

Exergy and environmental analysis of black liquor upgraded gasification in an integrated kraft pulp and ammonia production plant

*Meire Ellen Ribeiro Domingos^a, Daniel Flórez-Orrego^b, Moisés Teles dos Santos^c,
Silvio de Oliveira Junior^d*

^{a,c} Polytechnic School, University of Sao Paulo, Department of Chemical Engineering, Sao Paulo, Brazil,
^ameireallengorete@usp.br CA, ^cmoises.teles@usp.br,

^{b,d} Polytechnic School, University of Sao Paulo, Department of Mechanical Engineering, Sao Paulo,
Brazil, ^bdaflorezo@usp.br, ^dsoj@usp.br

Abstract:

Some byproducts of the Kraft pulp mills, such as the black liquor (1.4 t/t ADpulp, 15% solids), still contain more than half of the exergy content of the total wood fed to the digester. This residue represents a key supply of renewable energy to the pulp and paper plant, accounting for a power generation potential of about 670 TWh/y. In the customary practice, black liquor is concentrated in a multiple effect evaporator and burnt in waste heat recovery boilers in order to satisfy the combined power and steam demands. Moreover, as half of the steam generated is only used for evaporating the black liquor moisture, the efficiency of the electricity generation is relatively low. Additionally, the conventional process of concentration and combustion of the black liquor is responsible for a large amount of atmospheric emissions. Consequently, there is an interesting opportunity to improve the performance of the overall energy conversion process in the pulp and paper industry. Among the various upgrade routes for this byproduct, thermochemical conversion processes, such as improved drying approaches along with a pressurized gasification system, can be readily integrated to produce syngas from the concentrated black liquor. The produced syngas can be used for producing value-added products such as ammonia and CO₂, thus improving the environmental and exergy performance of the cogeneration plant and the entire mill, at the expense of a small capital investment. Accordingly, in this work, the conventional scenario of the black liquor use is compared with other enhanced energy conversion routes in terms of the economics, exergy efficiency and environmental impact. The combined energy integration and exergy analysis is used to identify the potential improvements that may remain hidden to the energy analysis alone, namely the mitigation of the process irreversibility.

Keywords:

Entrained flow gasifier, Black liquor, Kraft pulp mill, Exergy, Ammonia.

1. Introduction

Globally, the pulp and paper production is an experienced biomass-based industry and one of the most important economic activities, accounting for 5.6% of the total energy consumed by the industrial sector [1, 2]. This industry is also responsible for about 252 million tons of annual CO₂ emissions, equivalent to 2% of the total amount emitted by the industrial sectors worldwide [3]. Accordingly, various efforts are envisaged towards the mitigation of its atmospheric emissions, the improvement of the waste heat recovery and the enhanced utilization of its byproducts [4].

Moreover, due to its critical forest biomass dependency, the pulp and paper industry has sought for alternatives to its traditional processes, in order to identify and evaluate the opportunities that may arise with the maturation of the existing biorefinery concept.

The Kraft production process is the most traditional chemical pulping process, in which the organic matter extracted from the digested wood is largely found in the form of black liquor (BL), a product generated in the delignification process of the wood for the extraction of the cellulose fiber. Globally, it is estimated that about 170 Mt of black liquor (dry solids basis) is currently processed per year [5]. In this context, BL can be a key supply for renewable energy production systems, since it generates on average 1.3-1.90 tons of BL per ton of pulp [6], with an overall generation potential of 670 TWh/y [7]. Furthermore, BL has the advantage of already being partially processed as exists in a pumpable liquid form, thus simplifying the logistics of its handling and utilization in comparison with other potential biomass sources used for chemicals production in polygeneration systems [8].

On the other hand, in traditional Kraft pulping systems, BL is concentrated by using multi-effect evaporators until the solids concentration reaches 75-85 wt.%. Then, it is burned in the recovery boiler so that the power and steam requirements of the entire mill can be supplied by the cogeneration system [9,10]. However, the efficiency of the electricity generation by using conventional recovery boilers is low, since almost 50% of the steam used in the mill is consumed for evaporation of the water content of the black liquor [9,11], whereas the efficiency of the power generation based on the recovery boiler ranges between 9-14% [13,14]. Actually, the conventional concentration system and the subsequent combustion of the BL is reported to be the largest responsible for the overall CO₂ emissions [3].

Consequently, several opportunities to improve the exergy, environmental and economic performance of the conversion processes in the pulp industry are identified. Among these new prospects, the thermochemical routes, used to convert biomass into valuable products, have gained recent interest, particularly the pressurized entrained-flow, high temperature black liquor gasification (PEHT-BLG) technology. According to some authors, the PEHT-BLG is a promising technology expected to significantly improve the efficiency of energy and chemical recovery in the pulping industry [15,17]. Nowadays, there are more than 200 recovery boilers operating in pulp mills all over the world that have been in operation for more than 20 years and need to be replaced [16]. In contrast, gasification plants have a higher electricity efficiency, present fewer CO₂ emissions and endorse the same level of risk, compared with traditional recovery boilers [16].

The syngas produced from the gasification process of BL can be used either to generate electricity or produce chemicals and biofuels, expanding the product portfolio using the biorefinery concept [15,19]. Among the various alternatives, ammonia is one of the most demanded bulk chemicals in the world, mainly in the agriculture sector as fertilizer [16]. The global supply of nitrogen fertilizers faces an increasing trend estimated in 176.5 million of tons in 2018 [18]. However, in the same year, their reported atmospheric emissions were estimated in ca. 353 million tCO₂. In order to palliate the environmental impacts that nitrogen fertilizers production is responsible for, several efforts have been addressed to incentivize the decarbonization of the ammonia supply chain. Alternative pathways of hydrogen production, such as solar or wind energy, used for electrolyzing the water and for separating the nitrogen from air (cryogenic distillation, selective membranes, etc.), have been widely proposed [19]. However, the most promising alternative energy resources for hydrogen production remain to be the thermochemical conversion routes especially to capitalize on the underexploited biomass potential in tropical countries with a well-established biomass conversion expertise such as Brazil.

The main drawbacks of the biomass-based ammonia synthesis continue to be related to the high investment risk, the biomass availability and the scale-up of the gasification concept, as it may not fully compete with current fossil-based commercial production capacities, well above 1000 t_{NH₃}/day. In spite of this limitation, larger pressurized biomass gasifiers are expected to aid increasing the performance of biomass conversion process [20]. Fortunately, the technology is

revisited when the access to fossil resources such as natural gas and coal is limited, mainly due to scarcity or unstable international prices [21]. More stringent environmental regulations along with increasing concerns about the marked dependence on imported fertilizers have also led researchers to look for the use of the readily available biomass residues to produce commodities traditionally based on fossil resources. In this context, BL gasification may be considered more efficient and environmentally friendly alternative compared to current black liquor combustion, aside from promoting the diversification of the energy inputs requiring only a minimum additional investment cost.

Accordingly, in this work, the use of black liquor gasification in the integrated syngas and ammonia production plant is compared with the performance of the conventional conversion route (standalone Kraft pulp mill). Notwithstanding, by undertaking novel approaches, additional or radically different demands can be created. Consequently, the optimal integration approach between the chemical plants and the new utility systems must be updated, so that the power and steam requirements remain satisfied. To this end, a systematic framework that allows selecting the most suitable utility systems in the light of the exergy analysis (refrigeration, waste heat recovery and cogeneration), that satisfy the minimum energy requirements with the lower operating cost, is adopted.

2. Integrated Kraft pulp mill and ammonia plant description

Kraft process is the dominant chemical pulping process, in which the lignin present in the wood chips is solubilized by a strong alkaline solution (white liquor) at moderate temperature in order to extract the cellulose fibers. The process starts in the wood yard where logs are debarked, cut into wood chips and classified (Fig. 1, Kraft pulp mill section). It is estimated that about 90% of the wood mass (logs with bark) are sent to the pulping process, and the remaining 10% represents losses in the log debarking, chipping and chips classification [22]. Subsequently, the wood chips are impregnated with cooking liquor, and next fed to steam heated reactors called digesters [23]. This cooking operation is conducted under strongly alkaline conditions and in the presence of a sulphide solution (white liquor, approx. 60% NaOH, 25% Na₂S and 15% Na₂CO₃), at a temperature ranging from 145 to 180°C, depending on the size of the digester and the desired pulp production, on a residence time of several hours (usually between 1-5 h), in a batch or continuous process [24]. The pulp yield varies between 45-55% of the initial wood mass [25], depending of the pulping conditions and wood quality [24].

