Potential of hydrothermal black liquor gasification integrated in pulp production plant

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Abstract:
Greenhouse gas emission mitigation is one of the main motivations for increasing the use of biomass in providing environmentally friendly value-added products. The pulp and paper industry is a promising sector for the integration of biorefinery pathways. Among different technologies to produce pulp, the Kraft process accounts for 60% of the worldwide pulp production. The by-products of the Kraft process are major resources of biomass that can further be exploited. In the conventional Kraft process, black liquor is concentrated and burned in recovery boilers in order to satisfy the process heat demands and to recover the chemicals. Almost 40% of the heating demand of the process accounts for evaporators in which the black liquor is concentrated for utilization in the recovery boilers. The aim of this work is to investigate the potential of replacing conventional recovery boilers with a hydrothermal black liquor gasification unit. Hydrothermal gasification allows for having high water content black liquor (near 80%). This leads to an increase in energy efficiency of the process by reducing the overall heating demand (via eliminating the energy-intensive evaporation and concentrations stages) and simultaneously generating syngas that can be further processed into biofuels. In order to evaluate this potential, related process flow sheets are built and thermo-economic optimization of the integrated process is conducted. Furthermore, heat integration among the mill and the biorefinery is performed in order to identify the optimal operating conditions of the process. This work is a necessary preliminary step to provide incentives to further analyze the potential of the integration of the two.

Keywords:
Energy integration, Integrated biorefinery processes, Industrial energy efficiency, Energy optimization, Hydrothermal gasification.

1. Introduction and state of the art

One of the key challenges in energy sector of the future is a secure supply of affordable fuels with reduced environmental impact. The pulp and paper industry accounts for the sixth largest

European industrial energy user and is one of the major consumers of biomass resources [1]. This accounts for approximately 5% of the global industrial energy consumption [2]. It is important to improve the energy efficiency of the pulp production process as the its demand is growing rapidly throughout the world.
Most paper nowadays is produced via the Kraft process. Many studies have focused on improving the energy efficiency of the Kraft process. [3] developed a comprehensive methodology by identifying the interactions among utility systems and processes. They analyzed the system interactions and energy enhancement measures by taking into account the steam and water networks within a Canadian Kraft process. [4] developed an optimization methodology based on mixed integer linear programming (MILP) for the simultaneous optimization of water and energy. They applied the methodology on Canadian softwood Kraft pulp mill producing 1000 air-dried tonnes/day of pulp. By applying the simultaneous optimization approach, the water consumption could be reduced by 34%, while the hot utilities were reduced by 21%.
The usage of by-products of the pulp industry as feedstock for fuel integration pathways is another energy efficiency measure. Black liquor is a major by product of the pulp and paper industry. It consists of up to 45% of inorganic chemicals, which results in a relatively low heating value. For economic and environmental reasons, it is desired to recover the chemicals in the black liquor. In the conventional Kraft process, black liquor is concentrated, evaporated and burned in a recovery boiler for the provision of heat. Alternatively to the burning of black liquor, gasification has emerged as a promising option to generate fuel, chemicals and electricity simultaneously [5]. This has been addressed by [6], where the "Chemrec" gasification process -a pressurized, oxygen-blown high temperature entrained flow gasifier - for dimethyl ether (DME) and electricity production. The gasification process is compared to recovery boiler-based biorefinery concepts from an economic and climatic point of view. Furthermore, profitability and CO_2 emissions are compared for different future energy market scenarios. It is shown that commercialized black liquor gasification could be profitable for integrated mills. Combined electricity and DME production scenario has been shown to possess the best economic performance among all scenarios.
[7] performed pinch analysis of an integrated gasification cogeneration systems in combination with pulp mill in order to identify systems with maximum power and heat yield. According to [7], gasification holds promising potential for the simultaneous recovery of chemicals and energy when integrated into a pulp mill.
Overall, conventional gasification pathways suffer from poor efficiency when using wet biomass as a feed [8]. Black liquor as a side product from the pulping process exiting usually has a solid content of 17-18% [5]. To this end, hydrothermal gasification has emerged as a novel alternative technology to generate methane rich syngas from black liquor under supercritical water conditions that has recently been under major investigation. Hydrothermal gasification has been widely applied in combination with wet lingocelluosic feedstock. [8] identified the catalytic hydrothermal gasification of woody biomass to synthetic natural gas as a promising alternative to conventional gasification through experimental work using a laboratory batch reactor. They stated that the term hydrothermal indicates an aqueous system at elevated pressures and temperatures, near the critical point of water. It is discussed that the heat demand for bringing water to supercritical conditions is less than for evaporating it at subcritical pres-

