathways in literature [18,29]. The role of the downstream units is the removal of

oxygen and other hetero-atoms by the way of hydrogenation, followed by fractionation/distillation to renewable diesel, gasoline and a residue stream, similar to heavy fuel oil (HFO).

Figure 13. Overview process blocks for the different hydrothermal liquefaction of Forrest residue to renewable liquid fuels biorefinery configuration examined in this dissertation. HTL 1- 4: case studies. Large Square (blue): main process blocks. Small Square (shaded grey): HTL reactor system yield. Green Diamond: primary product. Yellow Diamond: co-products.

The examined feedstock is Finnish forest residues, a mixture of softwood and hardwood, collected during the harvesting of industrial wood. The feed elemental analysis is adapted from [32]. The biorefinery thermal feed is set at 300 MW on LHV basis, not considering auxiliary boiler consumption. This is equivalent to a solids throughput of around 1500 dry ton per day, similar to proposed technically feasible capacities in the literature [32,37]. The feedstock in all case studies enters a mechanical pretreatment block at the point of entry to the biorefinery. The solids content for the HTL reactor system is 15 wt.%, a conventional estimate similar to reported commercial pumping limitations [18]. The balance water mixed with the solid feed is recycled from the biorefinery operation along with a make-up stream (10% assumed as processing losses).

The HTL1 case, referred to as base case (BC) in **Publication I**, represents the conversion inefficiencies of the HTL technology. The hydrogen demand for HTL biocrude upgrading is procured offsite. Whereas the HTL gas yield is flared (around 85% CO₂) and the aqueous yield is treated in conventional WWT facilities. The solids from catalytic processing are proposed in the literature to be disposed-off in industrial landfills due to the low carbon and high mineral content [37]. In non-catalytic operations, significant mass and thermal yield remain. As such, it is considered to be sold for soil management and carbon sequestration purposes [55], or as a fuel or feedstock for biomaterial production [56].

The HTL2 case (case U1 in **Publication I**) considers the utilization of HTL solids for CHP purposes and the HTL gas for H₂ gas production within the biorefinery boundaries. The primary objective is to match both thermal utility and

material processing penalty. In the modelled hydrogen plant, the mixed biorefinery off-gases first enter a Selexol scrubber to remove acid gases (CO_2 and H_2S) [57]. The clean hydrocarbon-enriched gas then enters a series of catalytic reactors: steam reformer (at 650 °C reactor temperature) and a two-stage WGS reactor system (at 350 and 200 °C). The proposed reactor sequence is widely employed in commercial gas synthesis plants to reduce coke formation and increase H_2 conversion [58].

The solids CHP boiler is modelled similar to a bubbling fluidized-bed design proposed in [32,59]. Process heat demand is given precedence in utility network design. As such, the boiler is modelled as a heat only boiler (HOB) when available thermal load is insufficient to match both heat and power demand. An additional auxiliary boiler (if required) fired by Forrest residues is used to match hot utility demands not met by the HTL solids. The co-firing of HTL solids with Forrest residue was not examined in this study.

The HTL3 case (case U2 in **Publication I**) extends the biorefinery downstream valorization to the HTL water-soluble organics. The aqueous yield, mixed with other biorefinery condensates and wastewater streams, is fed to a SCWG reactor system, designed similar to the pilot setup reported in [40]. A common pressure swing adsorption (PSA) system for the product gas from the hydrogen plant and the SCWG reactor system brings gaseous product quality to Green hydrogen quality [28]. The HTL4 case (U3 in **Publication I**) expands the biorefinery product portfolio to include the three possible products: renewable liquid fuels, Green hydrogen and hydrochar. The case utility demands are met by the auxiliary boiler exclusively.

4.1.2 Gaseous carriers: Green hydrogen and Bio-SNG production

The production of the two H_2 gas carriers is through the common valorization of feed solids in the SCWG regime, followed by case specific downstream reforming. Fig. 14 illustrates the different process blocks present for each case study. For the detailed description of material flows, the reader is referred to **Publication II** for the grid quality Bio-SNG cases SCWG1A-B and **Publication III** for Green hydrogen cases SCWG2A-C.

Figure 14. Main process blocks for the different SCWG case studies examined.

The LEA feedstock is assumed to be delivered to all case studies in dry conditions. The feed is mixed with recycled water and a make-up stream to the desired solid content. The mixed feed is pressurized and then fed to the three-stage

SCWG reactor system, modelled according to [28]. The two selected reactor conditions, 450 and 600 °C, are meant to evaluate cases of both high fraction of CH₄ and H₂ gas, directly produced in the SCWG, respectively. In addition to cases with higher gas yields in the 600 °C. Similarly, the high solid content at 18 wt.% and the diluted feed at 5 wt.% evaluate the equilibria driven production of each gas, as shown earlier in Fig. 8.

The product gas then enters a thermal recovery block (independent block in the current conceptual design level). Case study SCWG1A, operating at a reactor temperature of 450 °C, is the only case, where only heat is recovered from the cooling of the SCWG product. Power production in the biorefinery is extracted from supercritical turbines, operating at inlet conditions of 600 °C, similar to expanders in commercial USC power plants or natural gas plants [20]. As such, all other examined cases, operating at high reactor conditions enter a power and heat recovery block. Where, the SCWG product first expands to 65 bar and then is further cooled to ambient temperatures similar to case SCWG1A.

In terms of design evaluation, the thermal penalty or benefit from the addition of excess power to the product portfolio could be observed by comparing the two Bio-SNG cases: SCWG1A and SCWG1B. The thermal and process design trade-offs evaluated in this research are listed in Table 2. The reader is directed to **Publication II** for a more detailed review on other proposed conceptual designs for SCWG Biorefineries in the literature.

Table 2. The design objective and thermal trade-off for the examined SCWG biorefinery cases.

SCWR Case	Biorefinery design tradeoff
SCWG1A	Base case at lower SCWG reactor temperature of 450 °C and high solids at 18 wt.%, with grid quality Bio-SNG as only target product.
SCWG1B	Higher reactor-operating temperature at 600 °C, to evaluate: 1. Excess power as an additional biorefinery product. 2. Higher gas yields in the SCWG reactor with lower CH₄ purity.
SCWG2A	Similar reactor temperature and solids to evaluate the Green hydrogen pathway at thermal self-sufficiency compared to the Bio-SNG cases.
SCWG2B	Diluted solids at 5 wt.% and temperature of 600 °C, to evaluate higher H ₂ purity in the SCWG reactor gas yield.
SCWG2C	No downstream utilization of off-gas at the higher H ₂ purity in the SCWG reactor gases.

In all case studies, the cooled down and depressurized SCWG product enters water and acid gas removal units, as shown in Fig. 14. The two-stage knockout drum system is designed to dehydrate the SCWG product, produce an off-gas stream rich in CO₂ and recycle process water. The balance gases in the dry SCWG product, with a high fraction of CH₄ or H₂, falls below bio-carrier target specifications. The following Selexol system selectively extracts 97% of CO₂ and 91% of the H₂S. The remaining impurities are removed in membrane units [57] to match

grid specification for the Bio-SNG cases or in a two-stage PSA system [28] to reach purity of 99.99% for Green hydrogen cases.

The separated off-gases are aggregated to an indirect production (or utilization) block to improve biorefinery material recovery. For the Bio-SNG cases SCWG1A-B, off-gases consisting of CO_2 and H_2 , with residual alkanes, enter a catalytic reverse water gas shift (RWGS) reactor at 500 °C to adjust the H_2/CO ratio for a following catalytic methanation reactor, operated at 300 °C. The CH_4 enriched gas is dried, and recycled to the membrane units in the upgrading block to augment the biorefinery Bio-SNG production capacity.

For the Green hydrogen cases SCWG2A-B, the raffinate stream (off-gas) from the PSA units, consisting of mostly CH_4 , is the only stream utilized in the indirect hydrogenation block. The hydrocarbon-rich stream enters a steam reformer followed by a two-stage water gas shift reactor system. The reactor sequence and operating conditions are similar to the hydrogen plant in the HTL cases. Where, the H_2 enriched gas is recycled to the PSA separator units to boost bio-carrier production.

The two indirect production pathways are evaluated by comparing cases SCWG1B for Bio-SNG and SCWG2A for Green hydrogen, both of which operate at the higher temperature and solid content conditions. The thermal penalty/benefit from a higher direct H_2 gas production in the SCWG reactor system is examined for a diluted solid feed of 5 wt.% in the case SCWG2B. The low solid content case reduces the hydrocarbon balance in the biorefinery off-gases. As such, the last case SCWG2C examines the thermal penalty/benefit trade-off of excluding the downstream upgrading pathway, in which the off-gases are simply combusted for insitu heat recovery.

4.1.3 Kraft pulp mill integration

In today's pulp and paper industry, large quantities of WBL are generated when the lignocellulose feed is digested with cooking chemicals (comprising sodium hydroxide and sodium sulfide) to separate cellulose fibers, used to produce specialty pulp, from other components. This side stream, rich in dissolved organic compounds (50% of original feed), makes WBL valorization an attractive pathway for valuable chemicals and energy recovery. The WBL mixture has a water content of around 80–85 wt.% and enters the Kraft recovery cycle for material and heat recovery, as shown in Fig. 15.

The aqueous WBL is first concentrated into strong black liquor (SBL) in a multi-staged evaporation step to remove ~ 80% of present water. The thermally densified SBL is then fired in a dual-purpose Tomlinson recovery boiler (RB). The boiler generates surplus heat (live steam) and recycles the cooking chemicals back to the pulping line as white liquor (WL), after a final recausticizing stage. The inorganic fraction in SBL (~45% on dry basis) lowers the fired heating value (13–15 MJ/kg) in the RB, and causes fouling and slagging throughout the recovery cycle. In addition, despite continuous improvement to the onsite steam economy, the recovery cycle is still characterized by poor thermal efficiency [60]. This is attributed to the evaporation stage, which consumes around one-third of steam produced insitu [61]. Nonetheless, the Tomlinson RB remains the most

widely adopted technology. This is credited to the economic and environmental importance of recovering and reusing the inorganic chemicals, where the RB is nearly 97% efficient in that regard [62].

Figure 15. The boundary conditions of the examined site integration of the SCWG reactor system in the operations of the recovery cycle in a Kraft pulp mill.

Commercially built KMs have continued to increase production capacities over the last 30 years to match increased demand in emerging economies [63]. Newly constructed mills have utilized excess carbon in the recovery cycle to expand their bio-product portfolios beyond the primary specialty pulp target. Crude tall oil (CTO), turpentine, biogas, sulfuric acids, methanol and bio-composites, are all by-products currently generated from mill side streams, albeit a small fraction of residual carbon [60]. The aqueous nature, as well as high alkali and available thermal content, of WBL qualifies it as an opportune candidate for the SCWR technology platform. The site integration includes redirecting the WBL stream to the parallel-aligned SCWG reactor system, rather than following the traditional recovery cycle, as illustrated in Fig. 15.

The objective behind the site integration is to evaluate displacing excess bioenergy (in the form of power) with additional bio-products from WBL organic valorization by the way of the SCWG system, while maintaining efficient recycling of inorganics.

The fixed solid content in the extracted WBL from KM operation, leads to the fine-tuning of the gasification regime temperature defining the primary product gas component, either H_2 in the high temperature case of 600 °C (SCWG3A) and CH_4 at 450 °C (SCWG3B case). The physical nature and chemical composition of the SCWG co-products are examined to identify possible “drop-in” points within the KM recovery cycle. The impact of co-firing the co-products (solids) on the RB chemistry is performed to evaluate the set integration constraint. In which, the RB continues to contribute in-situ bioenergy to match mill demands and maintaining the recyclability of inorganics. The examined mass, energy,

and cost balances for the KM operations include exchanged material (steam) and energy (power) streams with the pulping line, defined as the biorefinery balance of plant (BOP) in the context covered in the dissertation.

4.2 AspenPlus® process models

The following section selectively describes some of the models developed in AspenPlus® and other computational tools for different physical processes and unit operations within the biorefinery case studies investigated. For the detailed description of process units and modelling tools applied, the reader is referred to the appended publications in this dissertation.

The utility of AspenPlus® as a process modelling software to simulate thermochemical processes such as the SCWR reactor system and biorefinery thermochemical conversion steps is due to the built-in computational abilities. AspenPlus® contains libraries of industrially relevant unit operation blocks that calculate existing chemistry and phase equilibria based on extensive list of thermodynamic routines available in the literature, and compound databases available from the National Institute of Standards and Technology (NIST) Standard Reference Data Program (SRDP) [52]. Other process modelling tools such as CHEMCAD [64] and Belsim SA [28] have been reported, however Aspen Plus® remains the most extensively applied tool in the field [37,59,65-69].

4.2.1 Feedstock solids modelling

Publication I, II and III investigate the organic valorization of the solid feedstock in the SCWR reactor system. The inorganic (or ash) content of the feed is considered inert and is only accounted for in terms of respective mass yields. The solids flow in the reactor system (feedstock, hydrochar and ash) were defined as AspenPlus® non-conventional compounds, and were thermodynamically modelled based on built-in coal correlations, HCOALGEN and DCOALIGT, respectively. The calculation routines applied for the solids component in material streams are the Boie correlation to calculate the heat of combustion, the Kirov correlation for the specific heat capacity and IGT density equation¹⁶ [52]. The calculated HHV on dry basis, listed in Table 3, along with the feedstock elemental analysis reflect with reasonable accuracy experimentally measured heating values. The calculated heating values are used as the reference values (thermal input) for the biorefinery technical evaluations.