The pulp produced in the digester is washed in order to recover the cooking liquor (black liquor) and reduce the carryover of organic component to the oxygen delignification unit [23]. Black liquor contains approximately half of the organic material that was originally in the digested wood and almost all of the inorganic chemicals that were used for delignification [23]. The reported amount of dry solids in the black liquor per unit of pulp produced ranges from 0.86 up to 1.7 t_{BL}/t_{ADpulp} [23,26], whereas the higher the pulp yield the lower the amount of black liquor produced [27]. The pulp is then bleached with chlorine dioxide and hydrogen peroxide in a sequence of acidic and alkaline stages, with washing between them [28]. The bleached pulp is dried to about 90% solids, being cut in sheets and baled to be shipped to customers.

Traditionally, the available technology for recovering process chemicals and generate steam and power has been the chemical recovery boiler (Tomlinson boiler) integrated to a backpressure steam turbine [29]. This process is known as *recovery cycle*, which is reportedly responsible for making the pulping mill economically and environmentally possible [23]. After its separating from the cellulose fibers, the spent liquor (or weak black liquor) from the digestion step is concentrated in evaporators and burned in recovery boilers in order to recover the active cooking agents. In the combustion process, a smelt of sodium sulfide and sodium carbonate is produced (green liquor), regenerating over 90% of the pulping chemicals while producing steam and electricity for the mill [30]. Next, those chemicals are recausticized with lime and recycled back to the digester as an aqueous solution, the white liquor [31].

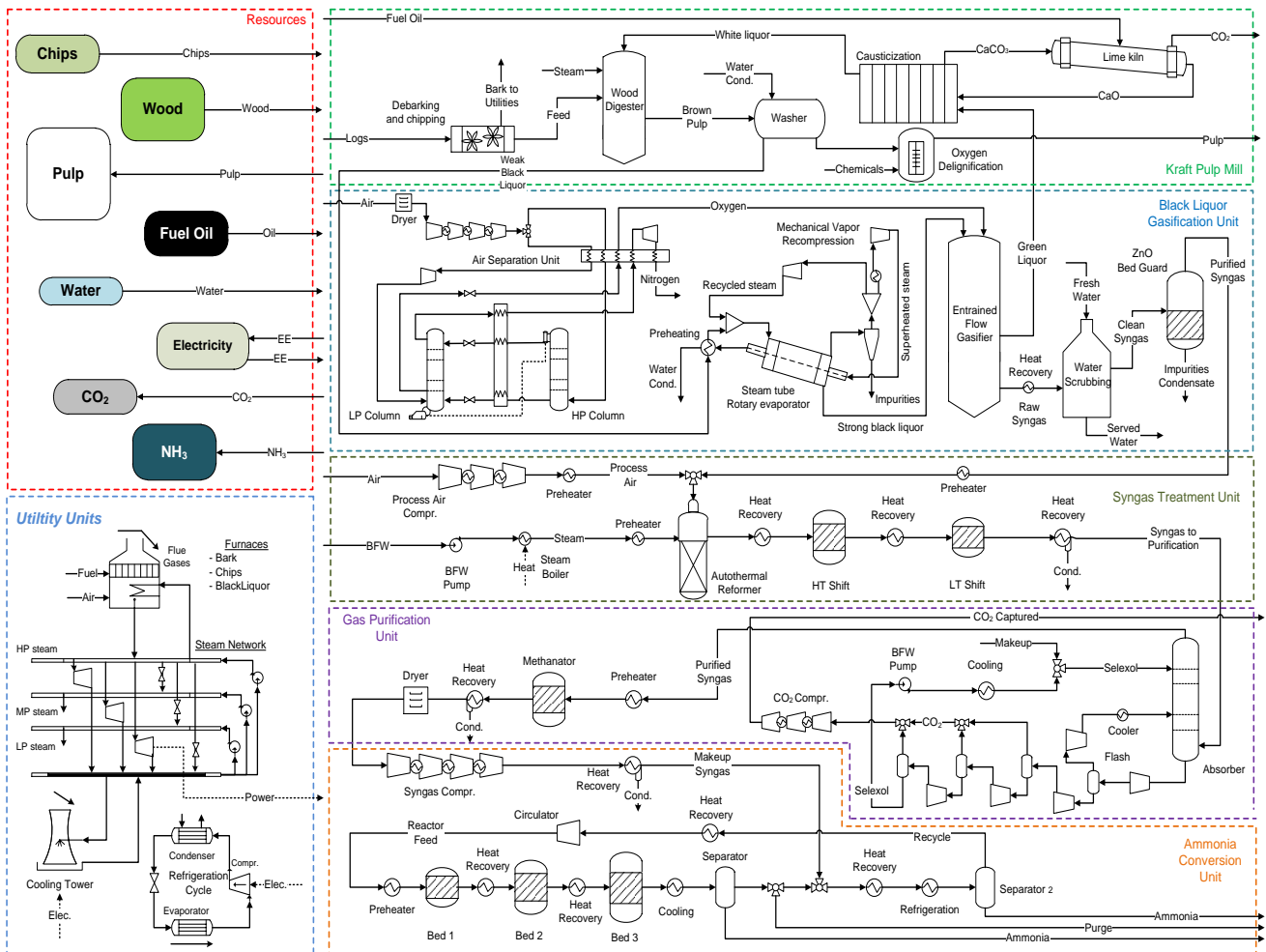


Figure 1. Flowsheet of the integrated Kraft pulp and Ammonia production plant.

Due to the potential improvement in energy efficiency, CO₂ emissions reduction and additional value added products commercialization, an alternative to the traditional chemical recovery process is proposed. This approach is based on the integration of a mechanical vapor recompression (MVR) system for black liquor concentration and subsequent gasification, along with a CO₂ capture system and ammonia production unit, as shown in Figure 1. Traditional evaporation is energy intensive and offers a great scope for reduction of costs by reducing the steam requirements [32], as proposed by [9]. MVR substitutes the large steam requirement by a demand of electrical energy, resulting in a very low operating cost compared to a multiple effect operation and higher efficiency when reducing the high moisture content of BL to about 15% wt. The drying process is composed of three consecutive stages, namely BL preheating, evaporation and steam superheating [9]. In the first stage, BL is preheated by using the compressed vapor before it enters in the steam tube rotary evaporator, wherein the weak BL evaporates in countercurrent heat exchange with the compressed steam. The heavy BL (85% wt. solids) leaves the evaporator and the extracted moisture is divided into a recycled stream and a purged steam. The first is recirculated back to the evaporator in order to improve the heat transfer performance, whereas the exhausted steam flows to the superheating stage. The saturated purge is superheated first in a heat exchanger that guarantees the vapor state and then recompressed in order to supply the energy required for evaporation [9,10] (see Fig. 1). The solid content of the dried BL has a great influence in the viscosity for concentrations above 60%, leading to pumping issues, formation of large liquor droplets, cracking and corrosion [33]. To overcome the high viscosity related drawbacks, some authors proposed a liquor heat treatment (LHT) [42], a thermal method consisting of the depolymerization of polysaccharides and lignin by raising the temperature of BL to 180-190°C, allowing the obtainment of a 90% dry solids BL in a pumpable form [34,35]

On the other hand, the pressurized entrained flow, black liquor gasification PEHT-BLG available in the market as Chemrec® gasifier [27] has the potential to double the power output comparatively to the conventional Tomlinson boiler when integrated with a combined cycle [36]. Other advantages, include tar-free and uniform temperature gasification at turbulent conditions which results in a high conversion efficiency and high reaction rate [16]. In the gasification step, the carbonaceous materials in the BL are converted into syngas rich in CO, H₂, H₂O and CO₂, while a smelt containing mainly Na₂CO₃ and Na₂S is formed in the bottom when a quench cooler separates the regenerated salts that will form the green liquor [9]. The gasifier pressure and temperature usually varies between 25-32 bar and 900-1100°C, whereas the oxygen-to-fuel ratio ranges between 0.40-0.55, with oxygen as agent [37]. After the syngas produced leaves the gasifier, it is cooled down and scrubbed with water, in order to remove the impurities that may affect the downstream equipment. As long as the syngas still contains methane and carbon monoxide, an autothermal reforming and a water gas shift reaction processes help increasing the hydrogen content, simultaneously producing more CO₂. A portion of the reformed mixture is burnt with air in order to provide the energy to the reforming reactions as well as to attain a H₂/N₂ ratio 3:1, suitable for ammonia production [38]. Henceforth, the hydrogen-rich syngas goes through a purification system composed of a physical absorption unit (DEPG) and a methanation system, is used to remove the carbon oxide components present in the syngas produced [39]. The purified syngas is compressed up to 200 bar and fed to a synthesis loop, where the H₂/N₂ mixture is partially converted into ammonia through a series of catalytic beds indirectly cooled [40].

