A Kraft Mill-Integrated Hydrothermal Liquefaction Process for Liquid Fuel Co-Production

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Abstract: There is a growing awareness of the need to mitigate greenhouse gas emissions and the inevitable depletion of fossil fuel. With the market pull for the growth in sustainable and renewable alternative energy, the challenge is to develop cost-effective, large-scale renewable energy alternatives for all energy sectors, of which transport fuels are one significant area. This work presents a summary of novel methods for integrating kraft mills with a hydrothermal liquefaction process. The application of these methods has resulted in a proposed kraft mill-integrated design that produces a liquid fuel and could provide net mitigation of 64.6 kg CO₂-e/GJ, compared to conventional petrol and diesel fuels, at a minimum fuel selling price of 1.12–1.38 NZD/LGE of fuel, based on the case study. This paper concludes that a hydrothermal liquefaction process with product upgrading has promising economic potential and environmental benefits that are significantly amplified by integrating with an existing kraft mill. At the current global kraft pulp production rate, if each kraft mill transforms into a biorefinery based on hydrothermal liquefaction, the biofuel production is an estimated 290 Mt (9.9 EJ).

Keywords: hydrothermal liquefaction; black liquor; process integration; techno-economic analysis; utility system; total site heat integration

1. Introduction

The World Commission on Environment and Development [1] defined sustainable development as development that meets the needs of the present without compromising the ability of future generations to meet their own needs. With the growing awareness on the need to mitigate greenhouse gas (GHG) emissions and the inevitable depletion of fossil fuel, the world is on the journey of transitioning towards more sustainable and renewable alternatives. The need to minimise fossil fuel use and mitigate its associated GHG emissions drives the ongoing growth in sustainable and renewable alternative energy.

In the world’s consumption of fossil fuel (coal, natural gas, and oil), 91% is used for energy applications. In crude oil consumption, 63% is for the global transportation sector and 16% is used to make building-block chemicals and polymers [2]. With transportation demand increasing globally, driven in part by population growth, the challenge to decrease the world’s reliance on fossil fuels requires the implementation of cost-effective, large-scale, renewable energy-based transport fuel projects.

Biorefineries are the most promising route to produce biofuel and platform chemicals to support a new bio-based industry [3]. A biorefinery is an industrial facility (or network of facilities) that covers a collection of technologies to sustainably convert biomass into basic building blocks for the production
of biofuels, energy, and chemicals [4]. It is analogous to current petroleum refineries. To be a feasible alternative, biorefineries must have a dependable supply of feedstock [5], which usually makes up 40 to 60% of the operating costs [6], and maximise the energy conservation between energy inputs and outputs.

Kraft pulping is a well-established process that can be converted into large-scale biorefineries, producing biofuels as a main product. Kraft mills contain critical components vital for a biorefinery [7], i.e., access to biomass feedstock and supply chains, understanding of biomass refining-type processes, and accessible residual feedstock, such as black liquor. Traditional processing in a chemical pulp mill, like a kraft mill, extracts between 40 to 60% of high-value pulp or paper products from the harvested logs while the remaining dissolved wood in the form of a liquor has relatively low economic potential. To maintain profitability, the kraft pulp sector is facing pressures to expand the range of products produced to more than just pulp, heat, and power production. A pulp mill processes a high volume of biomass feedstock and generates by-product streams like black liquor (a mixture of spent pulping chemicals and lignin), which is partially processed by the pulp production [7]. Biomass components—containing mostly hemicellulose and lignin in black liquor—supplies the energetic demand (heat and power) required by the kraft mill through combustion in a recovery boiler. The recovery boiler also plays a vital role in the inorganic chemical recovery process, which contributes to the overall economy of the kraft process. The organic component in black liquor has the potential to be transformed into bioproducts that have higher value than using black liquor as a fuel for heat and power.

Hydrothermal liquefaction (HTL) is a thermochemical process that depolymerises wet biomass into liquid fuels in a reactor operating at high temperature and pressure and sufficient time to decompose the solid natural polymeric structure to mostly liquid compounds [8]. It is a flexible conversion process due to the variability of bio-based or waste feedstock that have been successfully tested. The key advantage of why the HTL process is successful is because the feedstock of the HTL process does not have to undergo a drying process. Water in the HTL process serves as a reactant and catalyst in the subcritical region as the properties of the water change extremely. In the subcritical region, the dielectric constant of the water decreases significantly, as compared to ambient water [9]. Due to this, the solubility of hydrophobic compounds is higher than at ambient condition. In addition, the subcritical environment of the water increases the rate of acid/base-catalysed reactions due to the higher ionic product of water [10]. Liquid bio-crude is the key product of the process. With upgrading the process (like conventional fuel), this bio-crude can be transformed to the whole distillate range of petroleum-derived equivalent fuel products. When compared to gasification, pyrolysis and HTL have a simpler technical conversion of biomass to a liquid fuel [11]. However, when compared to pyrolysis oils, the lower oxygen content in HTL bio-crude makes it less corrosive and has higher heating value (30–36 MJ/kg). The higher calorific value of HTL bio-crude as compared to pyrolysis (15–22 MJ/kg) is more similar to conventional petroleum (43–46 MJ/kg) [12].

Numerous studies have been focusing on evaluating the technical and economic feasibility of the HTL process of different feedstock and algae, considering the various operating conditions of the reactors. However, techno-economic evaluation of HTL of black liquor still presents a research gap when compared to the other feedstock. Black liquor is a complex organic and inorganic mixture. The organic mixture in black liquor is mostly the remaining cellulosic fibres, lignin and hemicellulose, and the caustic inorganics that are used in the kraft process. The advantages of using black liquor in the HTL process are [13] (1) the organic component serves as feedstock to the process and (2) the inorganic component acts as a caustic catalytic solution, instead of sodium hydroxide, for the HTL process. Huet et al. [14] studied the integration of the HTL process of sulphur-free black liquor with a kraft mill, with the reactor temperature between 270 °C and 310 °C. HTL processing of black liquor produces both phenolic molecules and bio-crude. A sodium recovery of 97% was reported, which matches with kraft mill inorganics recovery technology. The sodium is recovered in the form of sodium carbonate, which is converted to caustic soda with the current available technology. Kosinkova et al. [15] conducted a
study of hydrothermal liquefaction of bagasse, using co-solvents, ethanol, and black liquor. The yield of the HTL bio-crude increases as the black liquor content increases. This is because black liquor in the co-solvent contains organic residues, which provide additional reactants for conversion and the basicity supports the base-catalysed condensation reaction that leads to oil formation.