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¹⁶ IGT (Institute of Gas Technology) equations give the solid-phase density of coal based on the ultimate and sulphur analysis. The standard deviation for 190 collected samples is 1.6% for a coal having a hydrogen content around 5%, in a similar range to biomass feedstocks.

Table 3. Elemental analysis in wt.% for the Forrest residue feedstock for case studies HTL1-4, and LEA for case studies SCWG 1A-B and 2A-C.

	Proximate analysis on dry basis		Ultimate analysis on dry ash free basis		
	Forrest residue	LEA		Forrest residue	LEA
Moisture content*	50%	5.6%	Carbon	51.99%	50.99%
Fixed carbon	19.4%	15.3%	Hydrogen	6.18%	7.44%
Volatile material	79.3%	79.8%	Nitrogen	0.41%	7.48%
Ash	1.3%	4.9%	Sulphur	0.02%	0.48%
HHV MJ/kg	19.9	21.9	Oxygen**	41.40%	33.61%

*on received basis, ** by difference.

Aside from using the correlations to model the slurry physical properties, the solids heat of combustion, calculated with the Boie correlation based on the dry elemental analysis is assumed to equate the enthalpic input into the reaction. The reactor thermal load (heat of reaction) is consequently the balance of heat of formation for liquefaction or gasification products and that of the solids enthalpy. The calculation and reference conditions for the stream enthalpy balance in Aspen Plus® is illustrated in Fig. 16. The enthalpy of departure (relative to standard conditions) are calculated with the selected equation of states (EOS) appropriate for the high pressure and temperature conditions examined in the SCWR reactor system¹⁷. The modelling approach has been validated in the literature for a wide range of biomass thermochemical processes such as CHP and in estimating the heat of pyrolysis and torrefaction processes [70].

Figure 16. Stream enthalpy balance calculation in AspenPlus®. DHFORM: heat of formation, IG: ideal gas and T: temperature. Reproduced from the software guideline materials [52].

The modelled WBL stream in **Publication IV**, is a mixture of organic (polysaccharides, lignin, phenolic derivatives, aliphatic acids, and extractives), and inorganic pulping by-products. The number of real compounds present in industrial liquors reaches hundreds, if not thousands [62]. The detailed characterization of the modelled organic compounds is listed in the appended publication. The solid lignin present in WBL mixture is modelled as non-conventional compound, similar to other organic solid flows in this research.

¹⁷ PSRK: Predictive for the subcritical conditions in Publication I. PR-WS: Peng Robinson with the Wong-Sandler mixing rule in Publications II and III for organic valorization in the supercritical phase. ELECRTL-HG: the modified Helgeson model for the electrolyte non-random two-liquid activity coefficient model, with the RK: Redlich-Kwong equation of state.

The physical properties for the non-solid components of material streams are modelled with the built-in electrolyte chemistry package in Aspen Plus®. The model combines solution chemistry with phase equilibria calculations. The list of reactions for salts formation, dissociation, and solids precipitation includes 12 WBL ions (Na^+ , K^+ , H_3O^+ , CH_3COO^- , CO_3^{2-} , SO_4^{2-} , S^{2-} , HS^- , OH^- , HCO_3^- , HSO_4^- and Cl^-) and 44 reactions. The list of possible solid salts included the original list of salts in the WBL and their hydrated forms, in addition to alkali bicarbonates and their double salts with carbonates, sulfate double salts with chloride and hydroxide, and finally carboxylic salt hydrates.

The modeled WBL has an inorganic (Na-K-Cl) to organic (C-H-O-S-N) ratio of 0.28 on a dry mass basis. The presence of inorganics characteristically alters the mixture physical properties. In mill operations, this is observed by increased energy demand to evaporate WBL by 4–6% compared to the latent heat of pure water evaporation [71]. When specific salts dissolve in water, the enthalpy of dissolution increases the enthalpy of the mixture, and, as a result, increases the boiling point of the mixture. The difference between the latter and the boiling point of water is known as the boiling point rise (BPR), and is commonly used to describe industrial liquors.

Figure 17 compares the modeled BPR in AspenPlus® against alternative correlations reported in the literature describing industrial liquors. The first data set (DS1) is modeled in Aspen Plus® properties and maintains solids composition while varying dilution. The second data set (DS2) is modeled with an adiabatic phase separation unit to take into account organic losses during evaporation. The present alkali dissolves released gases, while a fraction of volatile organics leaves with the vapors. As Fig. 17 shows, the modelling approach, while providing additional information on the existing inorganic chemistry, is consistent with the literature in predicting the WBL mixture's physical properties up to the 40–50 wt.% dilution, beyond which the absolute difference varies between two and seven temperature degrees.

Figure 17. The predicted boiling point rise (ΔBPR) of the developed WBL electrolyte chemistry package compared to industrial parametric correlations by Frederick et al. [72], Vakkilainen [60] and Adams et al. [62] and the Raoult's law model by Järvinen et al. [71].

4.2.2 Subcritical liquefaction model

The HTL reactor system block contains the principal de-polymerization step for feed solids into a hydrolyzed mixture of hundreds of organic compounds consisting of a wide range of acids, alcohols, aldehydes, esters, ketones, phenols and lignin derived oligomers [14]. The hydrophobic characteristic of the target biocrude is a function of the specific yields from the interacting chemical functional groups. Optimal reactor conditions for higher biocrude yields from lignocellulose feeds are reported between operating temperatures of 270 and 330°C in subcritical pressures [28]. The upper temperature restrains carbon partitioning into the gases, as it suppress secondary decomposition and Bourdard reactions. In addition, near to the critical point the recombination of free radical reactions into solids are activated in the presence of low ionic water conditions. The recent screening of HTL experimental work by Castello et al. [29], shows that feedstock nature and solids content dictate biocrude yield and quality, as well.

To model the fragmented nature of the reactor product and to account for the parallel and interactive conversion mechanisms, a predictive yield model was developed on the General Algebraic Modelling System (GAMS) software [73]. The highly non-equilibrium liquefaction yield is solved via a linear programming (LP) optimization routine. The modelling approach is a resource allocation type, with the objective function set to minimize mass balance error. The elemental feed is distributed to a predefined list of product compounds; and subject to the constrained yields for each of these compounds and the constrained phase distribution of the HTL organics.

The list of product compounds representing the liquefaction yield is determined by screening the reported GC-MS detected compounds in reported experimental HTL studies. The corresponding relative quantities is set based on reported percentage of a compound relative to the total chromatogram area. Although, GC chromatograms are limited by components' volatility and previous familiarity of potential product list to be expected, the analytical approach has demonstrated pragmatic feasibility in characterizing biomass-processed liquids [74].

The complete formulation of the optimization routine for the Forrest residue case, as well as the list of experimental references and compounds examined is found in the Appendix of **Publication I**, as well as in another publication by the author in [59]. Similar approach is adapted to close the mass balance of the hydro-treatment reactor in the upgrading block in the HTL study cases and in modelling the liquefaction of the lignin component in the WBL mixture in **Publication IV**.

Figure 18 illustrates the performance of the model compared to experimental data for different forestry lignocellulose feedstock. The two literature sources (Test exp. in the figure) were used to construct and validate the model performance based on biocrude compositions (carbon, hydrogen and oxygen wt.%), conversion (the solid residue yield) and thermal recovery (the HHV). When compared to the verification data, other experimental reports not used to construct the LP model, the relative error was found to be between 2 to 8 % for C wt.%, -1 to 8% for HHV and -3 to 0% for the solid yield. Larger deviations were

found for the hydrogen and oxygen content. However, that is expected due to oxygen transfers (hydration and dehydration reactions) between process water and the solid feedstock [31]. The lack of water consumption accounting from the experimental reactor setups limits the possibility to verify hydrogen and oxygen balance closure. The aqueous yield and the oxygen content of biocrude are regularly reported by difference in literature.

Figure 18. LP model validation for non-catalytic HTL reactors. Test exp. (1-2): experimental data sets used to build the model [75,76], Verif. exp. (1-3): external data sets for verification [31,77,78].

The composition of the HTL product from the predictive LP model is then used as the liquefaction output for the built-in AspenPlus® yield reactor. The developed AspenPlus® model for the biorefinery HTL reactor block, calculates the stream properties, reactor energy balance and the phase equilibria for the HTL product recovery units. The detailed description of the design criterion for process units (and model input conditions) could be found in the appended **Publication I**.

4.2.3 Supercritical gasification model

The adapted modelling approach for the gasification regime is the constrained equilibria (CE) method. The conceptualization of thermodynamic equilibria is based on minimizing Gibbs free energy (ΔG) for a given reactive system. The second law of thermodynamics dictates that all closed systems are driven towards equilibria, in which, by maximizing the entropy component (ΔS), shown in equation (1), all change (chemical reactions taking place) within the system are concluded. The process intensification nature of SCWR, namely the higher temperatures, is expected to accelerate equilibria driven mechanisms, leading to the suitability of the approach. Most importantly, the pragmatism of the approach remains in the simplification of the stoichiometric chemistry involved.

$$\Delta G = \Delta H - T\Delta S = \sum_{i=1}^{N_i} n_i \mu_i \quad (1)$$

Under equilibria-extent assumption, the non-stoichiometric model is constrained only by both: molar conservation, in which elemental feed (reactants) are partitioned to one of the pre-defined product components (n_i) and the non-negativity nature of such partitioning. The change in free energy is calculated in practice for isothermal reactor conditions (constant T). The departure in product mixture properties, enthalpy (ΔH) and entropy, is calculated in reference to standard conditions as explained by Fig. 16. The sum of chemical potential (μ_i) for each partitioned component, based on their respective molar volume, equates the minimized molar Gibbs energy change within the reactive system. The impact of molecular interactions on component's molar volume calculations is accounted for with the use of EOS for gaseous and activity coefficient models for condensed (liquid or solid) phases. The author in [59] detailed the derivation for the Gibbs minimization calculation routine.

However, real chemical reaction systems are characterized with conversion inefficiencies due to mass and heat transfer restrictions and the absence of indefinite time needed to reach equilibria. The CE modelling approach envisages the introduction of additional mechanistic and immaterial restrictions to account for such deviations [79]. The approach has been widely adapted in literature under different terminologies based on the nature of applied constraints.

Koukkari et al. [80] combined CE with the kinetic rate for selected governing reactions in multi-phase reactive systems. In another study by the same group, an extended list of constraints based on reported experimental deviations in gas compositions, tar and char formations were applied for thermochemical conversion of biomass [81]. The approach was first applied to SCWG systems in [82] for a glucose feed. Carbon conversion to gas was the only deterministic constraint. The model reportedly predicted gas composition more accurately than the equilibria –extent approach. Yakaboylu et al. [39] extended the non-stoichiometric approach with constraints for both carbon and hydrogen conversion to describe a multi-phase yield of the SCWG process. The group [39] concluded that the model could fairly predict the reactor performance; however, additional constraints, specific to the experimental validation are needed. This would restrict the model replicability for other setups. A more comprehensive literature review on other modelling studies applied for the SCWG process could be found in **Publication II**.

The CE gasification model applied in this research could be described within a period of two development stages. The first model, applied in **Publications II and III**, follows the approach by [39] and [81] in defining conversion inefficiencies as solids phase partitioning. The organic losses are assumed to be 10% of elemental feed following [28]. The solids are removed with the inert ash in an interstage solid separator, between the liquefaction and gasification units. The model validation discussed in detail in the appended papers showed that the predicted gas yields fell in line with experimental data with carbon recovery in the gas phase similar to the constrained value.

The gasification model was extended in **Publication IV** to account for the presence of inorganics in the reactor system, and to decouple the heat of reaction for solids liquefaction from that of gasification. The latter was performed to improve the characterization of enthalpic change and stream transport properties within the reactor system for the subsequent heat integration study. This is performed as the earlier study in **Publications II and III** showed that an optimal heat exchanger arrangement, even when considering available heat loads downstream, would include recuperating heat from the SCWG product stream to preheat the pressurized feed. Table 4 summarizes the difference in modelling assumptions applied for the gasification model in **Publications II and III** and that of **Publication IV**.

Table 4. Review of the modelling assumptions and applied calculation packages for the developed SCWG reactor models in this research.

Model design criteria	Publication II and III	Publication IV
Organic conversion inefficiencies	1. Solids partitioning is accounted for in the intermediate SCWG separator stage. The 10% assumed losses of elemental feed follows reported in [28]. 2. Losses in the aqueous phase are assumed to be based on the dissolution of gasified organics due to phase equilibria.	1. Organic solids (hydrochar) are calculated based on the lignin LP liquefaction model. The solids composition is based on biomass derived chars in [65]. 2. Losses in the aqueous phase are accounted for by: i) The Gibbs minimization routine for the formation of carboxylic salts and acids, along with captured gasified organics in the form of alkali salts. ii) Phase equilibria (dissolution) of gasified organics.
Inorganics	Modelled as a single inert component, separated ideally in the intermediate solid separator stage.	1. Solubility data, based on the modelled fluid density in the separation stage, was used to define partitioning into the solids. 2. Aspen Plus® electrolyte modelling to define composition of recovered solids. 3. Inorganic compounds from the Aspen Plus® chemistry package were defined as possible products for the Gibbs minimization routines in the supercritical phase.
Heat of reaction	The heat of reaction for both the liquefaction and gasification stages are combined as a single heat stream. This is performed to balance the exothermic energy released from the decomposition of solids to the elemental yield (in the liquefaction stage) with the formation of gasification products from that yield. The utility heat is assumed to be transferred at the SCWG reactor temperature.	The heat of reaction for each stage in the SCWG system is calculated independently based on the stream composition at each stage and the processing temperatures present in the specific process unit.