Finally, the Fig. 1 also summarizes the various alternatives of utility systems available for supplying the power and heat demands of the chemical plant including bark, chips, oil and black liquor fired furnaces, a cooling tower, a vapor-compression refrigeration system, as well as the resources consumed (e.g. wood, chips, black liquor, water, electricity) and the marketable products (pulp, ammonia, CO₂ and power). The waste heat available throughout the chemical processes is recovered by using an integrated steam network, so that more power can be generated by optimally profiting the thermodynamic potential of the waste heat exergy via backpressure and condensation steam turbines.

3. Methodology

In this section, the process modeling including the thermophysical properties and correlations used to evaluate the exergy performance, as well as the optimization methodology proposed for the minimum energy requirements and maximum economic revenues of the plant are described.

3.1. Process modeling

The thermodynamic properties of the flows as well as the mass, energy and exergy balances of each unitary operation are evaluated by using Aspen Plus® V8.8 software and the Peng-Robinson EoS with Boston-Mathias modifications [41]. The Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) is used to model the physical absorption of CO₂ with dimethyl ethers of polyethylene glycol (DEPG) as in [42]. The Kraft pulp modeling is based on the assumption of a pulp yield of 46.51% with respect to the total amount of digested biomass [22] and a production of 1.44 t_{BL}/t_{pulp}, as well as by considering the power and steam demands adapted from [24,29] to produce about 880 ADt/day pulp. The evaporation temperature (T , in °C) is estimated by using (1), which considers the concept of equilibrium moisture content, MC_{eq} , under the superheated steam condition [9,10].

$$MC_{eq}(\text{wt}\% \text{ wet basis}) = 54.678e^{-0.046T} \quad (1)$$

The simulation of the gasification process presents certain complexity as a reactive and separation system and, as such, it is simulated as consisting of several interrelated stages that occur simultaneously, namely drying, pyrolysis, gasification and combustion steps. The gasification pressure and the temperature are set as 30 bar and 1000 °C, respectively. In the quench zone of the

gasifier the smelt is separated, diluted with water and recycled back to the causticization plant in the form of green liquor to be regenerated and used again in the Kraft process. The oxygen-rich combustion of a fraction of the char produced in the black liquor pyrolysis step supplies the energy required by the endothermic drying, pyrolysis and reduction reactions. The ultimate and proximate composition (mass basis) for BL and other complex substances of interest are obtained from literature (see Table 1). Meanwhile, the lower heating value is estimated based on the correlations reported by Channiwala et al. [43] and the ratio of specific chemical exergy to the lower heating value, at standard conditions (298 K and 1 bar), is calculated by means of the correlations proposed by Szargut et al [44].

Table 1. Ultimate and proximate analyses, lower heating value (LHV) and specific exergy (b^{CH}) for selected material and fuel streams. FC: Fixed Carbon, V: Volatiles, M: Moisture.

Substance [Reference]	C	H	O	N	S	Cl	ASH	FC	V	M	LHV (MJ/kg dry)	b^{CH} (MJ/kg dry)
Wood [45–48]	49.90	6.14	42.85	0.27	0.00	-	0.83	-	-	40	18.85	21.23
Bark [49,50]	48.58	5.52	41.19	0.36	0.03	0.09	4.23	-	-	50	17.9	20.13
Black Liquor [51]	29.86	3.27	29.05	0.10	4.09	0.90	32.73	10.21	57.06	85	10.28	12.08
Oil [52]	85.10	10.90	-	-	4.00	-	-	-	-	2	40.56	43.38
Pulp [53]	44.44	6.17	49.39	-	-	-	-	-	-	10	16.32	19.80

3.2. Exergy analysis indicators

Some performance indicators for each ammonia plant configuration are proposed to allow for systematic comparisons between the different designed setups, namely *the conventional recovery boiler and two proposed based on the black liquor gasification process for simultaneous ammonia production with and without electricity import from the grid*. Table 2 compares the *rational exergy efficiency* (2), with the *relative exergy efficiency definition* (3). It must be noticed that, the former efficiency is higher than the relative one as it accounts for the outlet exergy of other byproducts (CO₂, purge gas).

Table 2. Plantwide exergy efficiency definitions of the integrated plants.

Definition	Formula	Equation
Rational	$\eta_{\text{Rational}} = \frac{B_{\text{useful, output}}}{B_{\text{input}}} = 1 - \frac{B_{\text{Dest}}}{B_{\text{input}}} = 1 - \frac{B_{\text{Dest}}}{B_{\text{oil}} + B_{\text{wood}} + B_{\text{chips}} + W_{\text{net}}}$	(2)
Relative	$\eta_{\text{Relative}} = \frac{B_{\text{consumed, ideal}}}{B_{\text{consumed, actual}}} = \frac{B_{\text{ammonia}} + B_{\text{pulp}}}{B_{\text{oil}} + B_{\text{wood}} + B_{\text{chips}} + W_{\text{net}}}$	(3)

B = exergy rate or flow rate (kW), $Dest$ = destroyed.

Physical and chemical exergy calculations, as well as exergy efficiencies are assessed using VBA® scripts as *user defined functions* [54].

3.3. Optimization framework and problem definition

In moderns chemical and industrial plants, processes streams and unit operations are interrelated through recycle loops and an extensive waste heat recovery network. Moreover, as long as electricity can be imported from the grid, a trade-off between additional fuel consumption for cogeneration and the extent of electricity purchase is expected. Since both resources can be used to supply the energy demand of the whole plant, the choice will be strongly influenced by the performance of the cogeneration and waste heat recovery systems, as well as by the cost of the electricity and the fuel consumed [55]. Thus, when competing energy resources are considered, the conventional process flowsheet may be drastically modified and additional or very different demands may be created. This circumstance requires a complete redesign of the energy integration

approach between the chemical units and the utility systems, so that the power and steam requirements remain satisfied.

In this way, depending on the availability and cost of the energy resources as well as on the desire of producing various value added products, cheaper energy resources, such as wood chips may be favored over more expensive energy inputs such as electricity [56]. On the other hand, by importing electricity in lieu of generating it in the own utility systems, the energy, economic and environmental impacts are transferred to the outside of the battery limits. Thus, depending on the electricity mix, it may bring more energy and environmental benefits than using wood chips as fuel in the cogeneration system. All these new features render the determination of the optimality a cumbersome task. Fortunately, the selection of the most suitable alternatives for the utility systems from a resourceful set of energy technologies allows reshaping the integrated curves of the chemical process aiming to minimize the exergy destruction by reducing the inherent driving forces through the optimization of the waste heat recovery and power generation. This procedure relies on an efficient mathematical programming approach in which all the potential energy technologies, resources and production routes are included (see Fig. 1). Additionally, by separating the chemical process simulation from the energy integration problem, the calculation of the mass and energy balances and the simulation of the complex energy conversion systems can be handled by using the Aspen® Plus modeler [57]. Meanwhile, the determination of the minimum energy requirements (MER) and the solution of the energy integration problem is handled by the OSMOSE Lua platform, developed by the IPESE group at the École Polytechnique Fédérale de Lausanne - EPFL, Switzerland [58].

