CHEMICAL ENGINEERING TRANSACTIONS

VOL. 70, 2018

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Timothy G. Walmsley, Petar S. Varbanov, Rongxin Su, Jiří J. Klemeš

**ISBN** 978-88-95608-67-9; **ISSN** 2283-9216

DOI: 10.3303/CET1870169

# Optimising Energy Recovery in Hydrothermal Liquefaction of Radiata Pine and Kraft Mill Black Liquor

Benjamin H. Y. Ong[a,*], Timothy G. Walmsley[b], Martin J. Atkins[a], Michael R. W. Walmsley[a], James R. Neale[a], Petar S. Varbanov[b]

[a]Energy Research Centre, School of Engineering, University of Waikato, Private Bag 3105, Hamilton, New Zealand
[b]Sustainable Process Integration Laboratory – SPIL, NETME Centre, Faculty of Mechanical Engineering, Brno University of Technology - VUT Brno, Technická 2896/2, 616 69 Brno, Czech Republic
bhyo1@students.waikato.ac.nz

The aim of this paper is to develop a heat exchanger network for hydrothermal liquefaction that is co-located with an existing Kraft pulp mill. Hydrothermal Liquefaction (HTL) is an energy-intensive process that operates at high temperature and pressure. Process Modelling and Pinch Analysis are used to develop a mass and heat integration system considering Total Site Integration with the Kraft pulp. The HTL process is simulated using Aspen Plus to extract and calculate the thermodynamic properties of the process. Stream data is then extracted and Pinch Analysis is applied to calculate the utility and heat recovery targets. Process data are varied to further maximise the heat recovery targets. Mass integration of compatible water-based flows is considered in this process to reduce the complexity of the Heat Exchanger Network, which is initially designed with the aid of SuperTarget™. The result showed that the procedure simplified the Heat Exchanger Network from 15 to 6 heat exchangers.

## 1. Introduction

The pulp and paper industry converts biomass into pulp that is further processed into paper and packaging material. The digested wood, lignin, hemicellulose, and other organic extractives and inorganics from the spent pulping chemicals forms black liquor. Black liquor is an intermediate product within the Kraft chemical recovery cycle that is combusted in the recovery boiler. The recovery boiler is integrated with a cogeneration unit to satisfy the demands of the heat and power of the mill. However, black liquor has the opportunity to be further converted into a higher value product through bio-refining. Ong et al. (2017) studied the material and heat integration of three biorefinery cases, which the work was later extended to Ong et al. (2017): gasification of black liquor, hydrothermal liquefaction (HTL) of biomass and simultaneous scarification and co-fermentation of biomass. As a basis, these processes were assumed to be co-located with an existing Kraft pulp mill in the Central North Island of New Zealand. One of the near-optimal solutions for that case study is hydrothermal liquefaction added to the Kraft mill with geothermal heat.

Hydrothermal liquefaction converts biomass into liquid fuels by processing in a hot, pressurised water environment for sufficient time to break down the solid biopolymeric structure to mainly liquid components (Elliot et al., 2015). The main product of HTL is bio-crude with a heating value of 30 – 36 MJ/kg that can be hydrodeoxygenated and upgraded to the whole distillate range of petroleum fuels (Demirbas, 2009). With the HTL reactor operating at very high pressure (220 - 250 bar) and temperature (315 - 355 °C), heat and exergy recovery during cooling and depressurisation of the product flow becomes non-trivial but essential to be economically competitive. In HTL, black liquor is used as an alkali catalyst to facilitate the conversion of biomass and also a source of feedstock material.