Ong et al. [16] analysed the techno-economic feasibility of HTL of radiata pine with black liquor from an existing kraft mill. The estimated minimum fuel selling price (MFSP) of this approach was 1.75 NZD/LGE of fuel (using a conversation rate of 1 NZD = 0.6 USD). Funkenbusch et al. [17] conducted a techno-economic analysis of HTL of lignin, where the lignin are extracted from BL, and determined a MFSP of 1.58 NZD/LGE. Melin et al. [18] experimentally investigated the optimum operating parameters for producing high-quality bio-oil from HTL of BL, using glycerol as the hydrogen donor and sodium hydroxide as the alkali for high heating value fuel. Lappalainen et al. [19] studied the effects of process conditions of the HTL process on the quality of bio-oil from HTL of black liquor. The process parameters studied are residence time and any additives (solvents, catalysts); these conditions are modified to optimise the quantity and quality of the bio-oil production and to minimise the production of secondary products such as biochar and gaseous products.

Prior to today, much of the research on the HTL process studies the process parameters of lab-scale batch reactors. There is, however, a shift towards commercialisation by scaling up the process to a continuous pilot-scale operation [20]. Due to the sub-critical condition required by the process, maximizing the energy efficiency of the HTL process is crucial. Okoro et al. [21] used pinch analysis to conduct heat integration for HTL of meat waste and successfully reduce the heating and cooling demands by approximately 36% and 32%, respectively. Shemfe et al. [22] applied pinch analysis to design the heat exchanger network for upgrading of bio-crude. Anastasaki et al. [20] studied the effectiveness of enhancing a custom-designed heat exchanger design through oscillating of the slurry. Magdeldin et al. [23] conducted a techno-economic assessment of a HTL process that is integrated with downstream combined heat and power (CHP) generation using waste heat and by-products of the process. The introduction of CHP in the HTL process increases the thermal efficiency of the process. Knorr et al. [24] recognized that the maximising the heat integration of the reactor design is a crucial gap. Ong et al. [25] used an iterative process integration and simulation methodology to improve the energy efficiency of integrating HTL with an existing kraft mill.

The aim of this paper is to carry out a techno-economic and carbon emissions assessment of hydrothermal liquefaction of radiata pine and black liquor to assess the techno-economic viability of the process, as compared to fossil fuel feedstock. This paper shows the benefits of integration of the HTL process with a kraft mill with a centralised utility system. The results include a thermo-economic assessment of two other options for reducing marginal fuel use in an existing kraft mill. These options are (1) black liquor evaporators with vapour recompression and (2) replacing the current aged recovery boiler with a high efficiency modern design. The study also explores the trade-off between the GHG emission cost and oil price increase on levelised profit.

2. Materials and Methods

The current study considers three scenarios and determines the cost-benefit of integrating the kraft mill with the new biorefinery technology by measuring how much the minimum fuel selling price changes for the different scenarios.

2.1. Total Site Heat Integration (TSHI)

Heat integration reduces heat demand on boilers and the consumption of fuel, e.g., natural gas, residual biomass, wood chips, and/or black liquor. The introduction of a new biorefinery process to an existing kraft mill significantly affects the site’s best heat integration design as well as its overall heat and power balance. The methods used throughout all two scenarios are TSHI with the kraft mill and site heat and power utility modelling.
A site utility model of the recovery boiler and supplementary boilers, turbine, and process heat demands has been implemented in an Excel™ spreadsheet. The boilers assume a constant thermal efficiency of 75%. The turbine model incorporates the extended Willan’s line approach of Medina-Flores et al. [26], where historical turbine performance data was used to define turbine model coefficients. Process heat demand from the utility system varies for each of the evaporation system options. The decrease in the low-pressure steam demand adversely impacts on turbine power generation. However, it reduces the required high-pressure steam from the marginal fuel boiler, which is fuelled partially by wood residue (50%) and natural gas (50%). The data is based on an existing kraft mill in the Central North Island of New Zealand.

2.2. Economic Assessment

The economic assessment is based on the methodology reported by Ong et al. [16]. The data used to estimate the operating costs are as presented in Table 1.

Table 1. Estimated material, utility, and carbon emission prices.

| Materials                        | Cost     |
|----------------------------------|----------|
| Radiata pine                     | 95.00 NZD/t |
| Radiata pine (+125 km)           | 160.00 NZD/t |
| Radiata pine (+350 km)           | 250.00 NZD/t |
| Sodium hydroxide                 | 500.00 NZD/t |
| Sodium sulphate                  | 220.00 NZD/t |
| Hydrotreating catalyst           | 50.20 NZD/kg |
| Utilities                        |          |
| Natural gas                      | 10.00 NZD/GJ |
| Electricity                      | 90.00 NZD/MWh |
| Cooling water                    | 2.50 NZD/MWh |
| GHG emission                     | 25.00 NZD/t |

2.3. Environmental Impact

A shortcut life cycle analysis of the GHG calculation uses the method in Martinez Hernandez and Ng [27]. The GHG emission is calculated for the HTL process and its downstream benefits using the GHG factors presented in Table 2.

Table 2. Environmental impact coefficients.

| Item              | GHG Factor t CO₂-e/Unit | Unit |
|-------------------|--------------------------|------|
| Electricity       | 0.085 [28]               | MWh  |
| Natural gas       | 0.058 [29]               | GJ   |
| Wastewater        | 0.188 [30]               | t    |

The main GHG emissions considered in this study are (1) electricity, (2) natural gas, and (3) wastewater. The Emission Trading Scheme (ETS) in New Zealand excludes emissions from biofuels and covers the conventional liquid fossil fuel emissions [31]. The main products converted from the upgrading of the bio-crude process are (1) gasoline equivalent, (2) diesel equivalent, and (3) heavy fuel oil equivalent. The flue gas emission only considers the emissions from the combustion of natural gas. The combustion of off-gas is considered emission free because the source is from the biomass and this falls outside the ETS. The flue gas emission data is extracted from the HTL process simulation model.
2.4. Process Flowsheet

The flowsheet for this paper is based on a PhD work that has been carried out [32]. The thesis started out with designing a kraft mill-integrated biorefinery system. The case study applies a process synthesis technique by developing a multi-dimensional, heat and mass integration methodology [33], which combines pinch analysis, total site heat integration [34], and P-graph [35] frameworks, to select a biorefinery option. The novel method takes into account heat and mass integration with an existing kraft mill in Central North Island of New Zealand and also first-order capital costs of the options at the selection process. The result from the paper shows that hydrothermal liquefaction was the optimal choice to be integrated with the existing kraft mill.

Figure 1 shows the final design summarised in the thesis. The biomass slurry consists of radiata pine, black liquor, and water. The biomass slurry is pressurised in multi-stage pumps and reacts to produce bio-crude, aqueous phase with a fraction of organic materials (hydrocarbons, alcohol), non-condensable gaseous products, and organic solid residues (biochar). Black liquor serves as an additional organic feedstock (hemicellulose and lignin) and a catalyst (Na and K) to the process. Kraft pulp residuals, combined with virgin wood chips and sawdust, can be considered to be the primary biomass feedstock, tapping into existing processes, supply chains, and infrastructure. The upgrading process, e.g., hydro-deoxygenation of bio-crude [36], reduces the oxygen content of the bio-crude, producing hydrocarbon fuels equivalent to petroleum products (45 MJ/kg). The process model based on Aspen Plus™ for the HTL process and upgrading of bio-crude is described in Ong et al. [16].