The inclusion of WBL inorganics, chemical composition and solubility, in the gasification model was to account for the impact of dissolved alkali in the supercritical phase on the gas yields and composition, in the SCWG reactor and product recovery system. The AspenPlus® physical property system bypasses all solution chemistry calculations for a dielectric constant around 10, as experienced in the supercritical phase [52]. As such, the solubility of present inorganics

was forced in the modelled solid separator based on reported values from [26], and shown earlier in Fig. 11. Earlier attempts to model inorganics in the SCWG system have only accounted for dissolution in the subcritical phase [83]. The positive impact of accounting for the remaining dissolved salts in the supercritical phase is evident in the model validation, shown in Fig. 19. The model predicts both gas yields and composition with reasonable accuracy. The composition of separated solid yield is calculated based on the solution chemistry package at recovered conditions, similar to earlier studies in literature [83].

Figure 19. The performance of the developed constrained equilibria model for the SCWG of WBL at 600 °C compared to reported experimental data from [84]. The blue data set uses reported carbon to gas conversion for the experimental setup and the orange data set assumes carbon conversion based on hydrochar formation from lignin liquefaction.

4.2.4 Balance of plant process units

The process design decisions for the BOP of each biorefinery case study is listed in the respective publication with justifications for the choice of each technology based on reported literature review of available commercial applications. The sequential processing configurations are developed based on sensitivity analysis of integral design variables. It is important to remind the reader that in the context of this dissertation, BOP refers to all non- SCWR reactor system units. This section briefly describes the modelling approach for selected process units and material conversion steps.

Renewable liquid fuels case

The selected mechanical pretreatment unit for all HTL case studies is coarse chipping to reduce the feed particle size to approximately 5-10 mm. The energy consumption (not modelled in AspenPlus®) is set at 0.18 MJ/kg dry feed similar to reported in [85]. Although, HTL product yields and quality have shown minimal correlation to smaller particle sizes [33]. Biomass processing pragmatism necessitates special consideration to the fibrous nature in the feed slurry, to avoid blockage and clogging in commercial scale units and instrumentation.

HTL biocrude properties such as heating value, fluid stability and viscosity, as well as the production of compatible liquid fuels with existing infrastructure for petroleum products, remain essential steps to realizing early commercial penetration. The upgrading sequence used in this study is adapted from [37]. The list of upgraded compounds is adapted from [68], and the upgrading hydro-deoxygenation (HDO) reactor yield is modelled with a LP optimization routine similar

to the HTL reactor for mass balance closure. The calculation routine included hydrogen consumption in the hydrotreatment conversion step as a free variable. The calculated consumption at 0.04 g H₂ per g of biocrude, falls in line with reports in the literature [37]. The product recovery units in the biorefinery are modelled following reported yields in literature with built-in Aspen Plus® separator units.

For the hydrogen plant, the hydrocarbon enriched off-gas mixture is converted to hydrogen via a sequence of reactor systems designed based on [58,86]. The steam-reforming step is modelled with the Gibbs minimization approach, followed by the reversible water gas shift step modelled in a stoichiometric reactor. The reformed gas goes through a knockout for water removal and hydrogen is separated in a PSA unit before it is sent to the upgrading block.

The WWT facilities for the aqueous yield are not modelled in detail except for the case studies with the SCWG system. Special attention would be needed in the future to investigate the design changes necessary for the WWT units of the HTL biorefinery. However, recent results have shown promising removal efficiencies for heavy metals, nutrients, and other pathogens to levels below environmental discharge regulations [47]. The solids and auxiliary boiler for matching heating utilities are modelled as part of the CHP Rankine cycle arrangement similar to the detailed in [59].

Downstream Green Hydrogen and Bio-SNG pathways

The downstream process blocks and reforming units are described briefly in section 4.1.2 and in detail in the appended **Publications II and III**. The reforming units are modelled as stoichiometric reactors, in which the extent of reaction rates are defined based on reported catalytic activity at the set operating conditions. The gas membranes and adsorbent systems are modelled with the standard separator unit in AspenPlus®.

Pulp mill integration case

As mentioned in the description of the biorefinery integration cases, only the RB unit among the KM process units is modelled in Aspen Plus®. The main chemical function for the RB is as a reducing reactor for cooking chemicals, specifically converting sodium sulfates (Na₂SO₄) to sulfides (Na₂S) [62]. The carbon-reducing mechanism takes place in the boiler's bottom section, known as char bed. Where, the inorganic flow leaving the boiler, known as smelt, includes mostly carbonated alkali and the reduced sulfur. The developed RB model assesses the participation of the non-volatiles fraction of fired SBL (along with SCWR solids in the site integration study) in the reducing mechanisms. The combustion of char bed gasification products, along with fired volatiles is modelled in an oxidizing upper furnace for steam production. The detailed Aspen Plus® model description as well as the underlying assumptions applied are listed in the appended **Publication IV**.

It is important to note that industrial RBs are dynamic reactors in which existing chemistry is dictated by the S/Na₂ molar ratio of fired SBL and the air-to-fuel ratio in different boiler sections [60]. Fig. 20 shows the impact of char bed temperature on the smelt composition and flow. The presence of operational

hot and cold “spots” in the bed between 800–1300 °C is well documented [62]. Alkali vaporization, reducing smelt flow, increases with temperature. While, in contrast, total sulfur released in vapors is reduced, leading to thermodynamically driven changes in the boiler’s exit material stream composition and flow. An average temperature of 1100 °C for the char bed was chosen based on a sensitivity analysis to represent the steady state design conditions.

Figure 20. The impact of char bed temperature on the smelt composition and flow leaving the modelled recovery boiler.

The modeled RB thermal efficiency¹⁸ is 84% (LHV) and 75% (HHV) on a wet basis, consistent with reported values in the literature [62]. If compared to the reference KM model in [53], the RB material flows modelled show good agreement. The modelled steam flow is 0.304 kg per MW of feed (0.291 in [53]) and smelt flow is 0.034 kg per MW (0.031 in [53]). The smelt composition shown in Fig. 20 is also consistent with reported in literature [53,60,62].

¹⁸ RB thermal efficiency = net heat for steam generation / incoming feed heating value.

4.3 Process integration

4.3.1 Heat integration

Pinch analysis method remains the cornerstone of process integration studies. The pinch method is usually applied in an iterative fashion to formulate or retrofit HEN(s), and/or the simultaneous optimization and synthesis of process schemes and subsystems based on targeting minimized energetic consumption. Gundersen [54] summarized the step-wise approach of the pinch method:

1. The determination of HEN principal targets, dictated by streams and equipment heat duties, along with operating temperature boundaries, collected from the AspenPlus® flowsheets in modelling levels 1 and 2.
2. Second is the development of the process composite curves (CC), in which process streams with a variable of quantity (heat duty) are expressed in terms of a specific quality (temperature). The graphical representation known as the T-Q diagram summarizes the available heating and cooling demands insitu of the biorefinery boundaries.
3. Finally, a numerical solution provides the fundamental pinch decomposition of the biorefinery streams into two subgroups of heat deficit and surplus. The calculated pinch temperature is considered the biorefinery thermal bottleneck. Heat exchange between process streams within the specific subgroup (with no crossover of the pinch temperature) enables maximum energy recovery and minimum heating and cooling utilities.

The pinch numerical solutions are conceptually simple, but with increased number of streams in the biorefinery, iterative calculations are required to cascade the present heat loads for the CC diagram. In this research, a minimum temperature difference, $\Delta T_{\min} = 10\text{ }^{\circ}\text{C}$ (except when reported otherwise), is set as the design condition trade-off between operational cost, the heat transferred across the streams, and the investment cost of heat exchanger units needed. A developed Mixed Integer Linear Programming (MILP) model on GAMS software performs the pinch calculations for **Publications II** and **III**. Aspen Energy Analyzer and Hint® software applying the same calculation routine were used for **Publications IV** and **I**, respectively.

4.3.2 Site integration in Publication IV

The developed KM model is used to calculate potential energy and resource savings. The general assumption is that changes to recovery cycle streams and subsequent impact on pulping line material and energy balance are directly correlated to the WBL flow into the recovery cycle and outlet streams from the RB and SCWR reactor system. This of significance when considering the sensitivity analysis conducted to study the impact of “economies of scale” from decoupling the recovery cycle and the Kraft pulping line. All relevant stream data for the KM model are listed in the appended **Publication IV**, and are based on [53] for a Nordic based mill with production capacity of 800 k ADt pulp per year.

4.4 Economic analysis

The economic assessment scrutinizes all case studies with economic indicators to establish feasibility constraints and potential for commerciality based on the bio-product portfolio selling prices. The assessment is developed under the Nth-of-a-kind (NOAK) plant assumption and follows the total revenue requirement approach reported by [87]. The break-even or MSP of bio-products is calculated based on the EBITDA approach (Earnings Before Interest, Taxes, Depreciation and Amortization). The approach is adapted to provide a standardized valuation of the different biorefinery case studies in this dissertation. In addition, EBITDA allows for pragmatic comparison with other biofuel technologies, emphasizing the cost of production, and excluding uncertainties around project-specific financing. The biorefinery case studies were assumed to have 100% equity, with no carry over debt and no salvage value for the biorefinery components at the end of the operation.

The MSP is calculated based on the levelized (annual) costs accrued. The levelized value considers both capital, and operating and maintaining (O&M) related costs over operational period of 20 years for **Publication I** and 25 years for **Publication IV**. The different lifetime scale between both publications is based on the standard life-time evaluation cycle for the reference technologies used for each, polygenerative power plants [87] and pulp mills [53] for the latter. The MSP is calculated for both publications based on a net present value (NPV) of zero for a reference start of operation year in 2016. The biorefinery NPV is calculated based on market escalation and changes in prices for the biorefinery material and energy streams over the period from 2002 to 2016. The respective data sets and calculation approach is presented in the Appendix of **Publication I**. The biorefinery location is assumed for Nordic conditions, with Finland as a representative case. The effective rate of return on investment and discount rate was set at 10%, with no revenue from a carbon tax policy or green incentive instruments considered.

4.4.1 Capital cost estimation

The capital investment for each case study is calculated based on the standard *study-estimate* approach with an uncertainty in the range of $\pm 30\%$ [51]. The approach includes consideration of biorefinery location, process flowsheeting of main process units, sizing and material specification, types of construction (excluding detailed piping, insulation and instrumentation diagrams) quantitate utility requirements and price-quotations sourced from the literature (not vendor data). The purchase equipment costs (PEC) formed the basis for the total capital investment (TCI) cost for each biorefinery case study. The PEC were calculated based on similar processing units, systems and blocks in the literature, listed in detail for **Publication I**, and based on [40] for the SCWR system and [53] for the KM units in **Publication IV**. The operating capacity scaling of all components was performed using the generally accepted six-tenths rule in chemical plant designs, with a scaling component (α) of 0.6, as shown in equation (2). $C_{PEC,study}$ is the PEC for the specific unit in this research and $C_{PEC,ref}$ is

for the reported values in the literature. Relevant stream and heat flows were used as the scaling variable, X_{study} and X_{ref} , for each process unit. In addition, all cost estimates were adjusted from reference years in the literature to the assumed end-of-construction (start of operation) common reference year of 2016, using the Chemical Engineering Plant Cost Indices (CEPCI) as shown in equation (3).

$$\frac{C_{PEC,study}}{C_{PEC,ref}} = \left(\frac{X_{study}}{X_{ref}} \right)^\alpha \quad (2)$$

$$\frac{C_{2016}}{C_{ref\ year}} = \frac{CEPCI_{2016}}{CEPCI_{ref\ year}} \quad (3)$$

The total capital investment cost (TCI) for the SCWR reactor system is calculated as following: At first, an installation factor ($a_{inst.}$)¹⁹ of 20% is added to the total calculated PEC. The fixed capital investment (FCI) is then calculated with an equipment capital investment factor (ECIF)²⁰ of 35%. Other outlay costs such as startup, working capital and funds utilized during the construction period are accounted for within the equipment capital investment factor. Finally, a 10% contingency is added, equation (4) summarizes the TCI calculation. The applied factors in this research are similar to adopted ones for other bio- energy and refineries in the literature [51,87]. In **Publication IV**, the TCI for the recovery cycle and BOP units were based on reported factors in [53]. At the end, the contribution of capital to the annual biorefinery cash flows, the annuity, was calculated based on the capital recovery factor (CRF), shown in equation (5), and calculated similar to [87]. Where, i_{eff} is the assumed effective rate of return and n is the operational lifetime of the biorefinery.

$$TCI = FCI \times (1 + Contingency) = \frac{(1 + a_{inst.}) \times PEC}{ECIF} \times (1 + 0.1) \quad (4)$$

$$Annuity_{capital} = TCI \times CRF = TCI \times \frac{i_{eff} \times (i_{eff} + 1)^n}{(i_{eff} + 1)^n - 1} \quad (5)$$

4.4.2 Operation and Maintenance cost estimation

The annual operation and maintenance (O&M) costs for each case study are divided into variable and fixed costs. The first is dependent on the annual production rate, and accounts for feedstock supply, make up (process) and cooling (utility) water, power consumption, catalyst cost, solids deposition, auxiliary hydrogen and wastewater disposal cost (post of the treatment units). The utilization factor was estimated to be 0.91 and as such, the annual operating hours for case studies was set at 8000 hr. Operational downtime is used to account for regular maintenance and equipment services.