This framework also allows to determine the most suitable utility systems (e.g. furnaces, refrigeration, steam network and cogeneration system) and their operating conditions that lead to the lowest resources consumption and optimal operating cost [59]. The computational framework manages the data transfer with the ASPEN Plus® software and builds the mixed integer linear programming (MILP) problem described in (4-8) that minimizes the operating cost of the chemical plant. In other words, the optimization problem consists of finding the integer variables, y_w , associated to the existence or absence of a given utility unit, ω , and its corresponding continuous load factor, f_w , that minimizes the objective function given by (4):

$$\min_{\substack{f_{\omega}, y_{\omega} \\ R_r, W}} \left[\begin{aligned} & f_{Chips}^{resource} (B \cdot c)_{Chips} + f_{Wood}^{resource} (B \cdot c)_{Wood} + f_{Oil}^{resource} (B \cdot c)_{Oil} + f_{Power}^{resource} (W \cdot c)_{Power}^{Net\ import} \\ & - f_{Pulp}^{resource} (B \cdot c)_{Pulp} - f_{NH_3}^{resource} (B \cdot c)_{NH_3} - f_{CO_2}^{resource} (\dot{m} \cdot c)_{CO_2} \end{aligned} \right] \quad (4)$$

Subject to:

$$\text{Heat balance at the temperature interval } r \quad \sum_{\omega=1}^{N_{\omega}} f_{\omega} q_{\omega,r} + \sum_{i=1}^N Q_{i,r} + R_{r+1} - R_r = 0 \quad \forall r = 1 \dots N \quad (5)$$

$$\text{Balance of produced/consumed power} \quad \sum_{\omega=1}^{N_{\omega}} f_{\omega} W_{\omega} + \sum_{\substack{\text{chemical} \\ \text{units}}} W_{net} + W_{imp} - W_{exp} = 0 \quad (6)$$

$$\text{Existence and size of the utility unit } w \quad f_{\min,\omega} y_{\omega} \leq f_{\omega} \leq f_{\max,\omega} y_{\omega} \quad \forall \omega = 1 \dots N_{\omega} \quad (7)$$

$$\text{Feasibility of the solution (MER)} \quad R_1 = 0, R_{N_r+1} = 0, R_r \geq 0 \quad \text{and} \quad W_{imp} \geq 0, W_{exp} \geq 0 \quad (8)$$

where N is the number of temperature intervals defined by considering the supply and the target temperatures of the entire set of streams; Q is the heat rate exchanged between the process streams ($Q_{i,r} > 0$ hot stream, $Q_{i,r} < 0$ cold stream) and R is the heat rate cascaded from higher ($r+1$) to lower (r) temperature intervals (kW); N_w is the number of units in the set of utility systems; B is the exergy flow rate (kW) of the resources going in and out of the plant; c stands for the purchasing cost (euro per kWh, m³ or kg/h) of the feedstock and electricity consumed, or the selling price of the marketable pulp, ammonia and CO₂ produced; q is the heating/cooling rates supplied by the utility systems (kW); W is the power produced by either the utility systems, the same chemical process or imported from/exported to the grid (kW). It is important to emphasize that the process modeling and

simulation of the chemical plant alone, including its mass and energy balances, is performed by using Aspen® Plus software. Meanwhile, the utility units are modeled via equation-oriented subroutines written in the Lua programming language. Therefore, the additional equations required for the mass and energy balances of those units rely on the concept of layer (water, natural gas, biomass, syngas, ammonia, power, carbon dioxide, heat, etc.) as shown in Fig. 2. To this end, representative market cost for wood (0.013 euro/kWh), chips (0.016 euro/kWh), oil (0.018 euro/kWh) and electricity (0.06 euro/kWh) consumed, as well as the selling prices of pulp (0.144 euro/kWh), ammonia (0.098 euro/kWh) and CO₂ (0.0084 euro/kg) produced are taken from sorted literature [24,60,61].

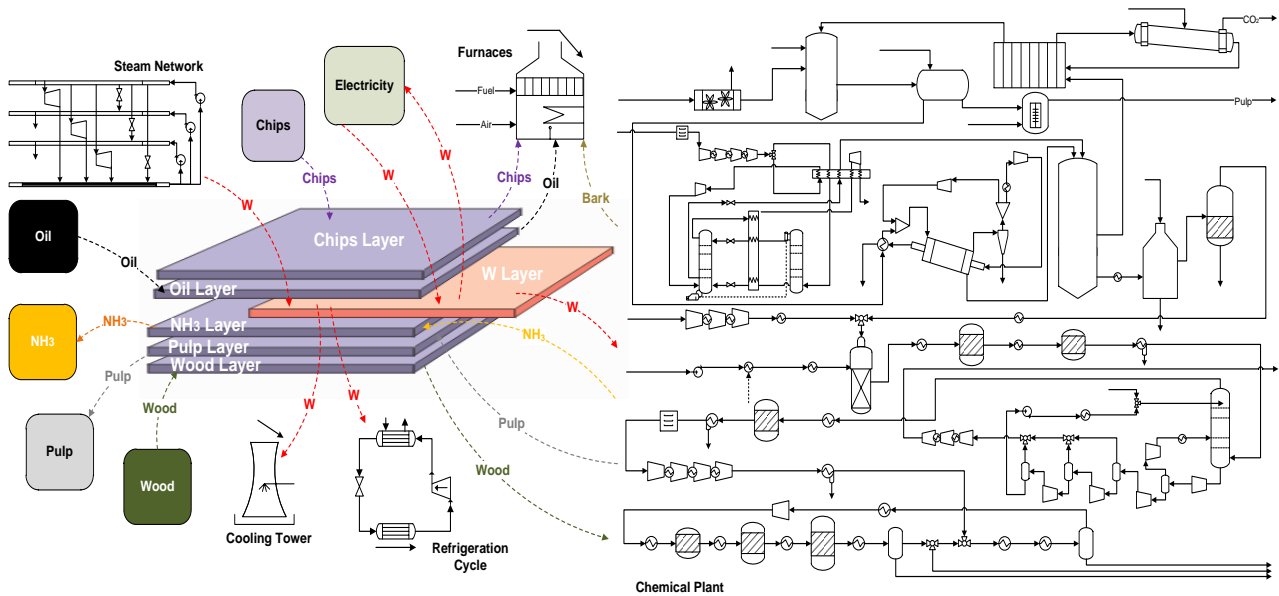


Figure 2. Concept of layer used in the optimization of the utility systems. *W*: power.

4. Results and discussion

Table 3 summarizes the results of the optimal process variables for the three scenarios considered. Two proposed scenarios, namely, the mixed mode (based on both chips fuel and electricity import) and the autonomous configuration (only chips import and cogeneration system enabled) are compared to the conventional configuration (recovery boiler application, no ammonia production). As it can be seen, the overall exergy consumption in the conventional case achieves 42.20 GJ/t_{Pulp}, whereas those figures for the two integrated ammonia plant cases have a marked increment between 10-36%. This is expected, due to the larger amount of biomass and electricity required to drive the compressors and other ancillary equipment of the ammonia production line. On the other hand, it is also evidenced that the integrated pulp and ammonia production configurations have higher operating revenues, due to the complementary value added CO₂ and NH₃, which are not produced in the conventional route. Moreover, even if the higher yearly investment cost of the integrated pulp and ammonia plants is considered, the net revenues only differ less than 5% compared to the conventional case.

According to some authors, the conventional scenario based on outdated recovery boilers (60 bar) may be improved by implementing various energy integration approaches. They consist of (i) the utilization of vapor cycles operating at higher pressures (100 bar), (ii) the substitution of the older technologies, such recovery boilers, by gasification systems handling black liquor with higher solids contents [23] and (iii) the diversification of the energy inputs and products such as the utilization of biorefinery residues and electricity generated from a more efficient Brazilian electricity mix.

Additionally, Table 3 also shows the *Extended Exergy Plant Consumption* that takes into account the exergy efficiency of the electricity generation (55.68%), as well as of the oil (95.20%) and

biomass (86.13%) supply chains [62,63]. Certainly, by adding the upstream inefficiencies in the feedstock supply chains to the conventional Kraft pulp mill analysis, the panorama the exergy destroyed in the feedstock acquisition further impairs the *extended* performance of the pulp and ammonia production process. Actually, the increase of the overall exergy consumption is remarkable, varying from 15.9-20.5% in the case of the simultaneous pulp and ammonia production routes. Although these figures may not be immediately interesting for pulp and ammonia producers when evaluating the performance of the plant itself, those figures are certainly useful to public policy and decision-makers in environmental and benchmarking frameworks, as they permit an holistic comparison of the impact of the fertilizers sector with other industrial sectors.