sure, which thus leads to energy savings compared to the conventional systems. Furthermore, tar formation is avoided due to supercritical conditions and the presence of a catalyst [8]. The fact that hydrothermal gasification allows for high water contents in the biomass makes the energy-intense concentration of the wet feedstock unnecessary.
An equilibrium model for hydrothermal gasification of waste biomass has been presented by [9]. It includes mass and energy balance models (using flow-sheeting software), heat and power integration and life cycle assessment. [10] present a model for the hydrothermal gasification of biomass that considers temperatures different from the equilibrium state. The energy conversion potential of woody biomass to methane is investigated including different gas separation options. The approach considers energy integration methods, thermodynamic models and optimization methods. It is found that product upgrading is an important factor regarding the economic and environmental evaluation of a process, since it highly affects costs, emissions and resource consumption. Only few studies have analyzed the implementation of catalytic hydrothermal gasification into a pulp and paper mill. [11] compares the potential technologies for the production of dimethyl ether and methane fuels from black liquor. The system performance is evaluated based on comparison with the reference pulp mill, fuel to product efficiency and the biofuel production potential. For methane production, catalytic hydrothermal gasification is considered as a replacement of the recovery boiler. The system proves to be self-sufficient but without any power export. Compared to the conventional pulp mill and the option of generating dimethyl ether, the overall steam demand can be reduced significantly. A large potential for the global production of both is indicated based on black liquor availability. [12] investigate the integration of biorefinery concepts into existing pulp and paper mills. A superstructure based process synthesis approach is employed to determine potential pathways for a long-term sustainable growth objective. The pulp and paper industry process network is divided into three sub-networks, a chemical pulping section, a biochemical production section and a black liquor utilization section. [5] provides a review of different gasification technologies as alternatives to replace the recovery boiler. According to [5], catalytic hydrothermal gasification has never been tested with black liquor as a resource. They point out that, compared to other gasification techniques, the high water content in black liquor leads to high conversion rates of organics to synthesis gas. This allows for the direct introduction of the black liquor into the hydrothermal gasifier, making energy-intensive evaporation and concentration units redundant. The goeal of this work is to investigate the potential of the energy integration of hydrothermal gasification in a conventional Kraft process. Related process flow sheets are built and thermo-economic optimization of the integrated process is conducted. This work is a necessary preliminary step to provide incentives to further analyze the potential of the integration of the two in terms of economic and environmental impact. In Section 2., the generic processes of a Kraft mill and a catalytic hydrothermal gasification unit are described. Furthermore, the integration of the two processes is described. Section 3. introduces the problem formulation of the energy integration. In Section 4., the results are discussed.

2. Process description and problem formulation

This section gives an overview of the conventional pulp and paper process and the hydrothermal gasification of biomass.

2.1. The Kraft process

Most of the European pulp and paper mills use wood as the basic raw material, which mainly consists of cellulose, hemicellulose and lignin [5]. Approximately 70% of the pulp production in Europe is taking place in the Kraft process. Therefore, a case study utilizing the Kraft process is considered.