The National Renewable Energy Laboratory (NREL) investigated a few process options to maximise heat integration, by changing the point where hot recycle or feed streams are added into the process (Knorr et al., 2013). However, the set points of the heat integration by NREL may impact the process in terms of the quality of biofuel, as these set points violate key requirements of the studied process. Arturi (2017) reviewed 34 peer-

Please cite this article as: Ong B.H.Y., Walmsley T.G., Atkins M.J., Walmsley M.R.W., Neale J.R., Varbanov P.S., 2018, Optimising energy recovery in hydrothermal liquefaction of radiata pine and kraft mill black liquor , Chemical Engineering Transactions, 70, 1009-1014 DOI:10.3303/CET1870169

reviewed studies to include different biomass type and process conditions on yields of the bio-crude and soluble organics and energy content of the bio-crudes. It was concluded that due to a lack of common correlation for different biomass feedstocks, each biomass requires a different approach for optimal bio-crude production.
The aim of this paper is to develop a mass and energy integration system for a HTL process by assessing the thermal benefits of Process Integration and Optimisation using Pinch Analysis techniques. The heat recovery system is designed to be integrated with an existing Kraft pulp mill in the Central North Island of New Zealand. To achieve the aim, the HTL process is modelled using a standard process modelling software package, Aspen Plus (Aspen Technology Inc., 2017), that is customised to simulate the complex behaviour of the HTL reactants and products. Stream data are then extracted to apply Pinch Analysis, to study the HTL process to determine the heat saving and utilities needed for the process. Soft process constraints are changed to achieve to maximum heat recovery. The heat exchanger network is then designed using SuperTarget™. The complexity of the heat exchanger is then decreased with mass integration.

## 2. Process specifications

In this paper, HTL process to convert biomass into bio-crude is studied. The studied HTL process is based on patent published by Canton Pulp Ltd and Licella Pty Ltd (Rowlands et al., 2017) and additional HTL process descriptions from NREL (Knorr et al., 2013). The HTL process is assumed to be co-located with an existing Kraft pulp mill in Central North Island of New Zealand.

### 2.1 Hydrothermal Liquefaction

The HTL process is based on an experiment carried out by Rowlands et al. (2017). Radiata Pine and weak black liquor are pumped to 10 bar and mixed in a mixing tank at a 1:1 ratio, water is added to the mixing tank to a biomass solid concentration of 10 %. The biomass-water slurry must then be then pumped to 230 bar across one or more compression stages. The pressurised feed is then heated to 355 °C. Pre-heating is allowed, however, rapid heating is needed from 250 °C to 355 °C. The biomass is then converted to bio-crude, water-soluble organics (WSO), water, gas and solid residues in the reactor. The conversion of the product is given in Table 1.

*Table 1: HTL conversion.*

| Components | wt % | HHV (MJ/kg) | HHV % |
|---|---|---|---|
| Bio-crude | 28.4 | 34.8 | 63.8 |
| Gas | 22.4 | 3.5 | 5.1 |
| WSO | 11.9 | 14.8 | 11.4 |
| Char | 13.1 | 23.4 | 19.8 |

In Aspen Plus, the HTL reactor is simulated as a yield reactor by specifying the concentration of the product yield distribution. After the product is produced in the reactor, it has to be cooled to a temperature of 200 °C or lower. After separation, the aqueous phase can be recycled up to 80 % of the water. The process block diagram of the HTL process is as shown in Figure 1.

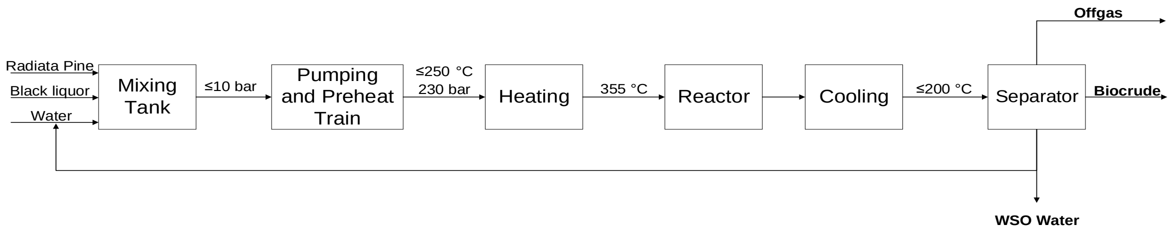



*Figure 1: Process Block Diagram of HTL with typical conditions*

## 3. Method

This paper aims to design a heat exchanger network for the HTL process. This is achieved by modelling the HTL process using Aspen Plus. The thermodynamic data were extracted from the process model and Pinch Analysis was used to determine the maximum heat recovery and utility targets of the process. The soft data are varied within the Aspen Plus model and the Pinch Analysis process is repeated. The HEN is designed with SuperTarget™. Mass Integration of certain water streams is then considered to further simplify the HEN design. The applied method for this paper is presented in Figure 2.