Furthermore, the indirect emissions related to the supply chains of the electricity, oil and biomass (e.g. production, distribution) shown in Table 3 have been also accounted for in the calculation of the fossil CO₂ emissions. Undoubtedly, such indirect contribution is not negligible and reveals environmental issues that otherwise may remain hidden if electricity imported or biomass are considered as *emissions free* inputs. For instance, the indirect emissions of the wood and chips supply are the largest share of indirect emissions (74-99% out of 0.25 tCO₂/t_{Pulp}), even higher than those directly produced by consuming fuel oil in the lime kiln furnace. It can be explained by the large amount of wood and chips required, which not only takes a toll to the efficiency of the overall plant, as it will be shown latter, but also proportionally increases the indirect emissions produced.

Table 3. Optimal process variables of the pulp and ammonia production facilities.

Process parameter	Conventional	Mixed	Autonomous
Utility system fuel input	--	Electricity/Chips	Chips
Feedstock wood consumption (GJ/t _{Pulp})	41.15	41.15	41.15
Utility chips consumption (GJ/t _{Pulp})	0.00	0.88	15.31
Utility electricity consumption (GJ/t _{Pulp})	0.00	3.43	0.00
Oil consumption (GJ/t _{Pulp})	1.05	1.05	1.05
Overall plant consumption (GJ/t_{Pulp})	42.20	46.51	57.51
Extended plant consumption (GJ/t_{Pulp})¹	48.87	56.06	66.65
Rankine cycle power generation (GJ/t _{Pulp}) ²	4.26	2.05	5.67
Chemical process power demand (GJ/t _{Pulp})			
- KraftPulp Mill	2.84	2.84	2.84
- Black Liquor Treatment and Gasification	1.20	1.20	1.20
- Syngas Conditioning and Ammonia Synthesis	0	0.58	0.58
Ancillary power demand (GJ/t _{Pulp}) ³	0.14	0.22	0.41
Min. Cooling requirement (GJ/t _{Pulp}) ⁴	1.36	2.68	2.68
Min. Heating requirement (GJ/t _{Pulp}) ⁴	8.22	2.33	2.33
Fossil CO ₂ emissions avoided (tCO ₂ /t _{Pulp}) ⁵	0.00	0.00	0.00
Fossil CO ₂ emitted –direct (tCO ₂ /t _{Pulp})	0.08	0.08	0.08
Fossil CO ₂ emitted – indirect (tCO ₂ /t _{Pulp}) ⁶	0.18	0.24	0.25
- CO ₂ emitted indirect – EE grid (%)	0.00	24.38	0.00
- CO ₂ emitted indirect – Biomass (%)	98.31	74.37	98.76
- CO ₂ emitted indirect – Oil (%)	1.69	1.25	1.24
Total fossil CO ₂ emitted (tCO ₂ /t _{Pulp})	0.26	0.32	0.33
Biogenic CO ₂ emissions avoided (tCO ₂ /t _{Pulp}) ⁵	0.00	1.38	1.38
Biogenic CO ₂ emitted – direct (tCO ₂ /t _{Pulp})	1.71	0.37	1.61
Total atmospheric emissions (tCO ₂ /t _{Pulp})	1.97	0.69	1.94
Overall CO₂ emissions balance⁷(tCO₂/t_{Pulp})	1.97	-0.69	0.56
Net CO₂ emissions balance⁷ (tCO₂/t_{Pulp})	0.26	-1.06	-1.05
Biomass consumption (t _{wood} /t _{NH₃+Pulp})	3.23	2.64	3.54
Syngas production (GJ/t _{Pulp})	0.00	9.36	9.36
Ammonia production (t/day)	0.00	218.93	218.93
Pulp production (t/day)	877.83	877.83	877.83

Process parameter	Conventional	Mixed	Autonomous
Marketable CO ₂ production (kg/h)	0	50,518	50,518
Electricity export (kW)	878	0	0
Operating Incomes (euro/ t _{Pulp})	714.61	859.72	859.72
Operating Costs (euro/t _{Pulp})	-153.49	-214.64	-221.55
Operating Revenues (euro/t _{Pulp}) ⁸	561.12	645.07	638.17
Yearly Investment cost (euro/t _{Pulp}) ⁹	-262.17	-355.90	-353.97
Net Plant Revenues (euro/t_{Pulp})¹⁰	298.95	289.17	284.20
Revenues difference (Conventional case as reference)	0.0%	-3.3%	-4.9%

1. The overall exergy consumption increases if the extended efficiency of the electricity generation (55.68%), as well as of the oil (95.20%) and biomass (86.13%) supply chains are considered as [62,63]; 2. Steam pressure levels 100, 12, 4 and 0.10 bar, steam superheating 200°C; 3. Cooling tower and vapor compression refrigeration systems; 4. Heating requirements of the chemical processes (energy basis) determined from the composite curves; 5. CO₂ emissions captured through a physical absorption system; 6. It considers the indirect emissions due to the upstream supply chains of electricity (62.09 g_{CO2}/kWh), wood (0.0043 g_{CO2}/kJ_{Wood}) and oil (0.0029 g_{CO2}/kJ_{Oil}) [62,63]; 7. The overall CO₂ balance considers overall CO₂ emitted (either fossil or biogenic) minus CO₂ captured, whereas the net value subtracts the amount of CO₂ embodied by the crops, assumed as circular emissions; 8. Operating revenues (only) calculated as the difference between the gross operating incomes minus the operating cost; 9. Ammonia plant and Pulp mill investment costs scaled according to [60] and [64]; 10. Net revenues estimated as the operating revenues minus the yearly investment cost.

The avoided CO₂ emissions are related to the carbon capture system in the syngas purification section. Since direct biomass-derived emissions are considered as neutral (circular) emissions, the difference between the biogenic CO₂ captured and the overall CO₂ emitted is considered as the net balance of CO₂ emissions (see Table 3). The negative values indicate an overall positive impact towards the depletion of the CO₂ present in the atmosphere, meaning that for each ton of ammonia produced, around one ton of CO₂ is withdrawn from the environment when the alternative routes are used. As a result, the indirect emissions from the biomass utilization are not only offset by the captured biogenic emissions, but also the import of ‘greener’ Brazilian electricity leads to an attractive overall exergy consumption along with a radical mitigation of CO₂ emissions. In fact, in the integrated production facilities (mixed and autonomous cases), almost half of the power generated or imported is consumed in the Kraft pulp mill (see Fig. 3). However, the autonomous case presents the highest total power generation (5.67 GJ/t_{Pulp}), or 33% higher than in the conventional case. On the other hand, in the mixed mode configuration, there is a reduction in the power generation due to the diversification of the resources consumed, namely, a large proportion of the power demand comes from the electricity imported from the grid.

Meanwhile, the MVR drying system accounts for about 22% of the overall power consumed. Unlike the MVR systems, in the traditional drying systems, a large amount of steam must be consumed instead of power in order to increase the concentration of solid in the black liquor, leading to increased consumption of wood chips to balance the combined heat and power demands of the chemical plants. The MVR system not only allows reducing the excess steam consumption but also reduces the large driving forces arisen from the comprehensive heat exchange of steam generation. This maximizes the recovery of the thermodynamic potential by transforming low-grade waste heat into power via a heat recovery network. It is also important to notice that the air separation unit consumes about 12% of the total power generation in the utility system. Despite of this fact, this power intensive process avoids the dilution of the gasification syngas with nitrogen, which otherwise would require the integration of a downstream nitrogen separation system in order to control the suitable ratio of H₂ to N₂ required for the ammonia synthesis.