The ultimate analysis of the HTL bio-crude is presented in Table 3. However, the proposed HTL process in Ong et al. [16] does not address the black liquor inorganics recovery. Figure 1 is a process flow diagram of a new proposed HTL process.

| Component | Bio-Crude |
|-----------|-----------|
| Carbon    | 73.4      |
| Hydrogen  | 6.5       |
| Nitrogen  | 0.1       |
| Sulphur   | 0.6       |
| Oxygen    | 18.9      |
| Ash       | 0.5       |

The inorganic chemicals and sodium and sulphur (Na/S) balance in a kraft mill are crucial for the process economics and environmental viability. The key to that is recycling the Na/S balance at a rate of approximately 97% [37]. Black liquor offers a chemical balance of sodium and sulphur (Na/S balance), which reduces the production cost of pulp and paper. Sodium salts and sulphur anions are primarily in the water and condensates of the HTL process. The concentrations of sodium and sulphur, however, are low, in terms of ppm in the aqueous phase. Evaporating the water from the aqueous phase would incur a high thermal energy cost in an already thermally intensive process. To overcome this issue, supercritical water gasification of the aqueous phase is proposed.

Supercritical water gasification (SCWG) is considered the most appropriate separation approach because:

1. SCWG is able to treat the phenolic compounds that are in the aqueous phase,
2. SCWG produces syngas that has lower contamination, and
3. The alkali salts are insoluble in the SCWG processing conditions due to the change in thermophysical properties above the critical point, which is important in the inorganic recovery of the process.
Figure 1. Process flow diagram for the kraft mill-integrated HTL process.
Additional benefits for implementing this process are the elimination of a hydrogen production plant and the reduction in wastewater treatment requirements.

The HTL, upgrading, and SCWG processes are simulated in Aspen Plus™ v9.0 (AspenTech, Bedford, MA, USA, 2020). The biomass into the HTL process was based on 2000 t/day organic loading, which is converted into bio-crude through the HTL process and upgraded to produce a gasoline and diesel blend.

Hydrothermal liquefaction is an energy-intensive process that operates at high temperature (315–355 °C) and pressure (220–250 bar). With these high operating conditions, heat and exergy recovery during cooling and depressurisation of the product flow greatly affects the economic competitiveness of the process. There is still a gap focused on increasing the energy efficiency of the HTL process. In the HTL process, the process conditions affect the product characteristics, yield, and quality. However, the temperature and pressure set points of some streams can be altered without affecting the product characteristics.

Ong et al. [25] established a novel and iterative method to optimise the mass and energy flows and asset of the HTL process, using heat and mass integration simultaneously with process simulation. The iterative procedure uses a combination of existing frameworks and design tools (process simulation tools, pinch analysis, process optimisation, and heat exchanger network design), with the inclusion of the process constraints of the HTL process. The procedure includes the simultaneous need for process simulation to provide in-depth analysis of the multiple impacts of the process modification opportunities. An important section of the analysis and optimisation is the implementation of process constraints based on the best available process knowledge from literature. As a result, the stream parameters and flow sheet design are modified and improved within defined parameters that do not affect the integrity of the process and product and that respect technological limitations. Based on the possible process modification and process constraints of the HTL process that would not affect the yield and quality of the product, the optimised flowsheet of the HTL process is presented in Figure 1.

3. Results

3.1. Scenario 1: Kraft Mill with Hydrothermal Liquefaction System

Scenario 1 considers the HTL process of radiata pine and black liquor. Total site heat integration for the HTL process and kraft mill has been used to have an insight into the integration potential between the HTL process and the kraft mill. The utility model is designed to understand the reduction in power generation due to the lower production of steam from the boilers.

3.1.1. Integration of Hydrothermal Liquefaction with Kraft Mill

Figure 2 shows the utility system of the existing kraft mill. The black liquor solids (BLS) are burned in two recovery boilers, RB1 and RB2. PB1 and PB2 are the marginal fuel (MF) boiler that supplies steam to any deficit demands. The current turbine generates 30.4 MW of power, which is about half the power use of the kraft mill.

Figure 3 shows the utility system of integrating the hydrothermal liquefaction system concept with a kraft mill, using 18% of the black liquor. The three processes are internally heat integrated by exchanging mass and heat with the kraft mill, as outlined in Ong et al. [25]. The utility generated from the three processes are delivered to the kraft pulp process through the utility system. In Figure 3, it shows that the heat that is supplied from the HTL process reduces the marginal fuel of PB1 by 34.8%. Due to the lower steam production from the diversion of the black liquor solids and the decrease in the marginal fuel, the power generation reduced by 9.8 MW. The power generated is calculated using a correlated Willan’s line based on the current turbine size. As a result, the inherent cost of black liquor as a feedstock includes the power generation lost by using part of the black liquor. The marginal fuel that is reduced from PB1 is sent to the HTL process as feedstock, which is cheaper due to the lower quality.
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Figure 2. Simplified utility system of the existing kraft mill.

3.1.2. Economic Assessment

The economic assessment is presented in Table 4. The tax used in the study is the federal tax in New Zealand, 34% of the taxable income. The HTL process and the upgrading of the bio-crude are the two processes that contribute the highest to the capital cost, comprising 28% and 29% of the total installed cost (TIC). Efforts are needed to decrease the cost of these sub-processes. Zhu et al. [38] reported that the TIC can be reduced by approximately 10% through decreasing of the operating pressure by 37 bar and temperature of the HTL process by 20 °C. Zhu et al. [38] also investigated hydrocracking the heavy fuel oil and reported that it increases the production rate by 62.9% as compared with the case without hydrocracking. This is another important direction for further work in relation to the present study.