¹⁹ Installation factors account for labor, foundations, supports, platform, construction expenses and other equipment-erection related costs.

²⁰ PEC to FCI ratio.

Finnish energy and fuel market prices, over the prior 15 years (2002-2016) to the common year for this study, were adapted from [59]. The escalated O&M cost cash flows were assumed to follow the linear correlation of reported price fluctuations, shown in Fig. 21. The set escalation rates take into account changes associated with resource depletion, disruption in market supply and demand, and technological advances, among others. The impact of inflation in this research is ignored, and follows the constant dollar approach, as suggested by [87]. This is not to distort the calculated cash flows by the long lifetime scale (20-25 years) assumed. The annuity for all O&M flows is calculated from the constant-escalation levelization factor (CELF), as shown in equations (6) and (7), wherein, r_n is the assumed escalation rate for specific material or energy stream.

Figure 21. Finnish market price fluctuations and the calculated escalations for some of the biorefinery material and energy streams.

$$k = \frac{(r_n + 1)}{(i_{eff} + 1)} \quad (6)$$

$$CELF = CRF \frac{k(1 - k^n)}{(1 - k)} \quad (7)$$

The fixed costs including labor, maintenance and property insurance, along with variable costs without available market price data (e.g. catalyst) were assumed to have an escalation rate of 3%. The labor requirement for each case study was set according to the literature. The average personal salary was set at €36k per annum, with 50% and 30% overhead and personal insurance factors, respectively, as suggested by [87]. Finally, the maintenance and insurance costs were assumed to be 1.5% of the TCI of the system. All detailed cash flow assumption for each case study are listed in their respective **Publication I and IV**.

4.5 Biorefinery techno-economic performance indicators

4.5.1 Thermal performance

The thermal performance of the different biorefinery case studies follows the first and second law of thermodynamics for the conservation of mass and energy in the closed system (biorefinery system boundaries). The performance equation (8) could be expressed in both LHV and HHV basis. Where the divisor Q is on as received (wet) basis and represents the chemical energy stored within feedstock (to the SCWR reactor system) and the auxiliary boiler feed (based on minimum hot utility from the pinch analysis). The numerator E is the sum of the case study material and energy co-products.

$$\eta_{th} = \frac{E_{bio-products}}{Q_{feedstock} + Q_{auxiliary feed}} \quad (8)$$

Special consideration is given to insitu power production in the different biorefinery configurations. For **Publications I, II and III**, power is expressed with (-ve) sign as part of the numerator bioproducts for cases in which insitu deficit exists. In **Publication IV**, in which, the SCWR reactor system is designed to be thermally independent within the KM site integration, power is considered an energy input to the closed thermodynamic system, and is part of equation (8) denominator.

4.5.2 Economic performance

The MSP of the biorefinery product streams is the main economic performance indicator reported in this summary. The MSP is reported on per unit of energy (MWh) of bioproducts (irrespective of energy carrier) for **Publication I**. A series of sensitivity analysis based on available market prices was performed in **Publication I** to quantify the MSP of the biorefinery products, which nullifies the NPV. The calculation was based on the discount cash flow analysis. In **Publication IV**, the MSP was calculated per unit of mass (ADt) basis for the primary specialty pulp product. The MSP takes into account the levelized revenue and cost cash flows of the different case studies, following equation (9).

$$MSP = \frac{(TCI \times CRF) + \sum O\&M_i \times CELF_i - \sum co-product revenue_j \times CELF_j}{Annual Production capacity_{energy or mass}} \quad (9)$$

5. Research Findings

The main scientific contribution of this dissertation lies within the four appended publications. Summaries of the publications are given in this chapter.

5.1 Summary of the results from Publication I

In this publication, the topic was to study the thermal and economic constraints for the non-catalytic HTL technology platform.

5.1.1 Liquefaction reactor model

Non-catalytic process yields

The non-catalytic elemental and phase boundaries set for the LP liquefaction model lead to HTL product yields with a significant solids content, as shown in Fig. 22. The hydrochar carbon partitioning (32%) and mass yield (264 g/kg dry feed) are slightly higher than the lower constraint set in the LP model. This falls in line with other wood liquefaction studies such as [31], [77] and [78]. The organic solids, a result of lignin’s benzene ring cyclization and secondary condensation of phenolic monomers [88], and directly competes with organics (water soluble and insoluble) formation pathways.

Figure 22. The carbon balance and mass yields for the HTL and Hydrotreatment production pathway to renewable fuels.

Hydroxyl and methoxy groups, originating from various lignin monomers, dominate the composition of modelled biocrude as shown in Fig. 23. Water-soluble organics, mainly consisting of carboxylic acids, furfurals and aldehydes, products of hemicellulose degradation also could contribute to the solids formation under long reactor residence time and/or low heating rates [27].

Figure 23. Modelled HTL biocrude composition.

The impact of process and reactive water on product yields

In essence, the formation of large organic molecules (via a sequence of combination reactions) to form either solid or liquids yield is initiated by present de-oxygenation mechanisms, namely, de-hydration or decarboxylation, in the HTL reaction medium [16]. In the LP model, water released from feed de-hydration shown (as reactive water in Fig. 23) is not constrained. While gas formation mechanisms are limited by the reported experimental yields and the CO₂ dominant fraction within it [68]. The latter of which leads to the majority of elemental hydrogen partitioning to either solid or organic yields.

The modelling approach shows that with quantitate representation of water released from the biomass feed and/or the reactivity of the process medium, modelling the HTL conversion step based on elemental partitioning could accurately describe the chemical mechanisms taking place. The model solution for released water (104 g/kg dry feed) allows mass balance closure while matching chemical functionalities in biocrude. The gas yield was found to be 147 g/kg dry feed (9% carbon).

The high yield of water-soluble organics at 271 g/kg dry feed (32% carbon) is a result of the hydrophilic nature of oxygenated organics and the low extraction rate (34%) for the acetone scrubber. Separation via phase equilibria (in the decanter) to a light crude stream was only 5.4% of liquefied organics. It is reported in the literature that both higher temperature [33] and solid feed content [29] would improve light crude separation. However, both approaches are not considered in this study as they present challenges related to heat recovery and slurry pumpability limits [18].

Non-catalytic compared to catalytic HTL processing

The total biocrude recovery was found to be 219 g (wet) per kg of feed (27 % of carbon). The biocrude moisture content, originating from the modelled phase separation of the light fraction, was found to be 2.8 wt.%, consistent with literature [68]. The oxygen removal rate in the non-catalytic HTL system was nearly 40% from the original feedstock with a final carbon content at 67 wt.% dry and a higher heating value of 27.1 MJ/kg.

The level of de-oxygenation remains to be a clear disadvantage compared to catalytic HTL treatment, which reports oxygen removal between 60-85% in the literature [29]. The increased downstream demand is illustrated in Fig. 22 with the significant upgrading losses fraction. The carbon recovery in the HDO process is efficient at 94%. The mass loss is in the form of residue water produced from the de-oxygenation mechanism. Renewable fuel yield for the HTL biorefinery was found to be 149 g/kg dry feed, and 25% recovery of feed carbon. It is important to note here that modelled carbon recovery is around a third less to the 35% reported for catalytic processing [37].

5.1.2 Mass & energy balance

The primary biomass to liquid fuel conversion (BtL)²¹ for the different case studies, the green contribution in Fig. 24, is similar except for the amount of feedstock needed to the auxiliary boiler system. The reader is referred to Fig. 13 for the detailed process block schematic for each case study. The HTL2 case had the highest BtL efficiency due to the absence of auxiliary utility. The biorefinery thermal efficiency, following equation (8), for case HTL2 with solids combustion was found to be 36% (LHV basis) and 33% (HHV). This is lower than the reported 52% conversion (HHV) for a similar catalytic HTL biorefinery to renewable liquid fuels [37]. This is attributed to the lower HTL biocrude yields and higher hydrogen consumption in the upgrading step. The residue water yield from the HDO unit is 26% (5.4% overall) compared to 16% only for the catalytic process reported in [37].

Non-catalytic HTL a platform technology for waste to bio-carrier plants

The HTL byproduct utilization blocks is where the distinction between the biorefinery cases, and between the catalytic and non-catalytic HTL systems, becomes evident. Fig. 24 shows the contribution of the different bioproducts on the thermal efficiency on LHV basis. The lowest efficiency recorded for the HTL2 case, in contrast to the BtL efficiency, is due to the thermal penalty from internally utilizing the upgraded bio-product, rather than combusting low thermal grade feedstock in other cases. This could also be observed when comparing the HTL3 and HTL4 cases, where the higher efficiency for the latter is due to the higher thermal value of hydrochar (as a co-product) compared to the Forrest residue feed. This illustrates the thermal value for non-catalytic HTL as a waste valorization technology.

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²¹ Biomass to liquid (BtL) efficiency is the ratio of heating value of the product liquid fuels to the heating value of biomass feed to the biorefinery (for both production and utility purposes).

Figure 24. Contribution of material and energy streams to the biorefinery thermal performance. Dashed line is the efficiency for the catalytic process based on reported energy flows in [68].

Interestingly to note, the higher efficiency for the HTL3 case compared to the HTL1 case in Fig. 24, shows that the combustion of solid yield from non-catalytic processing offsets the introduction of the energy intensive SCWG treatment of the aqueous yield. The reader is referred to Fig. 7 in **Publication I** for the graphical representation (composite curves) of the heat loads present in each case study. The presence of the SCWG system amplified the excess Green hydrogen production due to the significant fraction of water-soluble organics produced in the non-catalytic HTL reactor system. In addition, the residue gas from the SCWG reactor system accounted for around 90% of the off-gas feed to the hydrogen plant, with hydrocarbon content more than double of that in the HTL gas. The thermal penalty from employing the SCWG system is observable in the increased power demand for case studies HTL3 and HTL4. The efficiency for both cases were still found to be higher than the reported efficiency on LHV basis for the catalytic process reported in [68] for a similar forestry residue stream.

In evaluating the different HTL biorefinery designs proposed in the literature, special attention should be redirected toward the fate of water-soluble organics. The reported mass (and carbon) yield for the residual stream is reportedly anywhere between 20-50% for catalytic systems [36]. Many of the proposed continuous HTL systems in literature have reverted to the recirculation of HTL aqueous phase to the feed preparation unit [29]. This is often performed to lower make-up water consumption and due to reported marginal improvements in biocrude yield [89]. However, organic build-up in the reactor system is a threshold any system would need to adhere to, and fractional discharge is eventually necessary [29]. The nature of present organics (namely aromatic and phenolic substrates) [89] as well as inorganics [47] act as inhibitors for biological treatment options.

One thermal recovery possibility not considered in the appended paper is the utilization of available waste heat. The potential for district heat production

could possibly provide thermal efficiency improvements between 2-6%. In addition, low temperature power production is possible (e.g. via organic Rankine cycle or sterling engines). Another alternative includes utilizing oxidants in the SCWG reactor system for auto-thermal operations, replacing a fraction of hydrogen produced, in the form of H_2 directly from the SCWG or CH_4 directed to the hydrogen plant, with additional insitu CHP.

Another perspective to consider when comparing the different cases is the production capacities present for each bio-product. The primary product description for renewable liquid fuels might not be fitting to cases with aqueous yield valorization. Green hydrogen production at 0.43 and 0.36 MW per MW of feed (on HHV basis), for HTL3 and HTL4 cases respectively, exceeds that of both renewable liquid fuels at 0.31 and 0.26, and hydrochar at 0.25 MW (for case HTL4). The non-catalytic HTL platform could be considered more of a biomass fractionation technology.

5.1.3 Economic analysis

Figure 25 presents the results from the economic analysis of the HTL biorefinery cases. The average selling price of bio-products correlates with the thermal performance in Fig. 24. The HTL4 case with the highest thermal efficiency has the lowest MSP at €66 per MWh (LHV basis) of production, compared to the HTL2 case with the highest cost (and lowest efficiency) at €169 per MWh. This is unintuitive given that the HTL4 case records the highest utility consumption and the high contribution (around one-third) from feedstock procurement to the overall economic performance, a characteristic shared with other biomass to energy and fuel industrial systems [70]. However, the lowered MSP for the HTL4 case illustrates the ability of SCW reactor systems to valorize the low grade feedstock into high quality (thermal and economic) hydrogen carriers.

Figure 25. The leveled component costs (left axis) and the MSP (right axis) per MWh (LHV basis) of bioproducts for the HTL biorefinery cases.

Cost reduction drivers and breakeven prices of biorefinery co-products

The levelized cost for the upstream HTL reactor system ranged between €11 (HTL4) and €34 (HTL2) per MWh of product. The similarity of the solid feed throughput to the reactor system (300 MW on LHV basis) for all cases gives a uniform annual contribution. The interaction between reducing variable costs such as purchased hydrogen in HTL1 case and the introduction of hydrogen producing blocks in HTL2-4 shows economic improvement with lower MSPs for the latter. However, special attention should be directed to distribution, storage and end-user availability within the hydrogen value chain (not in the current scope). Similarly, by selling hydrochar rather than for insitu utilization, case HTL2 with the latter application has a MSP higher by 78%, 89% and 155% compared to the HTL1, HTL3 and HTL4 cases.