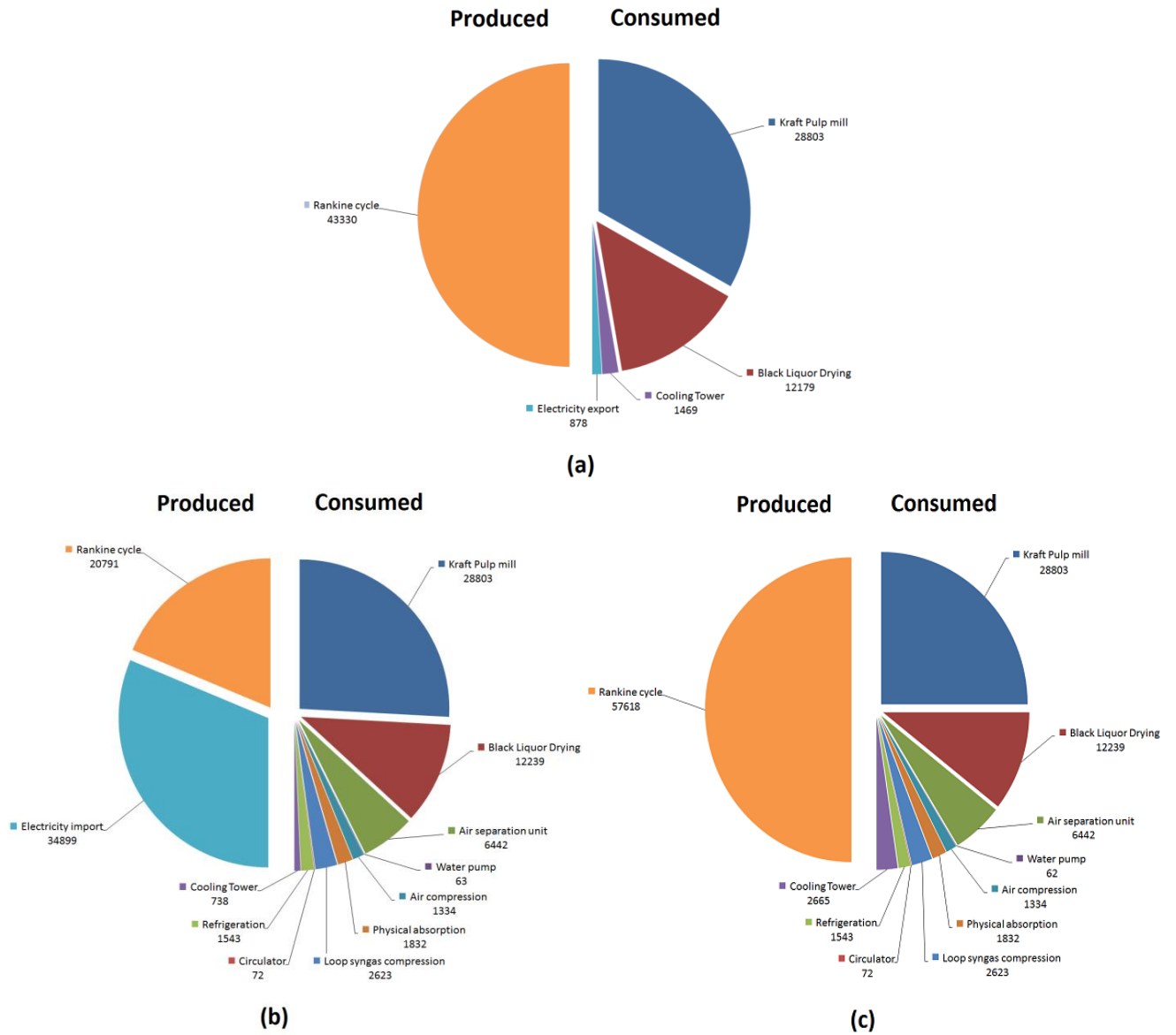


Figure 3. Power consumption breakdown (in kW): (a) Conventional configuration, (b) Mixed mode configuration, (c) Autonomous mode configuration.

Regarding the energy integration analysis, it can be observed a radical modification of the integrated curves due to the integration of an associated ammonia plant (Figs. 4b and c) when compared with conventional (standalone) Kraft pulp mill curve (Fig. 4a). Actually, a large amount of waste heat (pockets) is produced throughout the proposed chemical plants, which in turn can be recovered to preheat the process streams or raise high pressure steam, thus reducing the amount of external fuel (wood chips) imported. Moreover, a common characteristic of the tree scenario shown in Figs. 4 is the effect of the substitution of the traditional drying process based on a multiple effect evaporator by a mechanical vapor recompression system. This device allows reducing the amount of steam consumed in the concentration of the black liquor by using the waste heat available at lower temperatures to preheat the boiling feed water of a Rankine cycle that supply the compression system of the alternative drying technology.

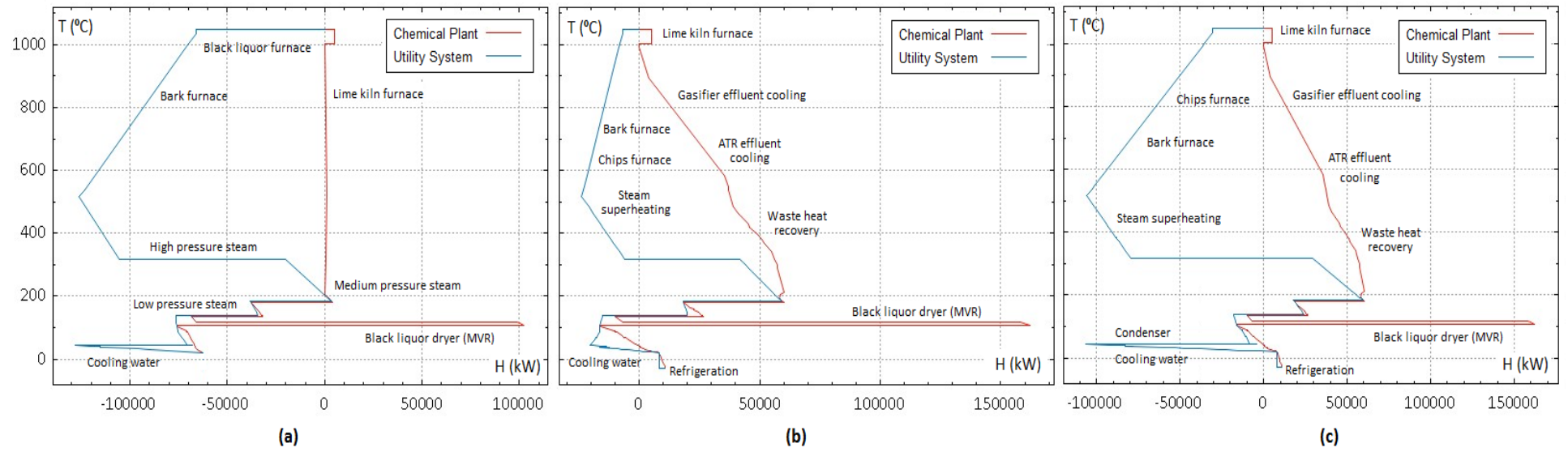


Figure 4. Integrated composite curves: (a) Conventional configuration, (b) Mixed mode configuration, (c) Autonomous mode configuration. MVR: Mechanical vapor recompression, H: Enthalpy flow rate, T: Temperature.

In contrast, in the conventional case, the heat requirements are totally supplied by the combustion of the residual bark and the strong black liquor in the recovery boiler, rendering the overall pulp production system self-sufficient in terms of both steam and power demands, and even allowing for a small amount of surplus electricity export. Unfortunately, this fact also leads to an increased amount of exergy destruction per unit of product. This is also the case of the autonomous configuration (Fig.4c), which produces both pulp and ammonia, as long as additional chips must be burned in the wood boiler to balance the energy requirements of the Kraft pulp and ammonia plants. Finally, in the case of the mixed mode (simultaneous chips and electricity import, Fig 4b), the amount of chips is dramatically reduced by maximizing the waste heat recovery and also importing the major part of the power consumed in the plant. This solution is responsible for the reduction of the irreversibility linked to the extensive heat transfer rates inherent to the other two scenarios (i.e. the standalone Kraft pulp mill and the autonomous case), as it can be evidenced by the longer span of the integrated curves along the horizontal axis H. Clearly, the most suitable solution might not be only related to the reduction of the irreversibility and chips consumption rates, since there may be a tradeoff that potentially favors the electricity import only if this condition is both economical and environmentally friendly, considering the highly renewable Brazilian electricity and the energy intensive biomass and oil supply chains.

Actually, according to Table 4, there is a significant reduction of the exergy efficiency for all the studied scenarios ranging from 14 up to 21% when the rational and extended relative efficiencies are considered. This is a consequence of the inclusion of additional sources of irreversibility such as the raw material obtainment into the originally standalone plant analyses. As concerns the exergy destruction, the mixed mode seems to outperform the other scenarios. However, by looking to the extended exergy destruction indicator, an apparently more efficient process can be deteriorated by the intensive consumption of raw materials with an important carbon footprint associated to its production, which finally results in a slightly better performance of the conventional case. As a result, better plant configurations may be offset by the performance of the extended production process.