Table 4. Cost results for HTL system with 18% black liquor.

| Installed Costs                  | NZD Million | Operating Cost            | NZD Million/y |
|---------------------------------|-------------|---------------------------|---------------|
| Biomass preparation             | 33.3        | Variable operating cost   | 65.1          |
| HTL                             | 111.7       | Feedstock                 | 8.2           |
| Upgrading                       | 124.7       | Natural gas               | 6.3           |
| SCWG                            | 60.0        | Catalysts and chemicals   | 21.5          |
| Utilities                       | 39.8        | Utilities                 |               |
| Contingency                     | 40.9        | Fixed costs               | 40.3          |
| Total installed cost            | 423.5       | Revenue from by-products  | 33.2          |
| Indirect costs                  | 234.3       | Capital depreciation      | 22.5          |
| Total capital investment        | 657.8       | Annualised investment     | 52.9          |
|                                 |             | Tax                       | 11.8          |

MFSP per L of product: 1.11 NZD/L
MFSP per LGE of product: 1.23 NZD/LGE
Figure 3. Simplified utility system of integrating the hydrothermal liquefaction process with the existing kraft mill.
Figure 4 shows the MFSP for redirecting a range of fractions of weak black liquor from the kraft mill to the hydrothermal liquefaction process for biofuel production. The figure shows that the MFSP decreases up to 20% of the kraft black liquor and the MFSP starts increasing again. This is due to the increase in the cost of radiata pine.

| % Black Liquor to HTL | Cost (NZD/LGE) |
|-----------------------|----------------|
| 10%                   | 0.80           |
| 15%                   | 0.90           |
| 20%                   | 1.00           |
| 25%                   | 1.10           |
| 30%                   | 1.20           |
| 35%                   | 1.30           |
| 40%                   | 1.40           |

**Figure 4.** MFSP and the breakdown of the levelised production costs of the HTL process with different processing size.

At the current forestry activity, there is an excess feedstock supply near the kraft mill [39]. However, at 25% of black liquor, the radiata pine feedstock at that vicinity is insufficient. The cost of the feedstock for the 25% black liquor case takes into account the additional 150 km needed to travel for feedstock collection and an additional 350 km for the 30% case and higher. The cost used to calculate the additional distance travelled for the delivery of the radiata pine is costed according to Robertson [40]. Therefore, the assumption of taking 18% of the black liquor used as the basis of the calculation is near the optimum.

The main products of the HTL process are biofuels, heat utilities, and heavy fuel oil. The biofuels are costed in the MFSP and the heat utilities are delivered back to the kraft pulp process. The heavy fuel oil, in this case, is equivalent to marine fuel oil. It is a revenue stream and is priced at the same cost of fossil fuel-derived marine fuel oil. In the last year, the marine fuel oil price has fluctuated at about 250 NZD/t [41]. The selling price of the heavy fuel oil is studied at low, average, and high values: 800, 1000, and 1150 NZD/t.

Figure 5 shows the change of feedstock (radiata pine and natural gas), electricity costs, and capital cost. The range of price shows the change from −30% to +30% based on the cost used in the calculation. The capital costs were estimates, the probable accuracy of the estimate is ±30% [42]. According to Figure 5, the cost of radiata pine (i.e., feedstock) has the highest effect on the MFSP, as reported in other studies [38,43].
3.1.3. GHG Emission

The calculated GHG emission for the HTL process is a credit of 97.5 kt CO\textsubscript{2}-e/y due the credits earned from sequestration of the solid residue outweighing the total emissions released by the process, 194.3 kt CO\textsubscript{2}-e/y.

In this work, the solid residue (biochar) produced from the integrated hydrothermal liquefaction process is used for soil amendment to earn GHG credits [44]. According to He et al. [45], 77.86% of the organic compound in the biochar would break down into the soil while the remaining carbon would be released into the atmosphere as GHG emissions. The net carbon credit of the biochar is estimated at 291.8 kt CO\textsubscript{2}-e/y. The carbon credit from the by-product earns 7.3 million NZD/y with a carbon price at 25 NZD/t. Sequestering the biochar for soil while producing emissions credits has economic and environmental merit. However, there may be extra opportunities for higher-value markets for the biochar in the future.

Due to the high pressure of the HTL process, a substantial amount of electricity is required by the process. The emissions shown in Table 5 are low because 90% of the electricity in New Zealand is renewable. Table 5 compares the GHG emissions of the HTL system by comparing the emission factor for electricity in Australia. The GHG emission factor for Australia assumed is the National Electricity Market’s emission factor [46]. The results in Table 5 show that the HTL production system is carbon neutral fuel, which provides a net reduction in New Zealand, due to the source of the electricity.

| Table 5. Comparing GHG emissions between New Zealand and Australia. |
|---------------------------------------------------------------|
| **Gr\textsuperscript{i}d emissions factor (t CO\textsubscript{2}-e/MWh)** | New Zealand | Australia |
| Natural gas | 0.085 | 0.830 |
| Electricity | 160.8 | 160.8 |
| Wastewater | 27.0 | 263.7 |
| Carbon sequestration | 6.5 | 6.5 |
| Net GHG emissions from HTL system | 291.8 | 291.8 |
| GHG emissions offset from fuel substitution | −97.5 | 139.2 |
| Total net GHG emissions reduction | −344.3 | −344.3 |
| | −441.8 | −205.1 |

A high amount of natural gas is used in the HTL process to supply the required heat demand of the kraft mill. Due to the energy-intensive HTL process, the net GHG credit is less than 100%.
One of the ways to reduce heat consumption is in the SCWG process. In the current SCWG process, the reaction process is an endothermic process. The natural gas needed by the SCWG process is used to solely heat the feed and maintain the temperature of the reactor. Studies from Castello [47] and Gutiérrez Ortiz et al. [48] suggest that the reaction process achieves an auto-thermal regime at a biomass concentration of 15 to 20 wt%. At that regime, maximum H₂ is produced, as well as methane production. Future work should include other biomasses to have a concentration that is beneficial for both hydrogen production and process energy sustainability.

Nie and Bi [44] carried out a life-cycle assessment of HTL fed with forest residues. They reported GHG emissions of 20.5 kg CO₂-e/GJ. In Nie and Bi [44], the natural gas needed for producing hydrogen (as feedstock and heating) is 3.0 kg of natural gas per kg of H₂ produced. Due to the high temperature in SCWG, the required natural gas for the hydrogen production is 6.2 kg of natural gas per kg of H₂ produced. However, the median value for the production of biofuel through the HTL process is 23.58 ± 4.18 kg CO₂-e/GJ [44].

### 3.1.4. Biofuel Policy Consideration

The question to answer is under what situation would the cost of biofuel be sufficiently profitable to compensate for the high level of investment risk. New Zealand’s fuel price is governed by global oil supply and demand factors. Table 6 shows the breakdown of the current petrol price in New Zealand.

| Components                        | NZD/LGE |
|-----------------------------------|---------|
| Refined Fuel                      | 0.559   |
| Fuel excise                       | 0.703   |
| Goods and Services Tax (GST)      | 0.269   |
| Emissions Trading Scheme (ETS)    | 0.062   |
| Shipping                          | 0.041   |
| Importer Margin                   | 0.450   |
| Total                             | 2.084   |

The ETS in New Zealand excludes biofuels from the emissions calculation. The overall carbon balance reported in the previous section only includes the carbon released by the HTL production system, which is calculated to be a carbon neutral system that provides a net reduction in GHG emissions. As a result, the use of biofuel would mitigate the emission of conventional fuel, which is covered by ETS. Therefore, it is assumed that because of the mitigation and that the biofuel is produced in New Zealand, the base cost for comparison with a fossil fuel should include the cost of the refined fuel, plus the ETS liability, shipping cost, and importer margin. The importer margin for the analysis is assumed as the average of 0.45 NZD/LGE. As a result, the current fuel price that the biofuel must compete against is 1.11 NZD/LGE.