Table 5 presents a sensitivity analysis for the two largest cost components (feedstock price and HTL capital costs) and the bio-product MSP for the HTL biorefinery. The NPV was calculated with a discounted cash flow rate of 10% over the 20-year operations. The existing commercial prices for the three bio-products yield a negative NPV for all case studies. It is important to note that no carbon-emission abatement incentives or bio-based production credits were considered in the evaluation.

Table 5. Sensitivity analysis of some of the economic estimates for biorefinery NPV calculation.

Sensitivity variable	HTL1	HTL2	HTL3	HTL4
NPV with current study estimates, M€-2016	-647.9	-806.6	-288.2	-104.4
NPV with 30% less HTL block PEC, M€-2016	-543.2	-702.0	-183.5	0.2
NPV with fuel escalation at 0%, M€-2016	-607.5	-768.7	-248.5	-57.0
Hydrochar MSP for NPV=0, €/MWh	123.4	N/A	N/A	51.4
Hydrogen MSP for NPV=0, €/kg	-17.7	68.7	3.07	2.46
Renewable fuels MSP for NPV=0, €/kg	2.45	2.86	1.51	1.03
Renewable fuels MSP for NPV=0, €/GGE	6.93	8.10	4.28	2.93

The feedstock cost escalation rate was examined at 0%, reflecting a purchasing agreement with no changes to the 2016 procurement prices. The biorefinery NPV improved between 6% and 45%, in the HTL1 and HTL4 cases respectively, yet remained negative. However, the reduction of HTL capital costs by 30%, the lower boundary for uncertainty in the capital cost estimation approach, yields break even conditions for the HTL4 case with existing market prices for renewable fuels, hydrogen and hydrochar (priced at €38 per MWh).

Comparing the economics of non-catalytic HTL with reference technologies

Under the existing capital estimation costs, the breakeven price of the HTL4 case for renewable fuels is €2.5 per kg (6.9 per GGE²²). This is equivalent to an oil barrel (bbl.) price of €150.²³ It is worth to note that the renewable fuel MSP price for the non-catalytic HTL4 case is lower than the price for the catalytic HTL system proposed by Zhu et al. [37] at ~ €3.4 per GGE (in the year 2016). The economic study by the PNNL team [37] remains the benchmark for the field as it relies on vendor proposed HTL reactor designs and quotation lists. This illustrates the competitiveness of the multi-product non-catalytic HTL platform proposed in this research as a logical trade-off to the single-product catalytic HTL platform. However, a more recent public statement by Steeper Energy (2018), a developer of the HTL catalytic upgrading technology for forestry biomass, claims that “upgraded biocrude to renewable fuels, lubricants or biochemicals could be produced for well under \$90 a barrel” [29].

The breakeven price for Green hydrogen was found to be €2.46 per kg, which remains higher than fossil based hydrogen (€1~2 in 2018 per kg) but more competitive than grid-connected electrolysis based H₂ reported in the range of €2.5 to €8 per kg in 2018 [12]. The absence of an established end-user or market for hydrochar gives larger uncertainties over selling the bio-product. The breakeven price for the HTL4 case is around €51 per MWh. Aside from the biomaterial pathway potential, hydrochar could also be sold as a green fuel for CHP plants. The breakeven price falls within the reported range in [70] for both wood pellets and torrefied wood pellets at €54 and €49 per MWh, respectively. In the scenario in which hydrochar is utilized insitu of the biorefinery (HTL3 case), the breakeven price for renewable fuels and hydrogen increases by 46% and 25% respectively.

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²² Conversion factors: Gallon Gasoline Equivalent (GGE) = 33.41 kWh and HHV = 42.1 MJ/kg.

²³ Conversion factor: barrel of oil = 1.7 MWh.

5.2 Summary of the results from Publication II and III

In the two publications, the topic was to study the thermal trade-offs for different operating conditions and downstream processing for the SCWG technology platform.

5.2.1 Mass balance of the biorefinery cases

The detailed SCWG reactor system and downstream process unit conversion and performance are listed in **Publication II** for the grid quality Bio-SNG cases SCWG1A-B and **Publication III**, for the Green hydrogen cases SCWG2A-C. Fig. 26 below gives a general outlook to the mass balance of each case study.

Figure 26. Mass balance results for the examined SCWG biorefinery cases.

The fate of carbon in SCWG

The gross mass yields, which account only for the product gas, are found to be 316 and 312 g per kg of solid feed (to the SCWG reactor system) for cases SCWG1A and 1B respectively. While cases SCWG2A, 2B and 2C had a gross hydrogen yield of 49, 151 and 82 g per kg of solid feed, only. The higher recovery in the Bio-SNG cases is attributed to the carbonaceous nature of the H_2 gas carrier. The organic losses in the solids and aqueous SCWG reactor yield ranged between 10-13% for all the case studies. In considering the entire biorefinery production platform, carbon balance in the Green hydrogen cases is in the form of released CO_2 in the residue gas streams. This could also be observed in the net mass yields, which take into account the combustion of additional LEA feedstock to match the biorefinery utility demands.

Aside from the molar shift in SCWG product gas, from CH_4 to H_2 , at higher temperatures leading to a higher fraction of directly produced CO_2 . When comparing the SCWG1B case to that of SCWG2A-C, the downstream reforming of off-gas (CH_4) to H_2 in the latter, followed by the WGS reaction for remaining CO, additionally contributes to the residue CO_2 flow. In contrast, for the Bio-SNG pathway, the employed downstream RWGS unit followed by the methanation step, acts as an insitu carbon capture unit. The directly produced CO_2 from the SCWG reactor system is recuperated into the target carrier.

This is further illustrated in Fig. 27, where the insitu CO₂ emissions from the two Bio-SNG cases are lower than the commercial technologies. The two Bio-SNG cases perform two functions, first as a biogenic carbon capture technology and second as a H₂ gas carrier producer. The nature of end-user utilization determines the effectiveness of the carbon capture function. In Fig. 27, when accounting for the end-user conversion step to H₂ gas (via steam reforming), both Bio-SNG cases record slightly higher emissions than reference technologies reported in [12]. The two Bio-SNG cases are shown in the figure for both theoretically stored H₂ within the Bio-SNG product stream, as well as reported emissions in industrial steam-reforming plants.²⁴

Figure 27. Carbon intensity per kg of bio-carrier for each of the SCWG biorefinery cases examined. theo. H₂: theoretical yield of H₂ gas from modelled Bio-SNG and ind. H₂: refers to industry reported emission increase relative to theoretical yield. Commercial technologies emissions are based on [12].

It is important to note that Fig. 27 accounts for emissions from the feedstock biorefinery gate to end user utilization, as such the fossilized nature of commercial technologies and the life-cycle carbon capture by biomass feeds are not considered. Nonetheless, the results show that in order to maximize the emission reduction of the SCWG Biorefineries, carbon in the form of CO₂ released needs to be recuperated to be stored or utilized. One approach is the use of alkali loading in the reactor system, as examined later in the WBL case studies in **Publication IV**. The alkali present, not only drives the equilibrium in the reactor system to hydrogen production, but also captures CO₂ in a recycable form. The experimental findings in [48] showed that with high alkali loading, the SCWG product gas could exclusively contain H₂ gas carriers, with balance carbon in the form of aqueous soluble carbonates and bi-carbonates.

The higher end-use carbon intensity for the Green hydrogen cases compared to the two Bio-SNG cases is primarily attributed to feed slurry dilution (for cases SCWG2B and SCWG2C) and lower direct production in the SCWG reactor system (for case SCWG2A). As shown in Fig. 26, the feed dilution to 5 wt.% solids

²⁴ Conversion: theoretically stored hydrogen is calculated following the combined stoichiometric reaction $CH_4 + 2 H_2O \rightarrow CO_2 + 4 H_2$, industrially produced emissions were assumed 113% of the theoretical based on the literature.

leads to higher utility demands and the amount of feedstock needed in the auxiliary boiler exceeds that of the actual feed to the SCWG reactor.

Interestingly, case SCWG2B has lower carbon intensity than cases SCWG2A and SCWG2C. This is due to the downstream processing for the Green hydrogen cases recuperating H_2 gas present in the off-gases, rather than partially combusted in case SCWG2A for thermal self-sufficiency and fully combusted in SCWG2C. However, downstream processing did not offset the processing penalty from operating at more favorable direct H_2 gas production in the reactor.

The role of reactive water on hydrogen gasification efficiency

The water consumed in the reactor is shown for each case study in Fig. 26. In comparing the base case SCWG1A to both SCWG1B and SCWG2A, reaction water increases with increasing the reactor operating temperature from 450 to 600°C. In comparing the latter two with cases SCWG2B and SCWG2C, consumption increases further with the dilution of the feed. The impact of consumed water on hydrogen gasification is evident in Fig. 28. When considering the hydrogen content in the solid feed, the hydrogen gasification efficiency for case SCWG2B (higher consumed water) is almost double of that for the Bio-SNG cases SCWG1A-B. Interestingly, case study SCWG2C, for Green hydrogen with no off-gas utilization, had a higher efficiency at 113% also compared to the Bio-SNG cases. On the other hand, the Bio-SNG cases recorded higher efficiencies when considering all hydrogen input to the biorefinery, a practice not applied in evaluation studies in the literature. Fig. 28 breaks down the contribution to hydrogen gasification efficiency from: feedstock, water consumption in SCWG reactor system and downstream, and in the utility systems. The holistic accounting of efficiency follows the order: SCWG1A (73%) > SCWG1B (64%) > SCWG2B (51%) > SCWG2C (34%) > SCWG2A (28%).

Figure 28. Hydrogen gasification efficiency in the examined SCWG biorefinery cases. The legend refers to feed: feedstock to the SCWG reactor system, cons. SCWG water: reactive water participating in gas reforming equilibria, total water cons.: includes SCWG reactor and reactive water in downstream units and utility: includes feedstock fired in the utility boiler.

5.2.2 Thermal performance of the biorefinery cases

Figure 29 presents the thermal performance of the examined SCWG case studies. The heat loads in the figure are presented on solids wet basis (excluding slurry water), compared to the dry ash free basis reported in **Publication II** and **Publication III**. The reader is referred to the detailed process CC illustrating the present thermal loads for each case study in the appended publications.

Figure 29. Energy balance and thermal performance of the examined SCWG Biorefineries.

Impact of solid content in the reactor system

The higher thermal value of the carrier, Green hydrogen at ~ 120 MJ/kg (LHV) compared to Bio-SNG at ~ 48.7 MJ/kg, led to the SCWG2B case recording the highest gross thermal production. However, the Green hydrogen cases are thermally penalized for the diluted nature of processing. This leads to a significant fraction of thermal input to the biorefinery utilized for elevating the thermal conditions of processing water for the SCWG reactor system. This is observed in the order of magnitude higher hot utility for Green hydrogen cases (excluding the self-sufficient SCWG2A) compared to the Bio-SNG production pathway.

The net thermal yield in kW per MW of total input (including solid feed and utility) followed a similar order to the holistic accounting for hydrogen gasification presented in the previous section: SCWG1A (753 kW) > SCWG1B (632) > SCWG2B (365) > SCWG2A (325) > SCWG2C (225). This is also reflected in the thermal efficiency, following equation (8), where the bio-carrier and excess power are considered the study case bio-products.

Impact of higher reactor gas yields and excess power production

The higher operating temperature in the SCWG reactor system leads to higher gross gas production and excess power available in the biorefinery, as can be seen from comparing the Bio-SNG cases SCWG1A-B in Fig. 29. However, that does not translate to improved thermal performance. The power penalty in case SCWG1A was found to not be offset by the increased gross production of co-products SCWG1B. This is attributed to the highest thermal utility demand being present in the temperature conditions of the SCWG reactor system. As such, the extraction of power at 600°C creates a thermal bottleneck at the reactor outlet and the hot utility doubles from 127 to 359 kW/MW of feed.

Thermal self-sufficiency of the SCWG biorefinery

The off-gas utilization in case SCWG2A was optimized (in the Aspen Plus® flowsheet) to match the present hot utility demand at high reactor temperature and solids content. The thermal performance compared to other case studies is penalized for insitu utilization of the valorized product. This illustrates the thermal cost for the chemical intensification step in the SCWR systems. In the literature, the SCWR technologies are revered for the ability to upgrade low value feedstock to a target intensified carbon and H₂ gas carrier. However, without the recuperation of heat supplied to the aqueous medium in the form of insitu CHP production, stand-alone concepts record low thermal conversion systems. One alternative to increase the added-value from SCWR systems would be to consider localization synergies with existing industrial infrastructure, as a by-product or waste treatment platform, as discussed in the cases presented in **Publication IV**.

5.3 Summary of the results from Publication IV

In this publication, the topic was to study the impact of inorganics present in biomass processing on the phase yields from the SCWG technology platform. The role of alkali in valorizing WBL feedstreams is investigated and possible processing synergies with Kraft pulp mill operations are reported.

