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Hydrothermal liquefaction of Radiata Pine with Kraft black liquor for integrated biofuel production

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ABSTRACT

This paper aims to evaluate the feasibility of hydrothermal liquefaction (HTL) of Radiata pine with black liquor from an existing Kraft pulp mill. The biomass into the HTL process was assumed at 2000 t/day and converted into bio-crude through the HTL process and upgraded to produce a gasoline and diesel blend. The HTL process was scaled-up based on an existing published patent. Mass and heat balance of the process was obtained through the process simulator, Aspen Plus. Process Integration was carried out to minimise the hot and cold utility of the process. The production rate of the process is 78.7 kt/y of fuel. The minimum fuel selling price (MFSP) was estimated at 0.95 USD/LGE (litre gasoline equivalent). A sensitivity analysis was carried out to determine the MFSP in 2017 and to study the changes of MFSP due to the uncertainty in the capital cost estimation.

1. Introduction

The forestry sector in New Zealand is the third largest export earner, exporting whole logs, pulp and paper, and other biomass residues. The pulp and paper industry market plummeted when the economic crisis hit in 2009, from which the industry is still recovering to pre-crisis levels (SETIS, 2011). The Kraft process is the main production method in New Zealand to produce chemical wood pulp. However, the Kraft pulp processing extracts only 50% of high-value product potential from harvested logs while the balance remains as low-value wood residues (Jack et al., 2013). Biomass components – mainly lignin and hemicelluloses in black liquor – are combusted in a recovery boiler to provide the heat and power needed by the pulp mill. The black liquor also serves an important role in the chemical recovery process, which creates the economy of the Kraft Process. The remaining organic content, i.e. the cellulosic fibres, have the potential to be converted into bio-products, which may be of higher value than supplying as thermal and power source. In additional, evolution towards an integrated biorefinery would allow the industry to diversify by manufacturing new high-value chemicals, fuels and export power, in addition to the traditional core products (van Heiningen, 2006). The use of black liquor as a raw material is favoured in comparison with other potential biomass sources for chemical production because the pulp mill economics is less sensitive to the fluctuation of pulp prices when diversified with additional products (Maniatis et al., 2007).

Black liquor can be converted to liquid fuels through thermochemical conversion, which includes gasification, hydrothermal liquefaction and pyrolysis. Ong et al. (2017) did a preliminary study to consider three biorefinery processes – gasification of black liquor, hydrothermal liquefaction (HTL) of forest residues and simultaneous scarification and co-fermentation of pine – with an existing Kraft pulp mill in the Central North Island of New Zealand. They concluded the HTL process had the greatest potential to be economic. One of the main advantages of HTL is the feedstock of the process does not have to be dried. This is attractive because most lignocellulosic biomass naturally contains moisture. Black liquor at the existing Kraft pulp mill is fired at 67% black liquor solids at the current recovery boiler and 20–30% of the thermal energy on site is consumed to evaporate water to concentrate weak black liquor into strong liquor.

Hydrothermal liquefaction converts biomass into liquid fuels in a reactor that operates at high temperature and high pressure with an aqueous slurry feed and sufficient time to break down the solid

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biopolymeric structure to mainly liquid components (Elliot et al., 2015). In HTL, the subcritical water acts as both reactant and catalyst. The solubility of hydrophobic organic compounds increases in subcritical water because the dielectric constant is significantly lower, as compared to ambient water (Uematsu and Frank, 1980). In addition, the ionic product of water is higher in the subcritical environment that accelerates acid or base-catalysed reactions (Toor et al., 2011). The main product of HTL is bio-crude and can be upgraded to the whole distillate range of petroleum-derived fuel products. In comparison with gasification, pyrolysis and HTL have a simpler technical conversion of biomass to a liquid fuel (Xu and Lad, 2008). As compared to HTL bio-crude, pyrolysis oils are more corrosive due to higher oxygen content and have lower calorific values (15–22 MJ/kg). HTL bio-crude, on the other hand, has a heating value of 30–36 MJ/kg, which is much closer to the heating value of petroleum (43–46 MJ/kg) (Demirbas, 2011).

The products of HTL of lignocellulosic biomass include non-condensable gases, solid residue, bio-crude and a water phase with small traces of bio-crude oil. These products are highly affected by the operating parameter of the HTL process. These parameters include the type of biomass, biomass to water/solvent ratio, temperature, pressure, retention time, the presence of a catalyst, and the recycling of the water phase. Akhtar and Amin (2011) studied the roles of these operating parameters and reported that the temperature of the HTL process is the most important parameter for bio-crude yield. The operating temperature varies with the type of biomass. Akhtar and Amin (2011) reported that temperatures higher than 350 °C decreases the bio-yield due to the preferential formation of the gas phase. This was supported by Wu et al. (2009), who showed the concentration of oil yield decreased after 350 °C. Zhu et al. (2015) found the bio-crude yield reached a maximum of 34.9 wt% at 200 °C but decreased to 19.9 wt% at 400 °C.