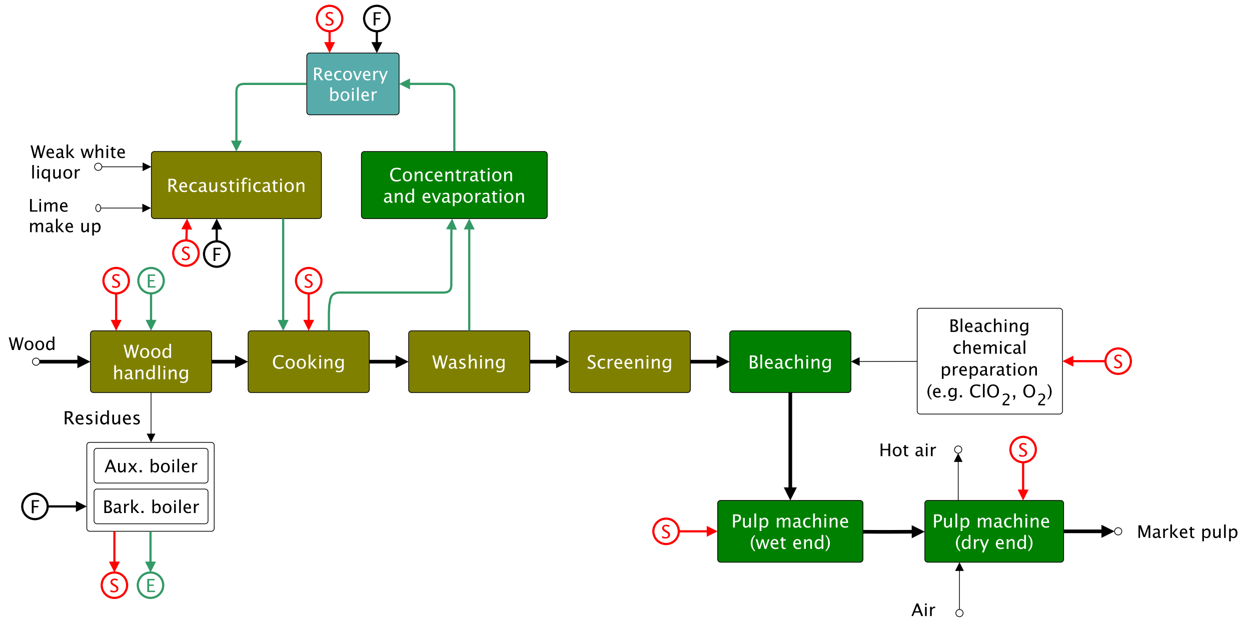

Figure 1: Block flow diagram f a generic Kraft process, adapted from [13]

In Figure 1, the block flow diagram of a generic Kraft process is presented. As a first step, wood is chopped, steamed and screened for non-wood materials in preparation of the cooking process. In the cooking process, also known as the digester, the processed wood chips are boiled under high pressure and high temperature, in order to remove cellulosic fibres. The chemical used in the digester (i.e. the liquor) is a mixture of white liquor, which consists of $NaOH$ and Na_2S and spent black liquor, which is recovered from the previous cooking process [14]. The outlet of the cooking process is washed to separate the fibers from spent liquor. The pulp exiting the digester is screened, bleached and dried. The black liquor (solid content of 15%) that is exiting the digester is fed through a recovery unit consisting of an evaporator unit, a concentrator unit and a recovery boiler. The concentrator yields black liquor with a dry solid content of 75%, which is burned in the recovery boiler. That way, the energy content of the burnt organic materials is recovered to run turbo-generators and to satisfy steam demands of the mill. Furthermore, inorganic chemicals are restored as chemical pulping agents, and by-products are recovered [14].
From an operational point of view , the major drawbacks of the recovery boilers are the risk of smelt water explosions and the relatively low efficiency of 12%. Even though the recovery boilers have proven over the last decades to be a relatively mature and reliable technology to

process spent cooking liquors and produce steam and electricity for process use, the pulp and paper industry has been exploring alternatives [5].
For modeling the Kraft process, the representative model of a pulp mill presented by [14] has been used. [14] models the Kraft process by generating three industrial clusters. The digester cluster includes the digester, washing and recausticization. It represents the process of breaking down wood chips for the pulp production. In the pulp machine cluster, the pulp machine, the bleaching unit and a ClO_2 unit are included. They represent the industrial site for producing pulp. The recovery boiler cluster includes an evaporator and a concentrator for black liquor as well as the recovery boiler, in which the processed black liquor is burned for the generation of process heat. No direct heat or mass exchange is allowed between the clusters. For cooling demands, a cooling tower operating at ambient temperatures is used.