5.3.1 Stand-alone reactor performance

Reactor system mass yields

Figure 30 shows the summary of the mass balance results for treating the Kraft process residual stream, WBL with 18 wt.% dry solids content in the SCWG reactor system. The three dry phase yields in Fig. 30(a) exceed 100% relative to dry WBL solids. The higher operating temperature at 600 °C in case SCWG3A leads to higher water reactivity, and an increase in gas production by around 14%. The solid yield is similar in both cases as the separation takes place in the pre-heating stage (post-liquefaction). Where, the radicals-based char formation in the gasification regime, at remarkably low levels calculated from the equilibria model, end as part of the dissolved organics in the aqueous phase. The slight difference in aqueous yields is attributed to increase in partial pressures (from higher gas production in the SCWG3A), with similar dissolved alkali present, leading to lower amounts of gases dissolved in the aqueous phase.

Figure 30. The SCWG reactor mass yields (a) on dry phase basis and (b) elemental partitioning in case SCWG3B.

Figure 30(b) shows the elemental yields in the reactor system. Carbon recovery in the product gas was 68%.²⁵ The carbon balance is split between mostly dissolved carbonates in the aqueous phase and the solid yield. Gas desulfurization was effective with 87% captured into the solid phase. However, it is worth noting, due to reported catalyst de-activation in the literature [90], the remaining sulfur in the gas yield necessitates a capture unit before any downstream reforming or upstream of the gasification unit when considering the catalytic SCWG3B case (at 450 °C). One uncertainty of the applied modelling approach is the simplified assumption that reduced sulfur follows the solubility of sulfates. The sulfur present in the gas yield is a product of the gasification of alkyl sulfides present in the WBL. The hypothesis falls in line with observations from [90] for elemental and oxidized sulfur deposits and that of [91] for organosulfur recalcitrance around the pseudo critical point.

Alkali recovery in the aqueous stream was found to be 55% and 39% for sodium and potassium, respectively. This follows a general solubility trend observed in the literature of K^+ ions being less soluble than Na^+ in [26] and [92]. However, such generalization should be applied with caution as the nature of anions present in the WBL mixture also plays a deciding role in any salting in or out effects.²⁶ Chlorine was also found to be 82% in solid phase yield.

Reactor system energy recovery

Figure 31 illustrates the energy flows for the two reactor cases for the WBL feed. The difference between the two cases stems from the higher utility in the SCWG3A case and the higher fraction of gross gas production being fired in the auxiliary boiler. The reactor system thermal products are SCWG gas yield, solids and heat recovery in the form of DH. The system efficiency, which follows equation (8), was found to be 83.4% for the 450 °C case (SCWG3B) compared to 80.2% for case SCWG3A. In contrast, the thermal efficiency, which does not consider the proposed heat recovery units, was found to be higher at 82.6% for the SCWG3A case. The absence of power production in the 600 °C case (SCWG3A) compared to cases with similar reactor conditions (SCWG1B and 2A) in **Publication II and III**, leads to improved efficiency in the high temperature case compared to lower operating temperatures. This is attributed to the higher gross gas production. In order for the reactor system to match the recorded thermal efficiencies at the set minimum hot utility and temperature difference ($\Delta T_{\min}$), a higher number of heat exchangers, leading to significantly higher costs would be required.

²⁵ This is commonly referred to as carbon gasification efficiency in the literature.

²⁶ Le Chatelier's principle for chemical equilibrium is observed when aqueous concentrations lead to an excess effect from one salt on another, commonly called "salting in" if increasing the solubility and "salting out" when decreasing it [26].

Figure 31. Sankey diagram for the energy flows present in the stand-alone SCWG reactor system for the treatment of WBL feed at the two reactor cases.

5.3.2 Reactor yield integration within a Kraft recovery cycle

The physical nature and composition of the SCWG phase yields was used as basis for initial screening of potential drop-in or integration within the reference Kraft recovery cycle.

Product gas as lime kiln replacement fuel

The primary product, SCWG gas, could potentially be fired in the existing recovery or power boilers on site, or as part of a retrofitted black liquor gasification combined cycle (BLGCC) system, as suggested for thermal gasification systems [61]. Another internal use in the mill is to be fired as a replacement fuel for HFO consumption in the limekiln (re-causticizing plant). The heating value (HHV on wet basis) of the gas is 21.2 MJ/kg and 23.2 MJ/kg for the SCWG3A and SCWG3B cases respectively, compared to the 40 MJ/kg for the reference HFO [53]. The product gas composition for both cases is shown in Fig. 32. The common restriction for fired fuels in the limekiln is the sulfur content, with a maximum reported threshold of 2 wt.% [93]. The SCWG gas in this study has 0.49 and 0.51 wt.% sulfur for the SCWG3A and SCWG3B cases respectively, which falls below low sulfur fuel oil classifications (<1 wt.%).

When considering the HFO consumed in the KM, a WBL split of 11.7% and 8%, to be directed to the reactor system, for the SCWG3A and SCWG3B cases, respectively, is sufficient to match limekiln thermal demand.

Figure 32. Molar composition of SCWG product gas from WBL for the two gasification temperature cases.

Aqueous yield bypass of the recovery boiler

The diluted SCWG aqueous yield with a water content of around 91 wt.% could potentially be introduced in the dissolving tank²⁷, rather than to the evaporation train. The mixing tank is the point of entry to the re-causticizing plant. This is primarily supported by the presence of reduced sulfur, as shown in Fig. 33, similar to targeting cooking chemicals form. The total alkali concentration in the aqueous yield was found to be 46–47 gNaOH/l for both reactor cases. Alkali precipitation in the solid separator reduces aqueous concentration than typically found in green and white liquor recycled streams in the mill, at 160–165 gNaOH/l [60]. The suggestion would be to mix the aqueous yield with outgoing RB smelt for alkali balance closure. The proposed integration would improve the performance of the existing recovery cycle by reducing the thermal demand for evaporation and reduction mechanisms in the RB.

Figure 33. The mass concentration of dissolved species in the SCWG aqueous yield of WBL.

²⁷ In the dissolving tank, green liquor is formed from mixing the smelt leaving the recovery boiler with recycled condensate streams from the mill. Green liquor is then causticized in the lime cycle to white liquor.

Co-firing reactor solids yield in recovery boiler

The proposed aqueous bypass of the RB alters the existing chemistry and material balance in the boiler. The modelled SCWG solids yield is a combination of separated inorganics and the lignin-derived hydrochar. The heating value of solids yield was found to be 1.9 and 3.5 MJ/kg for LHV and HHV on wet basis respectively. The low thermal value is attributed to the high apparent water content at 51.5% and inorganics (Na, K and Cl) to organics ratio of 0.52. The present water content, ~80% of which is bound in hydrated salts form, is a function of water separated along the brine in the separator unit. The modelled 7% of feed water partitioning to solids is based on reported in [49]. The sensitivity analysis shown in Fig. 34 illustrates that complete dehydration of separated salts takes place with only 4% of feed water separated in the solid yield (38% apparent water content). The hydrated nature of separated SCWG salts was also reported in the modelling study by [83]. It is important to note here, that a limitation of the applied electrolyte chemistry package is not accounting for the crystallization of either double salts burkeite or di-carbonate, two common salts in liquor evaporation [62].²⁸ The reported formation of the two double salts in the literature is at dry solids content beyond 50 wt.%, which falls in line with predicted dry solid precipitation in this study [60].

Figure 34. Impact of water partitioning into SCWG solids on the chemical composition. Free H₂O: stands for water not bound to hydrated salts. Apparent H₂O: water content including water in hydrated salts.

The high sulfates to sulfides ratio in the SCW solids, as shown in Table 6, requires firing them in the RB to return sulfur to the reduced cooking form. The dry composition of solids is similar to that of Kraft char, the non-volatile fraction of fired SBL. In industrial operation, the high temperature conditions in the lower furnace and the SBL spray nozzle design and location in the RB, enable the 30–40% mass loss of the fired solids during spraying and before particles are exposed to the char bed [94]. This is of practical importance as the release of bound H₂O in the fuel, as shown by the absence of oxygen in Kraft char in Table 6, limits the occurrence of smelt-water explosions.²⁹

²⁸ Molecular formula for Burkeite salt: $2(\text{Na}_2\text{SO}_4) \cdot \text{Na}_2\text{CO}_3$ and Di-carbonate salt: $\text{Na}_2\text{SO}_4 \cdot 2(\text{Na}_2\text{CO}_3)$.

²⁹ Violent heat releases because of incoming water reacting with molten char bed inorganics.

Table 6. Comparison between Kraft char composition released from fired liquors and that of the SCWG solids yield.

Component	Kraft char [95]	SCWG Solids
Organic Carbon	24.9%	17.8%
Organic Hydrogen	0.7%	1.1%
Organic Oxygen	0	5.9%
Na ₂ CO ₃	49.0%	31.5% *
Na ₂ SO ₄	16.4%	19.8% *
K ₂ SO ₄	-	3.0%
Na ₂ S	9.0%	-
S- and HS-	-	5.6%
Total Carbon	30.5% **	21.8%
Total Sodium	31.9% **	30.2%
Total Sulfur	7.1% **	10.7%

* Exist in hydrated form, value reported in dry salt basis.

** Calculated based on reported values in [95].

The sensitivity analysis for SCWG solids composition showed that all hydrate salts are found in anhydrous form in the temperature conditions found in the location of spray nozzles in the RB. As such, the assumption of co-firing the solids, after mixing with incoming SBL from the evaporator plant was deemed practical. Another alternative to reduce risk in industrial scale operation was demonstrated in a desalination setup reported in [49]. The dehydration of solids was performed through sequential flashing of the stream during the cooling stage. In which the majority of present water would be separated prior to saturation. However, it is important to note that challenges related to solids recovery might arise as the formation of double salts might lead to inorganics sticking to separator walls as reported in studies such as [43] and [43].

Table 7 lists material and energy performance indicators for the impact of co-firing wet SCWG solids with incoming SBL from the evaporator plant in the RB. The clear impact of the integration scenario, represented as a fraction (X) of WBL directed to the SCWG reactor system, could be observed in the mass reduction of the feed stream. The evaporator train removes water and tall oil components (given that separated condensable gases are fired in the RB) leads to 0.22 kg of RB feed per kg of WBL. While, the treatment in the SCWG reactor leads to 0.11 kg of solids per kg of WBL feed. As a result, the listed indicators in Table 7 correlate exponentially to the split fraction. If to be plotted against the fraction of hydrochar co-fired in RB feed, a linear correlation would be observed. This is evident of the processing objective of the proposed SCWG integration, where volatiles present in WBL are utilized to produce H₂ gas carriers, while non-volatiles, including inorganics, are directed to the onsite reducing reactor, the RB.

Table 7. Impact of co-firing the SCWG solids with SBL on RB material and energy flows at different WBL integration fractions. Values in ( ) are relative difference to reference case.

(X) split fraction	Hydro-char in feed	Fired heat (HHV)	Smelt flow	Steam flow	Furnace Adia-batic T.	Eff. (HHV)*	Smelt Na ₂ S	Smelt Na ₂ CO ₃
unit	wt. %	kJ/kg wet feed	g/g dry feed	g/g dry feed	°C	%	wt. %	wt. %
Ref. mill	0%	12144	0.43	4.01	1570	75%	19%	75%
10%	5%	11686	0.44 (+2%)	3.89 (-3%)	1542	74%	20%	74%
20%	11%	11179	0.45 (+4%)	3.75 (-7%)	1509	73%	21%	73%
30%	18%	10611	0.46 (+6%)	3.57 (-11%)	1469	71%	22%	71%
40%	25%	9974	0.47 (+9%)	3.37 (-16%)	1419	69%	23%	69%
50%	34%	9250	0.48 (+12%)	3.13 (-22%)	1357	66%	25%	67%
60%	43%	8432	0.50 (+17%)	2.82 (-30%)	1275	63%	26%	65%
70%	54%	7485	0.52 (+22%)	2.44 (-39%)	1166	58%	28%	62%
80%	67%	6383	0.55 (+29%)	1.92 (-52%)	1005	50%	31%	59%
90%	82%	5091	0.59 (+38%)	1.21 (-70%)	754	36%	34%	55%

*Boiler efficiency refers to heat transferred to steam compared to fired heat on wet basis.

Sulfur balance in the recovery cycle

The higher sulfur flow in SCWG solids at 11 wt.% (dry basis) compared to only 3.7 wt.% in the SBL, contributes to the higher smelt flow per dry solids listed in Table 7. In addition, the fraction of Na₂S in the smelt gradually displaces that of Na₂CO₃. The design specifications in the RB model: reduction efficiency (at 95%), flue gas O₂ wt.% (at 3%) and air distribution (50% to the char bed) lead also to continued increase of sulfate flow in the smelt (not shown in the table). This is attributed to the set char bed temperature of 1100 °C (steady state conditions) reducing sulfur vaporization in the boiler.

The ratio of oxidized sulfurs compared to reduced form in solids is higher than that of SBL. The increased thermal demand for reduction mechanisms in the char bed (along with lowered fired heat) could be observed from the decreasing adiabatic temperature in the upper furnace. The energy balance around the char bed showed that at split fractions beyond 60%, the bed becomes endothermic. As a result, the RB thermal efficiency (with respect to steam production) reduces significantly with higher split fractions. At the 100% redirection of WBL flow scenario (not listed in the Table 7); fired heat in the RB is insufficient to generate upper furnace temperatures necessary to produce steam.