These results can be compared with similar studies reported in the literature. Akbari and coworkers [65] studied the ammonia production from BL gasification at 27 bar and 1050°C, obtaining an energy yield of 31.07%, defined as the ratio between the HHV of ammonia and BL. For the sake of comparison, the integrated setups evaluated on the present study achieved 31.94% for this indicator. However, neither the Kraft pulp mill responsible for the production of such BL nor the utility systems that must satisfy the overall energy requirements of both pulp and ammonia production are explicitly modeled. In this way, this energy yield indicator is only based on the amount of black liquor consumed. This circumstance renders difficult the comparison with the proposed systems studied in this paper, since the interrelation between the waste heat recovery, the cogeneration system and the chemical plants is not evident in the previous work. In other words, the irreversibility associated with the conversion of the energy resources required for supplying the steam and power of the integrated systems is missing, once the proposed energy yield should account for them in order to highlight the actual specific energy consumption.

Andersson and Lundgren [66] performed a techno-economic evaluation of the simultaneous pulp and ammonia production in a Kraft pulp mill via integrated biomass gasification (bark, 30 bar and 1200°C). The authors compare a stand-alone ammonia production plant operating separately from the Kraft pulp mill, both plants consuming external wood as fuel. In a second scenario, the authors consider the energy integration of both facilities, so that the bark from the Kraft pulp mill can be used as the gasification feedstock by replacing the original bark boiler. Meanwhile, the black liquor produced is still consumed in a typical recovery boiler. The results showed that the overall efficiency calculated in terms of what the authors defined as 'electricity equivalents' (analogous to the exergy concept, but strongly reliant on arbitrary power conversion factors) for the stand-alone ammonia production plant achieves 44%, whereas for the integrated system an efficiency of 54% is obtained. According to the authors, this increment in the electricity equivalents-based efficiency is a

consequence of the enhanced utilization of bark in the gasification system and the integration of both plants. Other works [67] dealt with the evaluation of the marginal energy efficiency of methanol and dimethyl ether production by considering an additional biomass consumption, where this biomass energy is added to the pulp mill and is converted to automotive fuels via gasification of the black liquor. The overall energy efficiency of the conversion into fuels of the additional biomass added to the mill is reportedly between 65-70%, depending on the efficiency of the bark boiler. In other words, the energy efficiency is calculated for the increase of the energy flows of both biomass and motor fuels.

Table 4. Exergy destruction and exergy efficiencies for the studied configurations.

Process parameter	Conventional	Mixed	Autonomous
Rational exergy efficiency (%)	42.46%	51.63%	41.75%
Extended rational exergy efficiency (%) ¹	36.66%	42.83%	36.03%
Relative exergy efficiency (%)	42.25%	48.99%	39.62%
Extended relative exergy efficiency (%) ¹	36.48%	40.64%	34.19%
Exergy destruction (GJ/t _{Pulp})	24.28	22.50	33.50
Extended exergy destruction (GJ/t _{Pulp}) ¹	30.96	32.05	42.64

1. Overall exergy consumption increases if the cumulative efficiency of the electricity generation (55.68%), as well as of the oil (95.20%) and biomass (86.13%) supply chains are considered as reported by [62, 63].

5. Conclusions

In this work, the use of black liquor gasification in the integrated syngas and ammonia production plant is compared with the performance of the conventional conversion route (standalone Kraft pulp mill), aiming to reduce the amount of non-renewable exergy consumed and net CO₂ emissions, whereas maintaining attractive the integrated plant revenues. The combined energy integration and exergy analyses performed allowed spotting the best alternatives of utility systems that ensure competitive revenues, while maximizing the recovery of the available waste heat exergy. As a result, the exergy efficiencies of the conventional and integrated cases average 40% and 42%, respectively, whereas the overall emission balance varies from 1.97 to -0.69 tCO₂/t_{Pulp}, respectively. The negative values point towards the environmental benefits brought about by the production of chemicals through the use of alternative energy sources such as biomass. As it is evidenced, renewed efforts on research and development of more efficient conversion technologies of renewable energy sources must look towards the introduction of alternative ammonia production routes at larger scales in the fertilizer industry, in spite of the current high investment risk and less mature energy conversion technologies of biomass. Moreover, the electricity import, whether available, may help reducing the extent of the irreversibility and chips consumption rates in the integrated systems, as well as reducing the overall CO₂ emissions. Despite the increased investment cost, due to the complementary value added CO₂ and NH₃ produced, the operating revenues of the alternative configurations are not considerably impacted in comparison with the conventional route. Finally, it must be noticed that by defining extended plant consumption and efficiency concepts, the whole effect of the production process, including the inefficiencies of upstream feedstock supply chain can be evaluated. The results show to be strongly dependent on the indirect emissions, the energy resources used (chips, electricity or black liquor) and the market costs adopted for the resources and products.

Acknowledgements

The first author acknowledges CAPES Proex for her MSc grant. The second author would like to thank the National Agency of Petroleum, Gas and Biofuels, ANP (PRH/ANP Grant 48610.008928.99) and the Colombian Administrative Department of Science, Technology and

Innovation - COLCIENCIAS. The fourth author thanks to the National Research Council for Scientific and Technological Development, CNPq (grant 304935/2016-6).

References

- [1] M. R. Naqvi, Analysing performance of bio-refinery systems by integrating black liquor gasification with chemical pulp mills. PhD thesis, KTH – Royal Institute of Technology, Stockholm, Sweden, 2012.
- [2] International Energy Agency, “Tracking Clean Energy Progress 2017,” *Technology*, pp. 1–82, 2017.
- [3] D. Leeson, N. Mac Dowell, N. Shah, C. Petit, and P. S. Fennell, “A Techno-economic analysis and systematic review of carbon capture and storage (CCS) applied to the iron and steel, cement, oil refining and pulp and paper industries, as well as other high purity sources,” *Int. J. Greenh. Gas Control*, vol. 61, pp. 71–84, 2017.
- [4] E. K. Vakkilainen and H. Tran, “The kraft chemical recovery process,” *Tappi Kraft Recover. Short Course*, no. January 2015, pp. 1–8, 2008.
- [5] Y. Wang, X. Yang, M. Sun, L. Ma, X. Li, and L. Shi, “Estimating carbon emissions from the pulp and paper industry : A case study,” *Appl. Energy*, pp. 1–11, 2016.
- [6] C. Gaudreault, B. Malmberg, B. Upton, and R. Miner, “Greenhouse gas and non-renewable energy benefits of black liquor recovery,” *NCASI Tech. Bull.*, no. 984, 2011.
- [7] G. Zhang, J. Yan, H. Jin, and E. Dahlquist, “Integrated black liquor gasification polygeneration system with CO₂ Capture in pulp and paper mills to produce methanol and electricity,” *Int. J. Green Energy*, vol. 8, no. 2, pp. 275–293, 2011.
- [8] I. Bioenergy, “Black Liquor Gasification: Summary and conclusions from the IEA Bioenergy ExCo54 Workshop.” pp. 1–12, 2007.
- [9] A. Darmawan, F. Hardi, K. Yoshikawa, M. Aziz, and K. Tokimatsu, “Enhanced process integration of black liquor evaporation , gasification , and combined cycle,” *Appl. Energy*, vol. 204, pp. 1035–1042, 2017.
- [10] A. Darmawan, F. Hardi, K. Yoshikawa, M. Aziz, and K. Tokimatsu, “Enhanced Process Integration of Entrained Flow Gasification and Combined Cycle: Modeling and Simulation Using Aspen Plus,” *Energy Procedia*, vol. 105, pp. 303–308, 2017.
- [11] Å. Ab, “Energy consumption in the pulp and paper industry - Model mills 2010 Integrated fine paper mill Contents,” no. 20, 2011.
- [12] P. Bajpai, “Black Liquor Gasification,” *Black Liquor Gasif.*, pp. 1–92, 2014.
- [13] A. Darmawan, M. W. Ajiwibowo, K. Yoshikawa, M. Aziz, and K. Tokimatsu, “Energy-efficient recovery of black liquor through gasification and syngas chemical looping,” *Appl. Energy*, vol. 219, no. March, pp. 290–298, 2018.
- [14] M. Naqvi, J. Yan, and E. Dahlquist, “Black liquor gasification integrated in pulp and paper mills: A critical review,” *Bioresour. Technol.*, vol. 101, no. 21, pp. 8001–8015, 2010.
- [15] M. Marklund, “Pressurized Entrained-flow High Temperature Black Liquor Gasification CFD Based Reactor Scale-up Method and Spray Burner Characterization”. Luleå, Sweden: Luleå University of Technology; 2006.
- [16] M. Akbari, A. O. Oyedun, and A. Kumar, “Ammonia production from black liquor gasification and co-gasification with pulp and waste sludges: A techno-economic assessment,” *Energy*, vol. 151, pp. 133–143, 2018.
- [17] H. Wiinikka, A. Johansson, J. Wennebro, P. Carlsson, and O. G. W. Öhrman, “Evaluation of black liquor gasification intended for synthetic fuel or power production,” *Fuel Process. Technol.*, vol. 139, pp. 216–225, 2015.
- [18] FAO, *World fertilizer trends and outlook to 2018*, vol. 2, no. 3. Rome, 2015.
- [19] D. Frattini, G. Cinti, G. Bidini, U. Desideri, R. Cioffi, and E. Jannelli, “A system approach in energy evaluation of different renewable energies sources integration in ammonia production plants,” *Ren. Energy*, vol. 99, pp. 472–482, 2016.