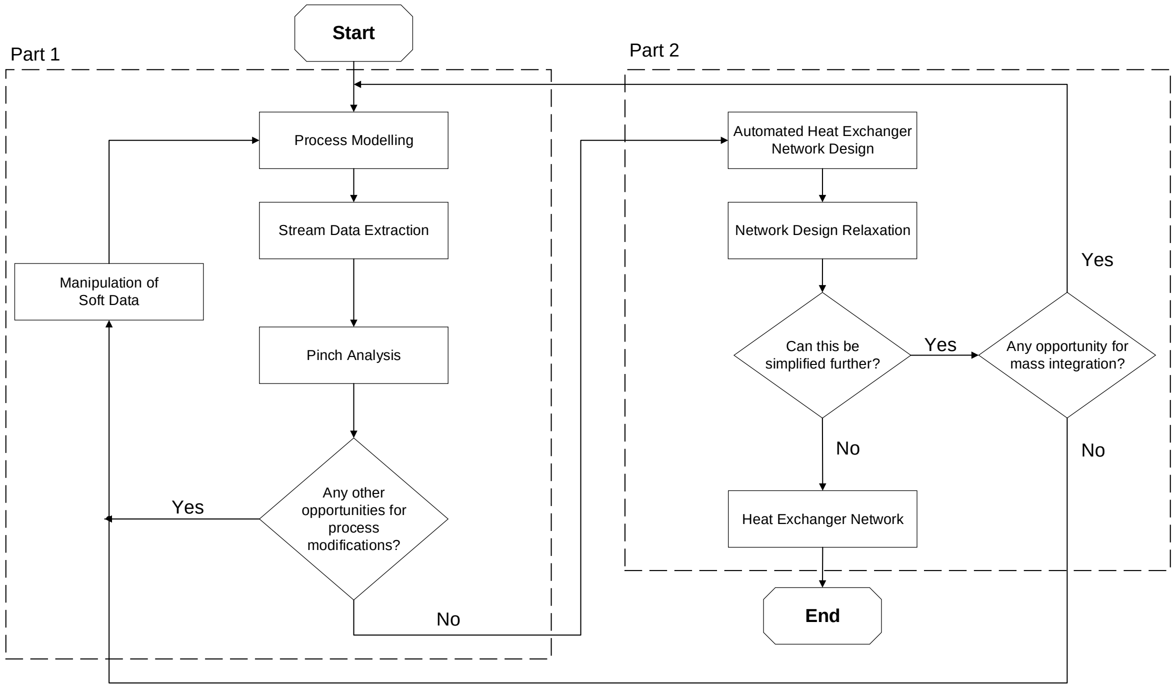



*Figure 2: Methodology of maximising mass and energy integration*

### 3.1 Process modelling

The process model is developed using Aspen Plus v9. The base case of this study is based on process simulation carried out by Ong et al. (2018). The process model is modelled based on 2,000 t/d of organic content with 450 t/d of bio-crude production. The feedstock, Radiata Pine and black liquor from the pulp mill, bio-crude, ash, and char are modelled as non-conventional components using the Aspen Physical Property System, as listed in Table 2. The thermodynamic properties of these elements are simulated using Aspen's Enthalpy and Density Coal Correlations, HCOALGEN and DCOALIGT. The mass balance and the stream data are then extracted from the Aspen model.