2.2. Catalytic hydrothermal gasification

In a gasification process, biomass is gasified in a pressurized reactor under reducing conditions. After being separated from inorganic ashes and smelt, the raw synthesis gas can be further processed to dimethyl ether, synthetic natural gas, methanol, hydrogen or synthetic diesel [5]. Since conventional gasification processes suffer from a poor efficiency, hydrothermal gasification has emerged as a promising alternative for the conversion of biomass. Catalytic hydrothermal gasification, also known as supercritical water oxidation is a novel technology that allows the production of methane rich synthetic gas from biomass with water content above 80% [15].
After the feedstock is heated up to supercritical conditions, the salt is separated from the hydrolyzed products using a reversed flow vessel. The gas phase is leaving the separator, is cooled down and passes through the catalytic fixed bed reactor, where the organic components are converted to syngas. The gasification in the aqueous system is taking place at elevated pressures and temperatures, near the critical point of water. The model of the hydrothermal gasification is based on the work presented by [15] and [10]. In the selected model, the catalytic hydrothermal gasification unit is followed by a hybrid Selexol/Membrane separation process. This configuration allows for accounting the combined heat and power generation from the high pressure syngas cooling and expansion (Figure 2).

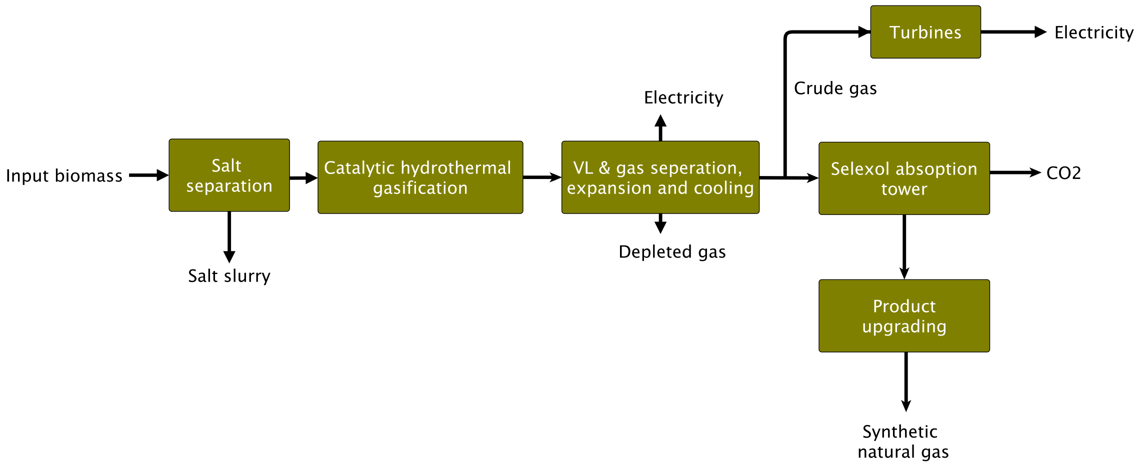

Figure 2: Block flow diagram of the catalytic hydrothermal gasification model, adapted from [15]

2.3. Integration of the catalytic hydrothermal gasification in the Kraft process

In order to combine the Kraft process with hydrothermal gasification, the complete recovery boiler cluster of the model described in Subsection 2.1. has been replaced by the hydrothermal gasification model. Since hydrothermal gasification requires cooling at temperatures lower than ambient temperature, the cooling tower is not sufficient to fulfill the demands. For that reason, a refrigeration unit is included in the model.

2.4. Integration with steam network

Energy integration between the clusters of the mill is performed via the integration of a steam network, as described by [13]. The steam network operates as a cogeneration unit on four different pressure levels, as shown in Table 1.