Studies have shown that the use of catalysts in HTL of biomass promotes the yield of bio-crude oil, improves its heating values, and inhibits the formation of solid residues. Research shows that using an alkali catalyst leads to the formation of aromatic oils as opposed to an acid catalyst that contributes to the formation of solid products (Elliot et al., 2015). Karagöz et al. (2005) investigated the effect of the presence of NaOH, Na_2CO_3, KOH and K_2CO_3 in HTL of wood biomass on product yields. The oil yield was 6–12 times greater than HTL without a catalyst for the various base solutions. They also reported that the presence of a catalyst favours the formation of certain compounds. For example, base catalysts favour the formation of phenol and benzenediol derivatives. Nazari et al. (2015) reported that the solid residues reduced significantly from 33.4 wt%, without a catalyst, to 10–14 wt% in catalytic runs.

Lignin, cellulose, and hemicellulose are the major constituents of the lignocellulosic materials and reaction of these components vary with temperature (Akhtar and Amin, 2011). Feedstock with higher content of cellulose and hemicellulose yields more bio-oil. Bhaskar et al. (2008) studied the HTL of two different wood biomass samples, which differs in the three major constituents. It was reported that the hardwood sample produced more oils than the softwood, due to the higher lignin content in the softwood. In HTL process, the amount of solid residue increases with the lignin content. Free phenoxyl radicals form when lignin is decomposed thermally above 250 °C. These radicals then result in solid residues through condensation and repolymerization processes, especially with the longer retention time (Demirbaş, 2000). However, this can also be overcome by adding a catalyst.

Many HTL studies and techno-economic analysis have been done on different lignocellulosic feedstock and algae, with different operating parameters. However, only a few studies on HTL of black liquor has been undertaken and this represents a gap in the current literature. Black liquor is a complex mixture of organics (mostly lignin and hemicellulose) and inorganics. Black liquor serves two purposes in HTL according to Rowlands et al. (2017): (1) BL contains a significant amount of cellulosic fibres which can be used as the organic matter feedstock for the HTL process and (2) the inorganics in black liquor is a basic solution which is a suitable substitute of NaOH as the catalyst for the HTL process. Huet et al. (2016) studied the HTL conversion of sulphur-free black liquor between 270 and 310 °C and its integration with a Kraft pulp mill. The hydrothermal liquefaction of BL produces both phenolic molecules and bio-crude simultaneously. The presence of carbohydrates, in addition to the cellulosic fibres, encourage the formation of bio-crude. The sodium recovery was 97%, which is compatible with Kraft mill, and in the form of sodium carbonate, which can be converted to caustic soda with the current technology. Kosinkova et al. (2015) studied the HTL of bagasse using ethanol and black liquor as solvents. The oil yield of the HTL increased as BL content increased because BL contains organic residues, which provided additional reactants for conversion and the basicity supports the base-catalysed condensation reaction that leads to oil formation.

The aim of this paper is to conduct a comprehensive techno-economic analysis of hydrothermal liquefaction of Radiata pine feed with black liquor as the catalyst. The approach taken for this analysis includes a process simulation of the process with Aspen Plus, to obtain the material and energy balances for capital and operating cost estimates and a pinch analysis study of the HTL process pathway. The hydrothermal liquefaction process is assumed to be co-located with an existing Kraft pulp mill. The black liquor for the process is taken from the Kraft pulp mill. Therefore, the effect on the integration with the Kraft pulp mill in terms of, sodium recovery and energy are examined as well.

The novel contributions of this work include:

- Techno-economic analysis of the HTL process using Radiata pine with Kraft pulp black liquor as biomass.
- The analysis of the integrating of HTL process with an existing Kraft pulp mill, in terms of chemical balances, heat and power.
- Process Integration study of the HTL process to determine the heat saving and utilities needed for the HTL process.

2. Process description

The process flow diagrams and models for the hydrothermal liquefaction process chosen for this study were from the patent published by Canton Pulp Ltd and Licella Pty Ltd (Rowlands et al., 2017) and research results from PNNL and NREL. The HTL process is co-located with an existing Kraft Pulp Mill in Central North Island of New Zealand.

Hydrothermal liquefaction and the upgrading are defined by five major processing areas: (1) biomass handling and preparation, (2) HTL of biomass, (3) product upgrading through hydrotreating of bio-crude to renewable fuel, (4) hydrogen production, and (4) wastewater treatment, as shown in Fig. 1.

The feedstock used in this case study is Radiata pine, with a moisture content of 50 wt%, and weak black liquor at 18.3 wt%. The elemental analysis for the feedstocks is adapted from Rowlands et al. (2017), as shown in Table 1, on a dry basis. The black liquor is rich in organic compounds, lignin, hemicellulose, carbohydrates, and alkali salts, which present an economic opportunity to reduce the operating cost by contributing organic compounds to be converted into bio-crude and their use as a catalyst, to promote the conversion of biomass into biofuel due to the alkali nature of black liquor.