*Table 2: Ultimate analysis of Radiata Pine, black liquor, and bio-crude (Rowlands et al., 2017)*

| Components | Radiata Pine (wt%) | Black Liquor (wt%) | Bio-crude (wt%) |
|---|---|---|---|
| Carbon | 52.30 | 37.50 | 73.40 |
| Hydrogen | 6.20 | 0.17 | 6.50 |
| Nitrogen | 0.06 | 0.01 | 0.10 |
| Sulphur | 0.01 | 4.77 | 0.60 |
| Oxygen | 40.80 | 3.20 | 18.90 |
| Chorine | 0 | 0.21 | 0 |
| Ash | 0.60 | 47.10 | 0.50 |
| Moisture Content | 50.00 | 81.40 | 8.00 |

### 3.2 Process Integration

With the thermal data calculated by Aspen Plus, Pinch analysis is applied to the both the HTL and upgrading process to calculate the required utility and recovery targets. The required utility and recovery targets are calculated by shifting individual streams with a global $\Delta T_{min}$ of 20 °C because of the high pressure of the streams. This is carried out in an Excel$^{TM}$ spreadsheet.

### 3.3 Soft data manipulation

There are three key process constraints in the HTL process. The constraints in the HTL process are (1) the rapid heating of the pressurised feed from 250 °C to the reaction temperature, which is 355 °C in this case, (2) the cooling of the product to 200 °C, and (3) the high-pressure pump has a maximum 15 % organic loading.

The soft data are defined after identifying the Pinch temperature. The soft data, such as the temperature of the outlet of cooling and/or heating streams, changing column and valves pressures, are manipulated to ensure that the changes made increases the heat recovery. The considered streams and process design are

(i) Inlet pressure and temperature of the Radiata Pine and black liquor
(ii) Presence of intermediate feed pump and the pressure
(iii) Presence of a preheating of feed and the temperature
(iv) Temperature of the cooling of the product after the reactor
(v) Temperature of the recycle stream between depressurisation
(vi) Depressurised pressure of the recycle stream
(vii) Temperature of the cooling of the depressurised recycle stream

When these process conditions varied, the process simulation solved using Aspen Plus, the heat data are then extracted again and Pinch analysis is carried out using an Excel™ spreadsheet.

### 3.4 Network design relaxation

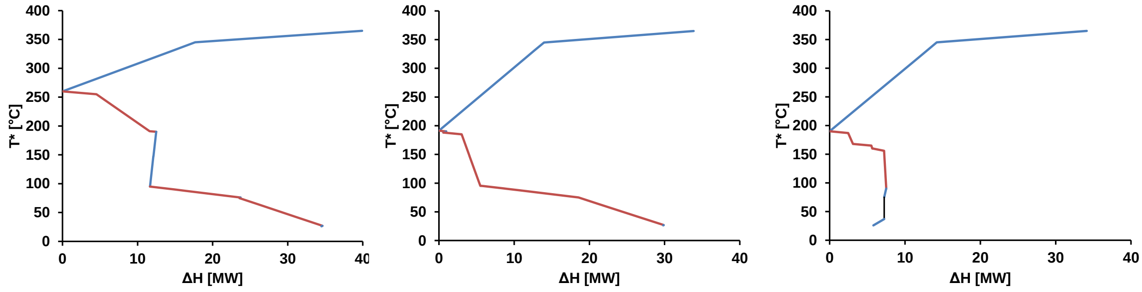
SuperTarget™ is then used to design the heat exchanger network. SuperTarget™ generates an automated design, which is used as the base case of the heat exchanger network. The interactive grid diagram allows flexible manual changes to the automated network.

The manual design is used to eliminate small heat exchangers to simplify the network. In this case, the modified network is developed by (1) matching process streams that have similar heat loads and (2) utilisation of the water process streams in the HTL process and Kraft pulp mill through mass integration.

## 4. Results and discussion

### 4.1 Pinch Analysis

Figure 3 shows the Grand Composite Curves of hydrothermal liquefaction (a) base case, (b) soft data optimization and (c) optimized integrated heat and mass of HTL process. The Pinch Temperatures are: (a) 260 °C, (b) 191 °C, and (c) 190 °C. The base case is the simulation according to the literatures. Figure 3b is the result of Part 1 methods of the Figure 2 and Figure 3c follows the Part 2 of the procedure in Figure 2. The key modification that changed the Pinch Temperature from Case a to b and c was the temperature of the preheating of the reactor feed. The feed was preheated to 245 °C in Case a and decreased to 175 °C for Cases b and c.




a b c

*Figure 3: Grand composite curves for (a) base case, (b) modified soft data, and (c) optimised integrated heat and mass of HTL process*

The utilities required and generated by the processes are shown in Table 3.