Table 1: Steam network characteristics

Level	Value	Unit
Level 1	58.7	bar
Level 2	12	bar
Level 3	5.2	bar
Level 4	1	bar

Turbines are placed between the highest pressure and subsequent lower pressures. Each defined cluster of the pulp mill can exchange heat with the steam network, while no direct heat exchange between the streams of different clusters is allowed due to geographical constraints. The energy-integration model is necessary to compute optimal heat-recovery in the system using heat-cascade constraints. Furthermore, it contains information about heat and power requirements of the processes.

3. Energy integration optimization problem

The process flowsheet models adapted from [15] for the superstructure of the hydrothermal gasification are defined in Belsim [16]. The material and energy flow model contains information about all process streams and their physical properties that can be used to define the energy requirements of the system. For the energy integration model of the pulp mill and the hydrothermal gasification unit, the approach presented by [17] is used. They propose a process integration methodology to satisfy the minimum energy requirements (MER) and close the energy balance of an energy system. The energy integration optimization problem is formulated as a MILP. The generation of a heat cascade combined with pinch analysis allows to obtain the MER and the optimal utility network of a system with regard to minimal operating cost. The overall problem is solved in LuaOsmose, a computational framework that is developed and continuously improved by the Industrial Process and Energy System Engineering group at the École Polytechnique Fédérale de Lausanne [18].

4. Results and discussion

Figure 3 displays the grand composite curve for the minimum energy requirement for all respective clusters. For the conventional Kraft mill, the grand composite curve of the individual clusters are represented in a) - c). For the hydrothermal gasification, Figure 3 f) represents the grand composite curves. Comparing the plots it can be observed that the thermal energy requirements of the recovery boiler and the hydrothermal gasification clusters are comparable, which makes the integration worthwhile investigating.