Figure 6 shows the effect of GHG prices on the fuel cost. As the GHG price increases, the biofuel MFSP decreases. The increase in GHG price increases the selling price of the heavy fuel oil and revenue earned from carbon sequestration through the solid residue. The current GHG price is assumed to be 25 NZD/t.

At the present time, the GHG price needs to increase its current price to about 47 NZD/t to reach the biofuel MFSP for the current oil price. This price is well within the anticipated range of GHG prices for New Zealand in 2030 [50]. Wetterlund et al. [51] mentioned that the feasibility of the process is highly dependent on policy framework and energy market conditions.
The price of crude oil plays a significant role in the economic viability of biofuels. The crude oil price is often volatile and closely linked to political and economic climates. At the beginning of October 2018, the oil price peaked at about 142 NZD/barrel before falling sharply to around 83 NZD/barrel by the year’s end. At the start of 2020, the price had slowly rebounded to 108 NZD/barrel. As a result, it is quite possible in the near future, a 25% increase in the current fuel cost is reasonable. Under this future oil price, the MFSP would be slightly exceeded, favoring implementation of the integrated HTL system.

With New Zealand on its transition to a sustainable economy, one of the ways to pull biofuels onto the market is through favorable policies [52]. In regions like Europe, the U.S., and South-East Asia, governments provide policies to grant biofuel producers tax exemptions and/or subsidies. With a similar effect, governments can also add a tax on specific classes of non-renewable energy fuels, beyond an ETS. To make the biofuel process economical, the New Zealand government could consider either to tax an extra 0.12 NZD/LGE on non-renewable fuels or give a subsidy of 0.12 NZD/LGE to the biofuel producer. An example of emerging markets is the biodiesel program in Colombia. The government implemented a combination of policies which includes the blending of fuels and tax credits for production and consumption, showing success in increasing biofuel production during the early stages of implementation [53]. Developing a comprehensive policy framework for biofuel uptake in New Zealand falls outside the scope of the current thesis but would be an interesting direction for further exploration.

3.2. Scenario 2: Mechanical Vapour Recompression of Black Liquor Evaporators

Black liquor evaporation in the recovery loop process of a kraft mill is an energy-intensive process. The energy demand of the evaporation process represents 20–30% of site-wide thermal energy demand. Usually, multi-effect evaporators (MEE) concentrate black liquor from about 18% to its firing solids (∼70% for older recovery boilers and ∼85% for modern ones). The first evaporator effect uses low-pressure steam (about 4.5 bar\text{ab}) and rejects heat through a condenser (about 0.18 bar\text{ab}) and cooling tower. To decrease this energy consumption, the integration of the evaporators with the kraft pulp processes is maximised. An alternate approach to energy reduction in evaporation systems is the use of vapour recompression technologies, thermal vapour recompression (TVR) and mechanical vapour recompression (MVR) [54]. MVR technology has rarely been considered for black liquor evaporators due to the availability of “free” energy gained from the recovery boiler as well as black liquor’s high boiling point elevation, which reaches about 15 °C at 67 wt% solids. However, some older kraft mills burn fossil fuels in supplementary boilers but have access to renewable electricity.
As a result, integration of MVR and/or TVR technology into the MEE may be an economic opportunity to reduce fossil fuel use and emissions.

The methodology for this scenario applies TSHI to correctly integrate MVR and TVR with MEE to significantly reduce the use of fossil fuel and its associated emissions. The methodology is further presented in Walmsley et al. [55].

### 3.2.1. Total Site Heat Integration for Conventional 7-Effect Black Liquor Evaporators

The total site profiles (excluding the evaporator) and the site utility grand composite curve for the studied kraft mill are shown in Figure 7. The $T^{**}$ denotes double-shifted temperature, a notation used in Total Site Heat Integration (information available in [34]). Weak black liquor enters at the lowest pressure effect at 85.0 °C, which initially operates with a saturation temperature of 66.8 °C. For each of the following effects, black liquor increases in pressure and enters at a temperature lower than its saturation temperature. At present, the 7-effect evaporators bleed 2.6 MW of steam from the 2nd effect to the foul condensate stripper column (in place of low-pressure steam). The net SEC (specific energy consumption) for the 7-effect evaporator is 420 kJ/kg$_{evap}$. 
3.2.2. Black Liquor Evaporators with Vapour Recompression

Figure 8 exhibits the TSHI of the 3-stage MVR system. There are two integration points: condensate heat recovery and a vapour bleed from stage 2 for the stripper column. Condensate from the 3-stage MVR system is available at 90 °C, which is hotter compared to 72 °C condensate from a conventional 7-effect set-up.
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A thermo-economic assessment of three options to retrofit black liquor evaporators with vapour recompression has been studied with results presented in Table 7. Table 7 shows a re-evaluated result from Walmsley et al. [55]. It is crucial to indicate that the modelling accounted for electricity use and includes the loss of cogeneration opportunity, increased heat integration, reductions in low pressure steam use, cooling tower expenses, carbon emission cost, and added maintenance due to MVR and TVR equipment.

The 2-stage MVR system attains a simple payback of 1.7 y and an internal rate of return (IRR) of 57%, which is better when compared with the 3- and 4-stage MVR systems. However, the challenge with implementing the 2-stage system is that the required saturation temperature lifts (8.8 and 9.5 °C) for the two MVR fans. These levels of saturation temperature lift push the upper design and operational limits of an MVR fan. The 3-stage MVR system requires lower temperature lifts (7.0, 3.3, and 8.0 °C) and achieves a greater levelised profit than the 2-stage MVR system. The 4-stage MVR uses less electricity than the 2- and 3-stage MVR systems but the higher capital of a fourth MVR fan offsets the energy benefit.