The increased sulfate smelt flow is considered chemical dead-load in KM operations as it will not participate in the pulping chemistry. [62] Sulfur mass balance closure in the dissolving tank (by mixing with aqueous yield) lowers the sulfate to sulfide ratio below operational limits in reference operations. However, in considering the overall flows, shown in Fig. 35, the rate of sulfur removal in the SCWG system leads to lower sulfidity in the recovery cycle. This could

lead to a negative impact on the Kraft cooking process. In practice, reference mill operations regularly include sulfur make-up streams (in the form of Na_2SO_4) to balance processing losses. Sulfur recovery in the reference mill is around 96% (excluding dust recycling), and decreases to 94% and 93% at 50% and 90% WBL split fractions respectively (including recycled aqueous yield). The addition of a sulfur gas absorber column following the L-G phase separation of the SCWG reactor product could possibly improve sulfur recovery.

Figure 35. Sulfur flows in the mill recovery cycle at different integration scenarios for the SCWG reactor system. Description arrows on the right are scaled according to the 90% case.

5.3.3 Economic analysis

The economic calculation in **Publication IV** for the SCWG integration scenarios addressed some of the uncertainties around biomass to fuel and energy systems through the following steps:

1. The biorefinery economic boundaries are applied based on a reference Nordic pulp mill, developed and validated, against industrial performance and historically cumulative technical documentation [53].
2. The site integration impact of the reactor on KM operation is evaluated and reported relative to the reference greenfield mill performance.
3. The WBL feed stream to the reactor system is not priced independently, but rather accounted for by the “missed production opportunity” from reduced existing power generation capacity.
4. The calculation method applied was tested with assumptions reported for the reference mill [53] such as i_{eff} , discount rate, life-time, end-of-construction year and others. The calculated MSP (with reference variables) for ADt pulp is €526, falls in line with reported by the reference study in [53] of €523. The relative difference was found to be less than 0.6%.

The different economic assumptions in this research are then easily traceable and could be summarized as different end-of construction year (2015 in [53] compared to 2016 in this study), different effective rate of return and discount rate (both 8% compared to 10% in this research), and no escalation of market

prices was considered in [53]. The differences lead to a MSP of €637 per ADt pulp used as the reference value when comparing the integration scenarios for a KM capacity of 800k ADt specialty pulp production per year.

Figure 36 shows the impact of integrating the SCWG reactor system on the reference mill economics. The economic indicators illustrated are the MSP per ADt of product pulp and the levelized contribution of different cost components for the mill (BOP and recovery cycle) and the reactor system. The integration is listed in the figure up to the 60% WBL split fraction to account for a single case with onsite power deficiency.

Figure 36. Comparison of the levelized cash flows and their contribution to the MSP per pulp product for a mill capacity of 800k ADt pulp per annum integrated with the SCWG reactor system. The MSP value is listed above each case for clarity of reading.

The difference in MSP between the two reactor cases is considerably small across the split fractions. The distinction is more observable in the levelized cash flows for the product gas revenues and the variable O&M (namely for catalyst replacement), both of which are higher in the lower 450 °C case (SCWG3B). Interestingly enough, the combined co-products (Gas, CTO and power) revenue flow for the 600 °C case (SCWG3A) increases by less than 1% compared the reference case at the 60% WBL split fraction. In other words, any new revenues from product gas selling are offset by the losses of CTO and power revenues. On

the other hand, the levelized revenues cash flow for the SCWG3B case continues to increase, up to 45% more than the reference case at the 60% WBL split fraction.

The breakeven MSP for the integration scenarios are found to be at a WBL split fraction of 31% and 35% for SCWG3A and SCWG3B cases, respectively. This is a result of increased revenues coupled with capital savings from smaller recovery cycle capacity offsetting capital cost increases from the SCWG reactor system. In considering the constraint for power self-sufficiency in mill operations, the thermal and economic feasibility range for integrating the SCWG technology would fall between the breakeven WBL splits (31-35%) and a 56% redirection to the reactor system.

6. Discussion

6.1 Comparing the supercritical gasification and subcritical liquefaction technology platforms

Figure 37 compares the thermal performance, following equation (8), for the stand-alone SCWG and HTL biorefinery case studies examined in this dissertation. The difference between Fig. 37 and earlier presented thermal performance for the SCWG cases in Fig. 29 and HTL in Fig. 24, is the inclusion of recovered heat from aqueous processing as an additional co-product. The product heat is assumed to be 90% of the available cooling utility above water saturation. This would represent available on-site heat for DH production.

Figure 37. The thermal performance on LHV basis of the developed SCWG and HTL standalone biorefinery cases examined. Cases with (*) refers to catalytic process and with (**) are cases which include both HTL (upstream) and SCWG (downstream) reactor systems.

The main takeaways from Fig. 37 could be summarized as:

- 1- The thermal opportunity from operating the SCWG process at higher temperatures (600 °C) remains lower at 82.7% for the case SCWG1B than found to be for the catalytic SCWG1A case (at 450 °C) with 83.5%.
- 2- In terms of thermal recovery, the HTL technology matches supercritical processing only when the valorization of the aqueous yield is included.
- 3- The inclusion of power production at higher SCWG temperatures allows for self-sufficient operation at considerably high efficiencies. Case SCWG2A, for Green hydrogen, has an efficiency of 67.5%.
- 4- The efficiency of Green hydrogen cases at 67-75% matches that of targeted efficiency improvements by the year 2030 in alkaline and PEM electrolyzers at 63-71% [12], however fall short of that for SOEC systems at 77-81% [96].

- 5- The thermal efficiency for the Bio-SNG cases are similar to reported upper limit efficiencies for synthetic methane (as an electrofuel) at 70-83% [96].
- 6- The multiproduct waste valorization case HTL4 reports the highest thermal recovery at 87%.

6.2 The liquefaction platform compared to alternative liquid hydrogen carrier pathways

Figure 38 compares the production prices for the HTL biorefinery cases with other liquid carrier production pathways. The costs for fossil-based fuels were estimated based on oil bbl. prices at two conditions, the highest (2011) and lowest (2016) recorded levels in the previous decade.³⁰ Fossil-based fuels, without policy imposed carbon tax, remain considerably cheaper than their biomass counterparts. The cheaper bio-based technologies remain those of the more mature biochemical platforms such as carbohydrates fermentation to alcohols and the transesterification of lipids to FAME (biodiesel). This is also attributed to the versatility and availability of feedstock at considerable lower costs. The large variation in production prices for both technologies in Fig. 38 is representative of the different commercial feedstock utilized, with lower boundaries accounting for 1st generation biofuels.

Figure 38. Comparison of technology-specific costs for the HTL case studies with other fossil and renewable based liquid fuel production routes. Average values highlighted with markers. Reported values are based on [32,96].

When considering the transition to advanced biofuels, the bio-product price projections for the HTL case studies are in-line and competitive with HVO, BtL and electro fuel technologies. However, it is important to note that commercial uncertainties around HVO, with high volume commercial production existing, and BtL, with several demonstration plants in place, are significantly less than that for the electro fuels and HTL technology platforms, with lower TRL levels.

The economic competitiveness of the HTL technology stems from another significant advantage compared to HVO, BtL or electro fuels, which is feedstock flexibility. The aqueous processing nature allows for the valorization of low thermal value and waste streams. The BtL cases in Fig. 38 represent production from the gasification of forest residues followed by gas reforming to liquids [32].

³⁰ Conversion factors: \$ to € = 0.9042 (2016) and 0.712 (2011), oil (bbl.) = 1.7 MWh and refinery yield of 94% consumer products.

However, when considering a wider feedstock list, the review of the technology presented in [97] shows that the selling price could reach as high as €128 per MWh (in the year 2016). This is mainly attributed to lower yields and higher gas cleaning costs from feedstock impurities and the sensitivity of reforming catalysts.

Similarly, the high variation for electro fuels represents fluctuating hydrogen costs from different electrolyzer technologies, along with low capacity factors for solar and wind technologies based power generation. On the other hand, economic evaluations for catalytic HTL systems for a wide range of feedstock such as dairy effluents, bagasse, algae and forestry feeds, reported in studies [37,66-69,98], show a smaller variation in production costs between €75 - €110 per MWh of co-products.³¹

In comparing findings from different techno-economic studies for biomass to fuels and energy system, one needs to consider:

1. The differences in the assessment methodology, key assumptions for economic factors and the fact that many of the reported findings are validated by relative proximity to previous literature.
2. Most studies follow the NOAK approach, which have been reported to significantly under-estimate costs related to introducing new technologies [11]. In addition, the reported economic uncertainties of $\pm 20-30\%$ consider deviations in capital cost estimations; however, are too simplistic to account for the compounding effect from inter-related economic assumptions such as operational capacity factors, financing rates and volatility in commercial pricing for energy commodities.
3. The absence of a standard biomass trading market adds to the uncertainty given the high contribution of feedstock gate fees to the final product cost in most conversion technologies.
4. For HTL studies specifically, scrutiny of the relied-on data sources highlights the limited (or lack thereof) economic data available in the literature. Most, if not all studies continue to rely on origin sources [37,99] for the catalytic HTL reactor system, the second largest cost component in proposed biorefineries.

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³¹ All reported prices are brought to €-2016 value, and due to the varied nature of the bio-carriers, renewable diesel conversion factors were applied to standardize reporting: liquid density of 0.85 kg/l, gallon diesel equivalence of 1.155 GGE and 1 GGE equivalence of 33.1 kWh.

6.3 Integration of the gasification platform in industry

Re-directing carbon emissions to new products

The design objective for integrating the SCWG reactor system in industrial bio-refineries in general, and KM(s) in specific, is illustrated in Fig. 39. The carbon flow balance in the recovery cycle shows the displacement of biogenic carbon emissions from the RB into the new mill bio-product (SCWG3B case from **Publication IV**). The insitu emissions from the recovery cycle are reduced by 34% and 61% at the 50 and 90% WBL split fraction respectively. It is however worth noting that the carbon flow in the product gas is 57 wt.% CO₂ (31 mol.%), with the balance mainly CH₄. As such, additional augmenting of carbon into the target bio-product could be performed in downstream reforming of the CO₂ fraction into a H₂ gas carrier, as was illustrated with cases SCWG1A-B from **Publication II**.

Figure 39. Carbon flows in the mill recovery cycle at different integration scenarios for the SCWG reactor system operating at 450 °C. Description arrows on the right are scaled according to the 90% split fraction case.

In addition, the retained carbon flow, ‘recycled to mill’ fraction in Fig. 39, increases with higher split fractions. Carbon flow to the recaustizing plant is mostly in the form of carbonates (smelt) and bi-carbonates (SCWG aqueous yield). A sensitivity analysis performed to assess the degassing of the aqueous yield showed that sulfur losses would be an undesirable side effect of such approach. The lowered sulfidity, shown earlier in Fig. 35, along with higher carbonate/bi-carbonate flow have direct impact on the subsequent re-causticizing chemistry. This typically would lead to increasing the lime demand in the mill, a sustainability challenge shared with black liquor thermal gasification (BLG) systems [61]. The lime-cycle chemistry as well as alternative causticizing technologies were not part of the scope in this study. Nonetheless, the high sulfur recovery at more than 93% (at 90% WBL split fraction) deems the applied assumption of re-causticizing plant scaling relative to WBL flow in the KM plausible.

De-coupling material production from chemicals and energy recovery

Figure 40 illustrates the potential for the SCWG reactor system to act as a H₂ gas carrier production block while processing requirements in the existing KM operations. The continued carbon removal from the recovery cycle and inorganic recycling at higher WBL split fractions allows for increasing pulping capacity without the need for RB capacity increases. Three different capacity-scaling variables were considered as part of the sensitivity analysis:

- 1- *Constant total steam production* aims to shift insitu bioenergy production (in the form of steam) from the RB to the bark boiler.
- 2- *Constant thermal load and flue gas flow in the RB* aim to maintain modern boiler design parameters. This is in order to minimize manufacturing changes needed for new installations or retrofit projects.

The technical feasibility of the capacity-scaling variables was examined based on the overall energy balance of the KM.

Figure 40. The potential mill capacity increases from the SCWG reactor system material decoupling of the Kraft recovery cycle and the pulping line.

All three design considerations led to a power demand deficiency near to the 50% WBL split fraction scenario. This is attributed to the utility design in the SCWG reactor system. The hot utility temperature demand is at the reactor conditions of 450 and 600 °C for both cases. The auxiliary boiler fired by a fraction of the product gas operates as HOB to match the higher temperature demand. While, power requirements for the reactor system is procured from the KM production balance (after matching steam demand). Savings from reduced power demand in the recovery cycle do not offset additional demand from the reactor system. For the 10% WBL split fraction scenarios, power demand increases between 5.2 to 5.9 times that of the savings for the three scaling-variables.

The thermal self-sufficiency of the reactor system, where the auxiliary boiler is independent from the KM steam network, eliminates the direct impact of increasing the reactor system capacity on the steam balance. If the restriction to match insitu power demand is excluded, the pulping capacity could be tripled while matching insitu steam demand. The increased capacities are plotted against historical development in commercial production capacities for context in Fig. 41. The proposed capacity increases while matching steam demand only (yellow scale in the figure) fall in line with similar KM production capacities commissioned in the previous 5 years.

Figure 41. Development of commercial pulp mill capacities as functions of the start-up year, adapted from [63]. The guiding lines on right vertical axis represent the reference mill capacity in this study (blue), and potential capacity increase while matching insitu steam and power demand (green) and steam demand only (yellow).

The bottleneck for higher production capacity (from integration at higher WBL split fractions) stems from the limit on available heat from the bark boiler, set similar to reference industrial operation [53]. The procurement of additional bark for the mill or utilizing digestive gas from WWT facilities was not considered in this study. Two alternatives proposed to make-up for the thermal penalty from replacing the RB with thermal gasification systems [61].