*Table 3: Targeted utilities required by the HTL process.*

| Utility | | a (MW) | b (MW) | c (MW) |
|---|---|---|---|---|
| Hot flue gas use | | 39.5 | 34.2 | 34.1 |
| LPS gen. | - indirect | 11.0 | 4.0 | 4.9 |
| HW gen | - direct | 0 | 0 | 28.3 |
| | - indirect | 19.4 | 22.2 | 1.3 |
| Cooling water use | | 3.4 | 3.8 | 0 |

Initially, in Case a, the recycled water, black liquor, and Radiata pine are isothermally mixed at atmospheric pressure and 85 °C, which is the black liquor temperature supplied from the Kraft pulp mill. In Case b, the pressure of the depressurised recycle stream was found to have a higher impact on the total heating and cooling utility of the process, as the process streams were not cooled, depressurised, then heated up again. The feed was mixed at 10 bar instead of 1 bar and the heating utility decreased from 39.5 MW to 33.9 MW and total cooling utility from 33.8 MW to 30.0 MW.

### 4.2 Heat Exchanger Network

The data from Figure 3b and c is then inputted into SuperTarget™. Figure 4 shows the automated design for the HEN design correlating to Figure 3b. The total HEN area for the automated design is 40,100 m$^2$ with 15 heat exchanger units. Figure 5 shows the optimised heat and mass integrated HEN with only 6 heat exchanger units and 31,800 m$^2$.