Figure 9 shows the MFSP of the kraft mill-integrated HTL process with the 3-stage MVR upgrade. The MFSP of the fuel is higher by 0.02 NZD/LGE, as compared to the base kraft mill due to the electricity use by the MVR process. The higher grid sourced electricity use in the HTL system increases the GHG emissions, and the production system is no longer a carbon credit production system.
Table 7. Thermo-economic assessment of retrofitting various multi-stage mechanical vapour recompression options with an existing effect evaporator. The assessment is compared to the conventional 7-effect evaporator.

|                        | 2-Stage MVR Benefits (NZD M/y) | 3-Stage MVR Benefits (NZD M/y) | 4-Stage MVR Benefits (NZD M/y) |
|------------------------|---------------------------------|---------------------------------|--------------------------------|
| **Electricity use**    |                                 |                                 |                                |
| MVR electricity use    | 8.3 MW –6.20                    | 7.5 MW –5.60                    | 7.1 MW –5.32                   |
| Cogeneration reduction | 10.0 MW –7.43                   | 9.8 MW –7.30                    | 9.5 MW –7.12                   |
| **Steam use**          |                                 |                                 |                                |
| LPS use reduction      | 37.9 MW 37.9 MW 37.9 MW          |                                 |                                |
| Increased heat recovery| 4.1 MW 3.3 MW 2.1 MW            |                                 |                                |
| **Steam flow reduction**|                                |                                 |                                |
| Cooling tower reduction| 35.1 MW 0.73 35.1 MW 0.73       |                                 |                                |
| **Carbon liability reduction** | 62.6 kt/y 1.56 61.4 kt/y 1.53 | 59.7 kt/y 1.49                  |
| Additional maintenance | 1.2% –0.14 1.2% –0.16 1.2% –0.18|                                 |                                |
| **Operation and maintenance** | 6.20 6.54 6.45 |                                 |                                |
| (O&M) cost reduction   |                                 |                                 |                                |
| Capital cost (uninstalled) | 3.49 3.91 4.32 |                                 |                                |
| Capital cost (installed) | 10.47 11.73 12.95 |                                 |                                |
| **Key Indicators**     |                                 |                                 |                                |
| Levelised profit       | 4.65 M NZD/y                    | 4.83 M NZD/y                    | 4.63 M NZD/y                   |
| Simple payback         | 1.7 y 1.8 y 2.0 y              |                                 |                                |
| Internal rate of return| 57% 53% 47%                     |                                 |                                |
| SEC<sub>net</sub>      | 145 130 130                     |                                 |                                |

* SEC<sub>net</sub> is the net specific energy consumption.
3.3. Scenario 3: New Modern Recovery Boiler

To increase the energy efficiency of the existing kraft mill, a new recovery boiler to replace the “old” style RB is considered. The aim of the new recovery boiler is to minimise the energy purchase and maximise power generation. This is achieved by producing higher steam parameters. The current recovery boilers in the existing kraft mills are fired with black liquor at about 67% dry solids to produce superheated steam at 400 °C at 45 bar. Over the years, recovery boiler technology has been improved and developed to fire black liquor at 72% to 85% dry solids. Environmental benefits include reductions in SO₂ and H₂S emissions with dry solids above 75% dry solids [56].

Figure 10 shows the utility system of replacing the old recovery boiler with a higher solids recovery boiler. As compared to the old recovery boiler, the new recovery boiler produces very high pressure (VHP) steam at 110 bar and 515 °C.

A mass and energy balance of the recovery boiler is carried out to evaluate the economics and operating costs using an Excel spreadsheet. The spreadsheet includes the existing supplementary boilers and turbine, process heat demands, and a new turbine. The design of the new turbine is based on satisfying the steam demand of the kraft pulp process. The new recovery boiler generates as much steam as possible and is primarily expanded in the new turbine. Any additional steam is sent to the existing turbine in the kraft mill. The splits of the expanded steam are determined by optimising maximum power generation in both turbines.

Comparing Figure 10 with Figure 2, PB2 was eliminated and the heat supplied by PB1 is reduced by half. The low-pressure steam demands increase slightly due to the higher evaporation demand needed to concentrate the black liquor solids. The difference in the performance of the boilers is presented in Table 8.

| Performance data. | Old Recovery Boiler | New Recovery Boiler | New Recovery Boiler + HTL |
|------------------|---------------------|---------------------|---------------------------|
| Steam produced (t/h) | 362 | 352 | 288.7 |
| Power generation (MW) | 30.5 | 54.1 | 41.7 |
| Wood residue used (t/h) | 72 | 8.4 | 5.4 |
Figure 10. Utility system for kraft mill with a new recovery boiler.

Table 8 also compares integrating HTL into the new recovery boiler case, taking 18% of the black liquor solids for biofuel production, as shown in Figure 1. The wood residue used as marginal fuel in PB1 reduces from 8.4 to 5.4 t/h. However, the power generation decreases with the reduction in the marginal fuel used.

Figure 11 shows the effect of increasing the black liquor solids in the HTL process on the power generation and marginal fuel used. The marginal fuel decrease is due to the lower steam demand from the kraft process, which is supplied by the HTL process. When about 52% of the black liquor is diverted to the hydrothermal liquefaction process, the kraft mill will be self-sufficient, in terms of energy demand. The 72 t/h of wood residue would be used as low-cost feedstock in the HTL process.

Figure 12 shows the MFSP of the kraft mill-integrated HTL process with a new recovery boiler. The new recovery boiler generates more electricity through the expansion of the VHP steam to lower quality steam as compared to the current recovery boiler. The decrease in black liquor flow has a higher impact on the decrease in electricity generation. Therefore, higher electricity is needed to replace the losses, which increase both the cost of electricity and the GHG emission cost.
diverted to the hydrothermal liquefaction process, the kraft mill will be self-sufficient, in terms of energy demand. The 72 t/h of wood residue would be used as low-cost feedstock in the HTL process.

Figure 11. Effect of black liquor solids in HTL.

Figure 12 shows the MFSP of the kraft mill-integrated HTL process with a new recovery boiler. The new recovery boiler generates more electricity through the expansion of the VHP steam to lower quality steam as compared to the current recovery boiler. The decrease in black liquor flow has a higher impact on the decrease in electricity generation. Therefore, higher electricity is needed to replace the losses, which increase both the cost of electricity and the GHG emission cost.

Figure 12. MFSP and the breakdown of the levelised production costs of the kraft mill-integrated HTL with a new recovery boiler, with different processing size.

4. Conclusions and Directions of Future Work

Hydrothermal liquefaction is a promising biorefinery technology that could be integrated with existing kraft mills. The comprehensive flowsheet of the hydrothermal liquefaction, upgrading of bio-crude, and auxiliary processes analysed in this study was developed in a PhD thesis. The economic evaluation of the integration of the HTL system design has been undertaken to establish key price points that would indicate full-scale implementation can compete with conventional fuels. The net reduction in GHG emissions of the system is 441.8 kt CO$_2$-e/y due to the substitution of conventional petrol and diesel fuels with the biofuel and sequestration of the biochar product. Vapour recompression technologies and a new high solids recovery boiler are considered for the integration with the HTL process. Vapour recompression can be economically integrated into a multi-effect evaporator at kraft mills with older recovery boiler technology, causing a step reduction in steam use. Since vapour recompression acts as an open cycle heat pump, the benefit gained from reducing carbon emissions in supplementary fossil fuel boilers is magnified. A new high solids recovery boiler produces very high-pressure steam that is expanded to generate electricity. The high solids recovery boiler eliminates...
the use of the natural gas boiler and increases the power generated by 76.8%. Integrating the HTL process in these scenarios increases the MFSP due to the higher electricity consumption of the process.