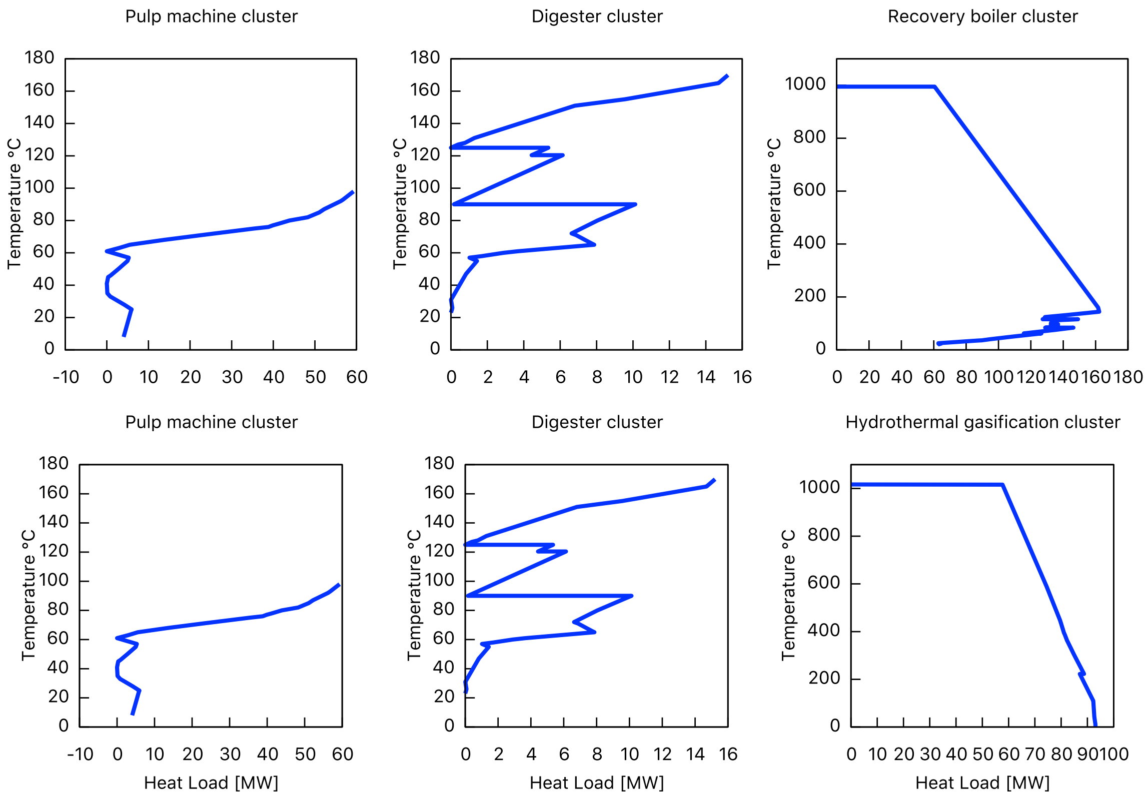

Figure 3: Grand composite curve of MER of conventional Kraft mill and hydrothermal gasification

Table 2 shows the sizing characteristics of the considered pulp mill, which are the same for both analyzed cases. Thus, the heating and cooling demands of the digester and the pulp machine cluster remain the same for both scenarios. In both cases, the pulp mill is self sufficient regarding the heating demand. The recovery boiler as well as the hydrothermal gasification unit generate enough heat to fulfill the demands of the other two clusters.

Table 2: Pulp mill characteristics [14]

Parameter	value	Unit
Biomass input	2000	$\text{tonnes}_{\text{air-dried}}/\text{day}$
Pulp production	1000	$\text{tonnes}_{\text{air-dried}}/\text{day}$
Electricity required by pulping process	25.1	MW

159 MW of steam is being generated in recovery boiler scenario (RBS) producing 28.1 MW of electricity. This amount is reduced to 58 MW of steam generation in the scenario considering catalytic hydrothermal gasification (HGS) where only 10 MW of electricity is produced. However, the expansion of gaseous products from the gasifier leads to an electricity generation of 30.3 MW. So overall, in the HGS, 12.4 MW of electricity can be sold. Furthermore, 0.4 kg/s of synthetic natural gas are generated and sold. In Table 3, the energy provided by the recovery boiler and the hydrothermal gasification unit are compared.

Table 3: Results for RBS and HGS scenario

	RBS	HGS	Unit
Heat transferred to steam network	159	58	MW
Electricity generated from steam network	28.1	10.0	MW
Electricity generated from gas expansion	0	30.3	MW
Excess electricity sold	0.2	12.4	MW
Synthetic natural gas sold	-	0.4	kg/s

The costs for cooling of the digester are reduced by 50%, while the cost for cooling refrigeration and the recovery boiler (hydrothermal gasification) unit increase by 48%. The costs for fresh-water consumption can be reduced by 5%. Furthermore, in the HGS, revenues are obtained from selling gridgas and electricity. As shown in Table 4, the annual revenues from selling electricity account for 6.1 Mio. USD, while revenues of 8.6 Mio. USD (0.745 USD/kg synthetic natural gas [19]) from selling gridgas are obtained.

Table 4: Annual operational costs for RBS and HGS scenario

	RBS	HGS	Unit
Cost for cooling of digester	0.8	0.4	Mio. USD
Cost for fresh water	3.1	2.9	Mio. USD
Cost for cooling/refrigeration of recovery boiler/ htg unit	0.6	0.9	Mio. USD
Revenues from sold electricity	0.1	6.1	Mio. USD
Revenues from sold grid gas	-	8.6	Mio. USD

5. Conclusion

Using the black liquor in a catalytic hydrothermal gasification unit instead of a recovery boiler allows the pulp mill to export electricity and heat while being self-sufficient regarding the heat demands of the the pulp production process. It needs to be taken into account that the aim of the current work is a preliminary step in investigating the potential of integrating biorefineries in Kraft pulp mills. This analysis has shown the great potential of energy integration of the two processes. Further assessment considering multi-objective optimization with economic and environmental impact criteria, and simultaneous process integration and optimization will be performed in the future. Furthermore, it needs to be investigated in further detail how the necessary chemicals for the pulping process can be recovered.

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Nomenclature

CO_2 Carbon dioxide

DME Dimethyl ether

HGS Hydrothermal gasification scenario

MER Minimum energy requirements

MILP Mixed integer linear programming

RBS Recovery boiler scenario

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