Figure 42 illustrates the integration impact on the KM economic performance indicator, the MSP of the specialty pulp product. The presented MSP(s) account for power deficiency cases: 60% for the reference capacity, 50% and 60% split cases for the two capacity scaling-variables. The benefits from ‘economy-of-scale’ are observed from improved MSP (compared to the ref. mill value) at the 10% WBL split fraction found for the scaling variables, compared to improved MSP beyond the 30% split fraction at reference capacity.

Figure 42. The compounded impact of ‘economy-of-scale’ factor and the SCWG system decoupling material flows on the MSP of the mill primary product.

The MSP at the 40% split fraction, with power and steam self-sufficiency at increased capacities was found to be between 16 to 17% lower than the reference case MSP. It is worth to mention that, revenues from increased bio-carriers co-selling and reduced capital costs in the recovery cycle offset power procurement costs at the higher WBL split fractions. This is attributed to two factors. First, the levelized selling price for the HFO-equivalent product gas at €29 per MWh is quite similar to the levelized price of power at €33. Second, the more efficient biomass to product gas conversion in the SCWG reactor system, compared to power from biomass in the recovery cycle.

Interestingly enough, the levelized product gas price as a hydrogen carrier is lower than the \$1 per kg of commercial H₂ (equivalent to €32 per MWh). This illustrates the conservative nature of the HFO-equivalency assumption for the SCWG product gas applied in this study.³²

³² All reported prices are in €-2016 year value.

7. Conclusion

7.1 Main findings and dissertation contribution

The objective of this dissertation was to better understand the thermal and economic constraints for commercializing the production of hydrogen carriers via the sub/supercritical water technology platforms. The advantageous thermo-physical and chemical properties from the aqueous processing medium enable low carbon and thermally efficient valorization mechanisms. The thesis was motivated by the available potential from industrial biomass, generated as residual streams from chemicals and materials manufacturing, to displace fossil fuels consumption.

Two primary production pathways were investigated. First, below water's pseudo critical conditions, the stand-alone non-catalytic HTL process was examined in **Publication I** for the production of liquid hydrocarbon carriers, to address demand in the transportation sector. The SCWG technology examined in **Publication II and III** addresses demand for gaseous carriers in both the power generation and chemical sectors. In the end, the holistic valorization potential of SCWR systems was examined in **Publication IV** to redirect excess carbon in Kraft pulp mills to new products, whilst serving a multitude of processing functions such as chemical recycling and waste treatment. The target bio-products are envisaged to contribute as hydrogen vectors in the necessary energy transition undertaken globally.

The devised biorefinery configurations in this dissertation were analyzed and systematically compared in reference to existing commercial technologies or similar production platforms under development. Chapter 6 presents the thermal and design trade-offs to be considered for SCWR systems as polygenerative platform Biorefineries. A summary of the main conclusions to the addressed research questions in this dissertation are listed below:

1. *What is the quantifiable contribution of water as a reactive component in SCWR systems in reducing the carbon intensity of hydrogen bio-carrier production?*

The study in **Publication II and III** showed that increased water participation in product formation mechanisms is driven by higher temperatures and lower solids in SCW systems. The study showed that although hydrogen gasification efficiency could reach up to 200% in the supercritical phase compared to hydrogen present in the feed. The intensification is penalized by increased energy utility. For the self-sufficient supercritical

reactor, the plant thermal efficiency, including the co-production of power and heat, was found to be 67.5%.

Intrestingly, operating at lower gasification temperature of 450 °C and 18 wt.% solid content for Bio-SNG production falls in line with the thermal performance of reference technologies such as electrolyzer based Green hydrogen and thermal gasification systems. This illustrates the processing opportunity for the reactor system to function as a H₂ gas carrier production unit, along with other functionalities such as CHP production and waste feed valorization.

While **Publication I** showed that the net contribution of the liquefaction platform is released water via-hydrolytic mechanisms such as de-oxygenation and dehydration. The presence of process water acts as a scrubber step to remove undesired organic and inorganic constituents in the liquefied product. This leads to a more hydrophobic crude, with desirable thermophysical properties, and lower upgrading requirements than reference pyrolysis oils from biomass.

2. *What is the role of biomass' inorganic-organic substrate interactions on the SCWR reactor conversion?*

The developed model in **Publication IV**, combining the constrained equilibria approach with electrolyte chemistry was shown to predict with reasonable accuracy the performance of the highly non ideal thermodynamic conditions in SCWR systems. The model showed that with current developments in salts capturing units around the critical point of water, the remaining (dissolved) alkali captures the CO₂ released from the partial oxidation conditions. This leads to improved equilibria towards the formation of H₂ gas carriers, increasing the thermal yield and reducing product gas impurities. Thermal recovery from the reactor system into product gas, solid hydrochar and DH was found to be 81-83% on HHV basis.

3. *Could the augmentation of carbon and hydrogen in the non-catalytic SCWR by-products, lead to both reducing the process residuals impact and matching the technical specifications and economic gains of reference technologies?*

The process models in **Publication I** illustrated that the displacement of organics into solids in the non-catalytic platform enables either: extending the product portfolio into bio-material production or could be used on site to offset the thermal penalty for valorizing the significant organic/carbon losses in the aqueous phase. The process modelling study showed that despite the lower quality biocrude from the HTL step, the thermal efficiency of the non-catalytic platform is between 60-87%, depending on the target products and utility availability.

The findings from **Publication II and III** illustrated that the SCWG biorefinery configurations for Green hydrogen as a gate product would require coupling with carbon capture technologies to reduce biogenic releases and realize the potential emission reductions of the technology. In addition, the targeted catalytic production of BioSNG remained the more favorable pathway among SCWR systems in terms of thermal recovery.

4. *What are the commercial feasibility drivers and constraints for potential co-products in the developed non-catalytic SCWR biorefinery concepts?*

The economic sensitivity analysis in **Publication I** identified two cost reduction measures: 30% lower capital costs for the HTL reactor system and establishing a hydrochar market valuation of €38 per MWh to make the non-catalytic HTL biorefinery economically competitive.

Under current market scenarios and investment cost assumptions, the breakeven prices for biorefinery co-products were found to be higher than reference commercial technologies. The study illustrated the importance of financial incentives to offset the additional capital and operating costs associated with industrial biomass valorization.

In addition, the site integration study in **Publication IV** showed that the co-location of the SCWG reactor system within Kraft pulp mill operations would match processing requirements while leading to a positive impact on the MSP of the mill's primary pulp product. The study showed that the optimal fraction of WBL to be directed to the SCWG reactor system is between 30-50%. The lower limit illustrates commercial feasibility defined as improved MSP of pulp. While, the upper limit represents the technical limit in the form of a power deficit in mill operations.

5. *What are possible material recycle synergies and added-value from the SCWR system site integration with existing industrial biomass processing plants?*

It was shown in the integration study with Kraft pulp mills in **Publication IV** that the organic-Na-S-K-Cl balance around the SCWG treatment of WBL showed processing synergies with the existing Kraft recovery cycle. The product gas could possibly be valorized as an additional bio-product from the mill or fired as a replacement fuel in existing limekiln operations. The solids and aqueous yield from the reactor system could be recycled back to the recovery cycle with minimal disruptions to sulfur and sodium recovery.

The study showed that the SCWG reactor system allows greater operational flexibility in the mill, where the material production line is decoupled from the chemical and energy recovery cycles. This is illustrated in the economies of scale opportunity by the SCWG technology, where the MSP of pulp could be reduced by up to around 17% while increasing production capacity anywhere between 165 to 178%.

7.2 Recommended future development and research questions

The direction for future research, process improvements and possible technology development for sub/supercritical water reactor systems is discussed and concluded in the reported techno-economic findings. In addition, considering the modelling nature of this study, certain limitations can be identified, and presented here as a guidance for future work.

- This study relies largely on secondary sourced data from the literature for the process modelling and economic assessment. It is suggested that future work runs concurrently with measurement campaigns to address newly identified knowledge gaps, reduce uncertainties around data quality as well as optimally utilize resources dedicated to data procurement, analysis and model validation. Some of the key performance parameters suggested for special attention going forward are water consumption in the elevated thermal conditions, reactor system energy requirements and reducing the impact on deterministic process yields from the analytical phase separation methods employed within laboratory setups.
- Many advances in modelling supercritical fluids, including the constrained equilibria approach proposed in this study, have delivered satisfactory and reasonably accurate predictions of thermodynamic properties. However, scaling of process units for commercial purposes, requires extending case-specific knowledge to transport properties and hydrodynamics. The computational fluid dynamic modelling challenge to be undertaken in this regard would be to account for the high variation at miniature temperature intervals of thermo-physical properties such as density, heat capacity, transfer co-efficients and mixing properties of multi-phase and various fluid-types within the reactive conditions.
- The complexity around experimental determination of inorganic mixtures solubility has hindered the availability of such data in literature. The developed model in this study predicts solvency in sub/supercritical water, specific to the set process conditions in the reactive system. The need for a predictive and mechanistic approach is evident to extend modelling capabilities to a wide range of industrial biomass feedstock and processing conditions.
- This study illustrated the processing opportunity from the co-location and site integration of sub/supercritical water systems in existing industrial infrastructure. Further studies examining similar synergies with other industries as part of sector coupling/ industrial symbiosis solutions would be beneficial for the wider commercial deployment. One potential industry is iron and steel production, where co-product hydrogen and hydrochar could be utilized on site as bio-based reducers. Other possible alternatives are cement, WWT and the petrochemical industry.

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List of Abbreviations and Symbols

ADt	Air-dried ton
bbl.	oil barrel
BECSS	Bio- energy with carbon capture and storage
BEVs	Battery electric vehicles
Bio-SNG	Bio-synthetic natural gas
BLG	Black liquor gasification
BLGCC	Black liquor Gasification Combined Cycle
BOP	Balance of plant
BtL	Biomass-to-liquid
CC	Composite curves
CE	Constrained equilibria
CELF	Constant-escalation levelization factor
CEPCI	Chemical Engineering Plant Cost Indices
CH ₄	Methane
CHP	combined heat and power
Cl	Chlorine
CO	Carbon monoxide
CO ₂	Carbon dioxide
CP	Critical point
CRF	Capital recovery factor
CTO	Crude tall oil
DH	District heating network
EBITDA	Earnings Before Interest, Taxes, Depreciation and Amortization
EJ	Exa joule

EOS	Equation of states
Evap.	Vaporization
FAME	Fatty acid methyl ester
FCI	Fixed capital investment
FT	Fischer-Tropsch
GAMS	General Algebraic Modelling System
GHG	Global greenhouse gas
GWP	Global warming potential
H ₂	Hydrogen
H ₂ S	Hydrogen sulfide
HDO	Hydro-deoxygenation
HEN	Heat exchanger networks
HFO	Heavy fuel oil
HHV	Higher heating value
HOB	Heat only boiler
HTC	Hydrothermal carbonization
HTL	Hydrothermal liquefaction
HVOs	Hydrogenated vegetable oils
IEA	International Energy Agency
IPCC	Intergovernmental Panel on Climate Change
K	Potassium
K ₂ SO ₄	Potassium sulfate
KM	Kraft pulp mill
K _w	Ionic product
LEA	Lipid extracted algal
L-G	Liquid – gas saturation line
LHV	Lower heating value
LP	Linear programming
L-S	Liquid – solid equilibria line
MILP	Mixed Integer Linear Programming
MSP	Minimum selling price

Na	Sodium
Na ₂ CO ₃	Sodium carbonate
Na ₂ CO ₃ .10H ₂ O	Sodium decahydrate
Na ₂ S	Sodium sulfide
Na ₂ SO ₄	Sodium sulfate
Na ₂ SO ₄ .10H ₂ O	Glauber salt
NaOH	Sodium hydroxide
NOAK	N th -of-a-kind
NPV	Net present value
O&M	Operation and maintenance costs
O ₂	Oxygen
PEC	Purchase equipment costs
PNNL	Pacific Northwest National Laboratory
PSA	Pressure swing adsorption
RB	Recovery boiler
RWGS	Reverse water gas shift
S	Sulfur
SBL	Strong black liquor
SCW	Sub/supercritical water
SCWG	Supercritical water gasification
SCWR	Sub/supercritical water refining
(SO ₄) ⁻²	Sulfate ion
TCI	Total capital investment cost
TCI	Total capital investment cost
TRL	Technology readiness level
USC	Ultra-supercritical rankine cycles
WBL	Weak black liquor
wt. %	Mass fraction
WWT	Wastewater treatment
α	Scaling component
ΔBPR	Boiling point rise

ΔG	Gibbs free energy
ΔH	Enthalpy
ΔS	Entropy
$\Delta T_{\min}$	Minimum temperature difference
ε	Dielectric constant
λ	Air to fuel ratio
μ	Chemical potential
ρ	Density

In order to facilitate a just transition to a future where our everyday energy and material consumption is environmentally concise, technical innovation needs to be accompanied with the necessary knowledge on the economical and societal impact of proposed solutions. This dissertation provides a summary of techno-economic bottlenecks facing sub/supercritical water as a technology to valorize industrial residues and wastes into value-added products for the energy, transportation and industrial manufacturing sectors. The results show that sub/supercritical water has the potential to function as a transitional low-carbon platform to reduce GHG emissions in areas where electrification could possibly be constrained.

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