Future work should focus on improving the economics of the process by reducing the temperature and pressure of the process. The current study of the HTL process is fixed at 355 °C and 230 bar due to the availability of data at this condition. Experimental testing on the effect of temperature and pressure on the bio-crude yield and quality should be tested, as the processing conditions play significant roles in the outcome. Looping of a co-solvent in the hydrothermal liquefaction process has been proven to reduce the energy requirement of the HTL process.

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References
1. Brundland, G.H. World Commission on Environment and Development. In Our Common Future; Oxford University Press: Oxford, NY, USA, 1987.
2. Statista. Oil Demand Distribution by Sector Worldwide 2016; Statista: Hamburg, Germany, 2019.
3. Fernando, S.; Adhikari, S.; Chandrapal, C.; Murali, N. Biorefineries: Current Status, Challenges, and Future Direction. Energy Fuels 2006, 20, 1727–1737.
4. Morais, A.R.C.; Bogel-Lukasik, R. Green chemistry and the biorefinery concept. Sustain. Chem. Process. 2013, 1, 18. [CrossRef]
5. Stephen, J.D.; Sokhansanj, S.; Bi, X.; Sowlati, T.; Kloeck, T.; Townley-Smith, L.; Stumborg, M.A. The impact of agricultural residue yield range on the delivered cost to a biorefinery in the Peace River region of Alberta, Canada. Biosyst. Eng. 2010, 105, 298–305. [CrossRef]
6. Ghatak, H.R. Biorefineries from the perspective of sustainability: Feedstocks, products, and processes. Renew. Sustain. Energy Rev. 2011, 15, 4042–4052.
7. Pettersson, K.; Mahmoudkhani, M.; von Schenk, A. Opportunities for biorefineries in the pulping industry. In Systems Perspectives on Biorefineries; Chalmers University of Technology: Göteborg, Sweden, 2013.
8. Elliot, D.C.; Biller, P.; Ross, A.B.; Schmidt, A.J.; Jones, S.B. Hydrothermal Liquefaction of Biomass: Developments from Batch to Continuous Process. Bioresour. Technol. 2015, 178, 147–156. [CrossRef] [PubMed]
9. Uematsu, M.; Frank, E.U. Static Dielectric Constant of Water and Steam. J. Phys. Chem. Ref. Data 1980, 9, 1291–1306.
10. Toor, S.S.; Rosendahl, L.; Rudolf, A. Hydrothermal liquefaction of biomass: A review of subcritical water technologies. Energy 2011, 36, 2328–2342. [CrossRef]
11. Xu, C.; Lad, N. Production of Heavy Oils with High Caloric Values by Direct Liquefaction of Woody Biomass in Sub/Near-Critical Water. Energy Fuels 2008, 22, 635–642. [CrossRef]
12. Demirbas, A. Competitive Liquid Biofuels from Biomass. Appl. Energy 2011, 88, 17–28. [CrossRef]
13. Rowlands, W.N.; Humphreys, L.J.; Thew, R.W.C.; Spankie, J.A.; Uloth, V.C.; Watson, P.A.; Pudlas, M.W. Integrated Kraft Pulp Mill and Thermochemical Conversion System. 2017. Available online: https://patentscope.wipo.int/search/en/detail.jsf?docId=WO2016058098 (accessed on 24 February 2019).
14. Huet, M.; Roubaud, A.; Chirat, C.; Lachenal, D. Hydrothermal treatment of black liquor for energy and phenolic platform molecules recovery in a pulp mill. Biomass Bioenergy 2016, 89, 105–112. [CrossRef]
15. Kosinkova, J.; Ramirez, J.A.; Nguyen, J.; Ristovski, Z.; Brown, R.; Lin, C.S.K.; Rainey, T.J. In the field: Hydrothermal liquefaction of bagasse using ethanol and black liquor as solvents. Biofuels Bioprod. Biorefin. 2015, 9, 630–638. [CrossRef]
16. Ong, B.H.Y.; Walmsley, T.G.; Atkins, M.J.; Walmsley, M.R.W. Hydrothermal liquefaction of Radiata Pine with Kraft black liquor for integrated biofuel production. J. Clean. Prod. 2018, 199, 737–750. [CrossRef]
17. Funkenbusch, L.T.; Mullins, M.E.; Vamling, L.; Belkhier, T.; Srettiwat, N.; Winjobi, O.; Shonnard, D.R.; Rogers, T.N. Technoeconomic assessment of hydrothermal liquefaction oil from lignin with catalytic upgrading for renewable fuel and chemical production. *Wires Energy Environ*. 2018, 8, 1–12. [CrossRef]

18. Melin, K.; Välimäki, A.; Oasmää, A.; Lehtonen, J. The Effect of Hydrothermal Liquefaction of Black Liquor in Bio-Oil Quality. In Proceedings of the 27th European Biomass Conference and Exhibition, Lisbon, Portugal, 27–30 May 2019; pp. 1144–1145. [CrossRef]

19. Lappalainen, J.; Baudouin, D.; Hornung, U.; Schuler, J.; Melin, K.; Bjelić, S.; Vogel, F.; Konttinen, J.; Joronen, T. Sub- and Supercritical Water Liquefaction of Kraft Lignin and Black Liquor Derived Lignin. *Energies* 2020, 13, 3309. [CrossRef]

20. Anastasakis, K.; Biller, P.; Madsen, R.; Glasius, M.; Johansson, I. Continuous Hydrothermal Liquefaction of Biomass in a Novel Pilot Plant with Heat Recovery and Hydraulic Oscillation. *Energies* 2018, 11, 2695. [CrossRef]

21. Okoro, O.V.; Sun, Z.; Birch, J. Techno-Economic Assessment of a Scaled-Up Meat Waste Biorefinery System: A Simulation Study. *Materiel* 2019, 12, 1030. [CrossRef]

22. Shemfe, M.B.; Fidalgo, B.; Gu, S. Heat integration for bio-oil hydropyrolysis coupled with aqueous phase steam reforming. *Chem. Eng. Res. Des.* 2016, 107, 73–80. [CrossRef]

23. Magdeldin, M.; Kohl, T.; Järvinen, M. Techno-economic assessment of the by-products contribution from non-catalytic hydrothermal liquefaction of lignocellulose residues. *Energy* 2017, 137, 679–695. [CrossRef]

24. Knorr, D.; Lukas, J.; Schoen, P.; Harris Group Inc. *Production of Advanced Biofuels via Liquefaction: Hydrothermal Liquefaction Reactor Design*; National Renewable Energy Lab.(NREL): Atlanta, GA, USA, 2013.