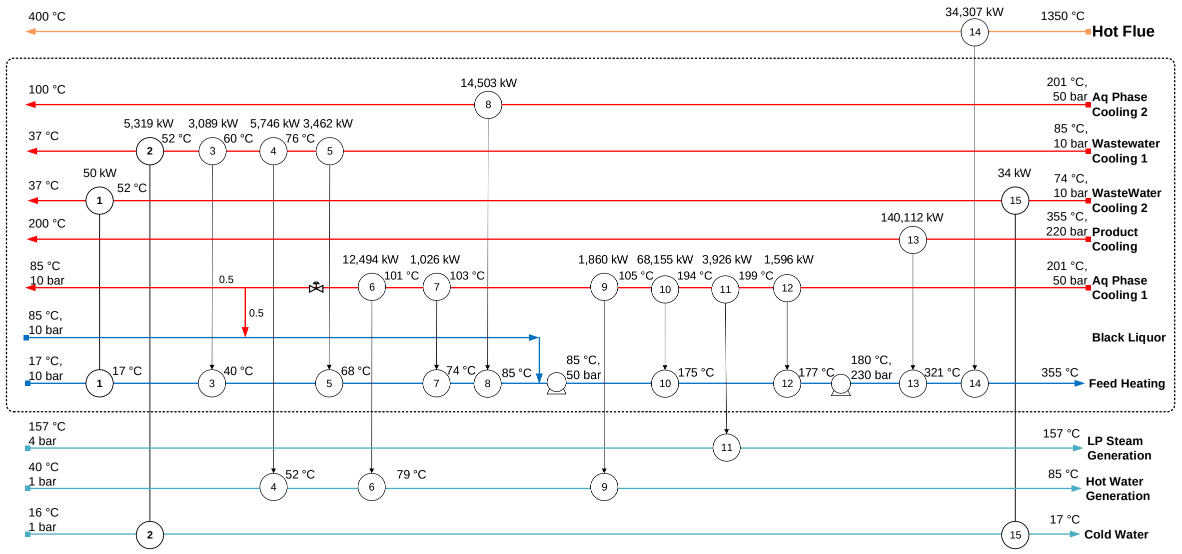



*Figure 4: Automated Heat Exchanger Network Design for HTL process.*

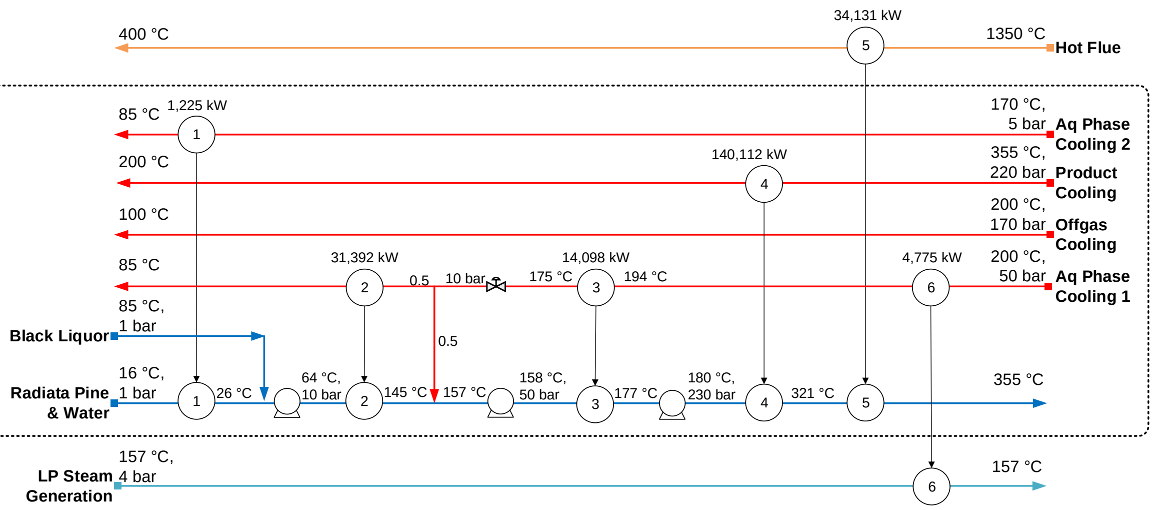



*Figure 5: Optimised Heat and Mass Heat Exchanger Network for HTL process.*

For Case c, the complexity of the network has been simplified from 15 heat exchangers to 6 heat exchangers. The overall heating requirement for the process in Cases b and c is the same. In Case b, the aqueous phase 1 is cooled to 85 °C and depressurised to 10 bar before being separated into wastewater and recycled water. The recycled water is isothermally mixed with the weak black liquor and later with the Radiate Pine with water slurry to form the reactor feed. In Case c, instead of cooling the recycled water down and then heating it up again after mixing with the feed, the recycled stream was mixed with the feed at different temperatures. The remainder of the aqueous phase 1 after preheating the combined black liquor and Radiata Pine slurry, has a water purity of about 99 %, which means if may be exported to neighbouring processes such as the Kraft process as hot water. This change in mass integration formed a key basis for significantly simplifying the HEN and reducing the required area by 21 %.

In Figure 5, the hot utility required by the process is according to the targeted value by Pinch Analysis. However, 5.8 MW of LP steam was generated and no hot water was generated, as compared to targeted values in Table 3.

## 5. Conclusions

This paper carried out a pinch analysis study on hydrothermal liquefaction, co-located with Kraft pulp mill on the Central North Island of New Zealand. An iterative method of using Aspen Plus simulation software, Process Integration and SuperTarget$^{TM}$ were used to generate a heat exchanger network for HTL process. By carrying out the novel method of heat and mass integration in heat exchanger network design, the number of heat exchanger decreased from 15 heat exchangers to 6 heat exchangers and a total area from 40,100 $m^2$ to 31,800 $m^2$. The future work is to apply the same procedure to the upgrading of bio-crude and determining a more accurate expectation of the heat transfer coefficients of the fluids. Integration of HTL and upgrading with CHP should be considered as well, as it provides additional heating and power generation to the processes and the Kraft pulp mill.

### Acknowledgements

This research is funded by the project “Catalyzing Investment in New Zealand Wood-Energy Industrial Symbiosis Opportunities”, a joint Scion/University of Waikato project, funded by the New Zealand Ministry of Business, Innovation, and Employment, in collaboration agreement and support from the EU project “Sustainable Process Integration Laboratory – SPIL”, project No. CZ.02.1.01/0.0/0.0/15_003/0000456 funded by EU “CZ Operational Programme Research, Development and Education”, Priority 1: Strengthening capacity for quality research.

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