25. Ong, B.H.Y.; Walmsley, T.G.; Atkins, M.J.; Varbanov, P.S.; Walmsley, M.R.W. A heat- and mass-integrated design of hydrothermal liquefaction process co-located with a Kraft pulp mill. *Energy* 2019, 189, 116235. [CrossRef]

26. Medina-Flores, J.M.; Picon-Nuñez, M. Modelling the power production of single and multiple extraction steam turbines. *Chem. Eng. Sci.* 2010, 65, 2811–2820. [CrossRef]

27. Martinez Hernandez, E.; Ng, K.S. Design of biorefinery systems for conversion of corn stover into biofuels using a biorefinery engineering framework. *Clean Technol. Environ. Policy* 2017, 20, 1–14. [CrossRef]

28. Ministry of Business, Innovation and Employment. *Electricity Demand and Generation Scenario*; Ministry of Business, Innovation and Employment: Wellington, New Zealand, 2018.

29. Ministry for the Environment. *Guidance for Voluntary, Corporate Greenhouse Gas Reporting: Data and Methods*; Ministry for the Environment: Wellington, New Zealand, 2008.

30. Ministry for the Environment. *New Zealand’s Greenhouse Gas Inventory for the 2007 Calendar Year*; Ministry for the Environment: Wellington, New Zealand, 2017.

31. Environmental Protection Authority. *Liquid Fossil Fuels 2019*. Available online: https://www.epa.govt.nz/industry-areas/emissions-trading-scheme/industries-in-the-emissions-trading-scheme/liquid-fossil-fuels?accordion-anchor=75 (accessed on 2 June 2020).

32. Ong, B.H.Y. A Kraft Mill-Integrated Biorefinery Design for New Zealand; University of Waikato: Hamilton, New Zealand, 2019.

33. Ong, B.H.Y.; Walmsley, T.G.; Atkins, M.J.; Walmsley, M.R.W. Total site mass, heat and power integration using process integration and process graph. *J. Clean. Prod.* 2017, 167, 32–43. [CrossRef]

34. Klemes, J.J. *Handbook of Process Integration (PI): Minimisation of Energy and Water Use, Waste and Emissions*; Woodhead Publishing in Energy, Woodhead Pub: Cambridge, UK, 2013; ISBN 9780857095930.

35. Friedler, F.; Tarjan, K.; Huang, Y.W.; Fan, L.T. Graph-Theoretic Approach to Process Synthesis: Axioms and Theorems. *Chem. Eng. Sci.* 1992, 47, 1973–1988. [CrossRef]

36. Elliot, D.C. Historical Developments in Hydroprocessing Bio-Oils. *Energy Fuels* 2007, 21, 1792–1815. [CrossRef]

37. Tran, H.; Vakkilainen, E.K. The Kraft Chemical Recovery Process; TAPPIE Press: St. Petersburg, FL, USA, 2012.

38. Zhu, Y.; Biddy, M.J.; Jones, S.B.; Elliot, D.C.; Schmidt, A.J. Techno-economic analysis of liquid fuel production from woody biomass via hydrothermal liquefaction ([HTL]) and upgrading. *Appl. Energy* 2014, 129, 384–394. [CrossRef]

39. Alcaraz, S.; Hall, P. Mapping of Primary Processing Heat Demand and Forestry Resources to Allow Identification of Industrial Symbiosis Opportunities at A Regional Level Scion Report for MBIE; Scion: Rotorua, New Zealand, 2018.
40. Robertson, K. *Estimating Regional Supply and Delivered Cost of Forest and Wood Processing Biomass Available for Bioenergy*; University of Canterbury: Christchurch, New Zealand, 2006.

41. Ship & Bunker. Singapore Bunker Prices. Ship Bunker 2019. Available online: https://shipandbunker.com/prices/apac/sea/sg-sin-singapore (accessed on 2 June 2020).

42. Gerrard, A.M. *Guide to Capital Cost Estimating*, 4th ed.; Institution of Chemical Engineers (IChemE): Warwickshire, UK, 2000.

43. Magdeldin, M.; Kohl, T.; Järvinen, M. Techno-economic Assessment of Integrated Hydrothermal Liquefaction and Combined Heat and Power Production from Lignocellulose Residues. *J. Sustain. Dev. Energy Water Environ. Syst.* 2018, 6, 89–113. [CrossRef]

44. Nie, Y.; Bi, X. Life-cycle assessment of transportation biofuels from hydrothermal liquefaction of forest residues in British Columbia. *Biotechnol. Biofuels* 2018, 11, 23. [CrossRef]

45. He, Y.; Zhou, X.; Jiang, L.; Li, M.; Du, Z.; Zhou, G.; Shao, J.; Wang, X.; Xu, Z.; Bai, S.H.; et al. Effects of biochar application on soil greenhouse gas fluxes: A meta-analysis. *Geb Bioenergy* 2017, 9, 743–755. [CrossRef]

46. Department of the Environment and Energy. *National Greenhouse Accounts Factors*; Department of the Environment and Energy: Canberra, Australia, 2017.

47. Castello, D. *Supercritical Water Gasification of Biomass*; University of Trento: Trento, Italy, 2013.

48. Gutiérrez Ortiz, F.J.; Ollero, P.; Serrera, A.; Galera, S. An energy and exergy analysis of the supercritical water reforming of glycerol for power production. *Int. J. Hydrog. Energy* 2012, 37, 209–226. [CrossRef]

49. Motoring, A.A. How Petrol Prices are Calculated. Available online: https://www.aa.co.nz/cars/owning-a-car/fuel-prices-and-types/how-petrol-prices-are-calculated/ (accessed on 1 June 2020).

50. New Zealand Productivity Commission. *Low—Emissions Economy*; New Zealand Productivity Commission: Wellington, New Zealand, 2018.

51. Wetterlund, E.; Pettersson, K.; Harvey, S. Systems analysis of integrating biomass gasification with pulp and paper production—Effects on economic performance, CO₂ emissions and energy use. *Energy* 2011, 36, 932–941. [CrossRef]

52. Suckling, I.D.; De Miguel Mercader, F.; Monge, J.J.; Wakelin, S.J.; Hall, P.W.; Bennett, P.J. *New Zealand Biofuels Roadmap Summary Report: Growing A Biofuelled New Zealand*; Scion: Rotorua, New Zealand, 2018.

53. Martins, F.; Gay, J.C. Biofuels: From Boom to Bust? 2017. Available online: https://www.bain.com/insights/biofuels-from-boom-to-bust/ (accessed on 1 June 2020).

54. Sharan, P.; Bandyopadhyay, S. Integration of thermo-vapor compressor with multiple-effect evaporator. *Appl. Energy* 2016, 184, 560–573. [CrossRef]

55. Walmsley, T.G.; Atkins, M.J.; Ong, B.H.Y.; Klemes, J.J.; Walmsley, M.R.W. Total site heat integration of multi-effect evaporators with vapour recompression for older kraft mills. *Chem. Eng. Trans.* 2017, 61, 265–270.

56. Hyöty, P.A.; Ojala, S.T. Super Combustion of Black Liquor. In Proceedings of the International Recovery Boiler Conference Tampere Hall, Tampere, Finland, 11 June 2014; pp. 49–53.

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