- [20] P. Gilbert, S. Alexander, P. Thornley, and J. Brammer, "Assessing economically viable carbon reductions for the production of ammonia from biomass gasification," *J. Clean. Prod.*, vol. 64, pp. 581–589, 2014.
- [21] NETL, "Gasification Background, Markets for Gasification," 2014. Available: <https://www.netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/markets>. [Accessed: 29-Oct-2018].
- [22] C. Foelkel, "The Eucalyptus Wood for Pulp Production - Understanding the Construction of the Indicator of Specific Consumption of Wood for Kraft Pulp Production [In Portuguese]," *Eucalyptus Online B. Newsl.*, 2017.
- [23] IEA, "Black Liquor Gasification." pp. 1–12, 2007.
- [24] F. de A. B. Moraes, "Model for the evaluation of the specific consumption of wood and energy input in the process of pulp and paper manufacturing [In portuguese]," MSc Thesis, Araraquara University Institute, Brazil, 2011.
- [25] Rural Technology Initiative, "Chapter 8 . Pulp and Paper." Available: http://www.ruraltech.org/projects/conversions/briggs_conversions/briggs_ch08/chapter08_combined.pdf. [Accessed: 17-Sep-2018].
- [26] D. L. Bachmann, "Benchmarking of pulp mill processes," *O Papel*, n. 8, p. 66-70, 2009.
- [27] S. Consonni, R. E. Katofsky, and E. D. Larson, "A gasification-based biorefinery for the pulp and paper industry," *Chem. Eng. Res. Des.*, vol. 87, no. 9, pp. 1293–1317, 2009.
- [28] M. Naqvi, J. Yan, and E. Dahlquist, "Black liquor gasification integrated in pulp and paper mills: A critical review," *Bioresour. Technol.*, vol. 101, no. 21, pp. 8001–8015, 2010.
- [29] E. T. D. F. Ferreira and J. A. P. Balestieri, "Black liquor gasification combined cycle with CO₂ capture - Technical and economic analysis," *Appl. Therm. Eng.*, vol. 75, pp. 371–383, 2015.
- [30] S. B. Alabi, "Development and Implementation of an Online Kraft Black Liquor Viscosity Soft Sensor," PhD Thesis, University of Canterbury, 2010.
- [31] M. Moshkelani, M. Marinova, M. Perrier, and J. Paris, "The forest biorefinery and its implementation in the pulp and paper industry: Energy overview," *Appl. Therm. Eng.*, vol. 50, no. 2, pp. 1427–1436, 2013.
- [32] R. Raghuraman, "Design and simulation of a multiple effect evaporator system," National Institute of Technology Rourkela, 2011.
- [33] SOFRASER, "Black liquor recovery (concentration for combustion)," 2013. Available: https://www.sofraser.com/images/images/applications/InlineControl_Combustion_BlackLiquor_Customer.pdf. [Accessed: 07-Oct-2018].
- [34] E. K. Vakkilainen, "Kraft Recovery Boilers - High Dry Solids Firing", 2006. Available: https://www.researchgate.net/profile/Esa_Vakkilainen/publication/279871546_Kraft_recovery_boilers_-_Principles_and_practice/links/561a6dba08ae6d1730898b68.pdf. [Accessed: 20-Dec-2018].
- [35] UNIDO, "Evaluation of technologies on recovery of black liquor chemicals for small and medium size pulp mills using non-wood fibrous raw materials," 1996. Available: [https://open.unido.org/api/documents/4808393/download/Evaluation Of Technologies On Recovery Of Black Liquor Chemicals For Small And Medium Size Pulp Mills Using Non-Wood Fibrous Raw Materials \(21704.en\)](https://open.unido.org/api/documents/4808393/download/Evaluation%20Of%20Technologies%20On%20Recovery%20Of%20Black%20Liquor%20Chemicals%20For%20Small%20And%20Medium%20Size%20Pulp%20Mills%20Using%20Non-Wood%20Fibrous%20Raw%20Materials%20(21704.en)). [Accessed: 05-Aug-2018].
- [36] A.-S. Näsholm and M. Westermarck, "Energy studies of different cogeneration systems for black liquor gasification," *Energy Convers. Manag.*, vol. 38, no. 15–17, pp. 1655–1663, 2002.
- [37] A. Larsson, A. Nordin, R. Backman, B. Warnqvist, and G. Eriksson, "Influence of black liquor variability, combustion, and gasification process variables and inaccuracies in thermochemical data on equilibrium modeling results," *Energy and Fuels*, vol. 20, no. 1, pp. 359–363, 2006.
- [38] M. Appl, "Ullmann's encyclopedia of industrial chemistry," in *Ullmann's encyclopedia of industrial chemistry*, Weinheim: Wiley-VCH GmbH, 2012.
- [39] D. Flórez-Orrego and S. de Oliveira Junior, "On the efficiency, exergy costs and

- CO₂emission cost allocation for an integrated syngas and ammonia production plant,” *Energy*, vol. 117, pp. 341–360, 2016.
- [40] D. Flórez-Orrego and S. de Oliveira Junior, “Exergy assessment of single and dual pressure industrial ammonia synthesis units,” *Energy*, vol. 141, pp. 2540–2558, 2017.
- [41] ASPENTECH, “Aspen Physical Property System - Physical Property Methods V7.3.” 2011.
- [42] F. Florez-Orrego, D., Sharma, S., Oliveira Jr, S., Marechal, “Combined Exergy Analysis and Energy Integration for Design Optimization of Nitrogen Fertilizer Plants,” in *30th International Conference on Efficiency, Cost, Optimization, Simulation and Environmental Impact of Energy Systems*, San Diego State University, San Diego USA, 2017.
- [43] S. A. Channiwala and P. P. Parikh, “A unified correlation for estimating HHV of solid, liquid and gaseous fuels,” *Fuel*, vol. 81, no. 8, pp. 1051–1063, May 2002.
- [44] F. Szargut, J., Morris, D, Steward, *Exergy analysis of thermal, chemical, and metallurgical processes*. New York: Hemisphere Publishing Corporation, 1988.
- [45] M. Dellavedova, M. Derudi, R. Biesuz, A. Lunghi, and R. Rota, “On the gasification of biomass: Data analysis and regressions,” *Process Saf. Environ. Prot.*, vol. 90, no. 3, pp. 246–254, 2012.
- [46] D. T. Pio, L. A. C. Tarelho, and M. A. A. Matos, “Characteristics of the gas produced during biomass direct gasification in an autothermal pilot-scale bubbling fluidized bed reactor,” *Energy*, vol. 120, pp. 915–928, 2017.
- [47] R. A. M. Boloy, J. L. Silveira, C. E. Tuna, C. R. Coronado, and J. S. Antunes, “Ecological impacts from syngas burning in internal combustion engine: Technical and economic aspects,” *Renew. Sustain. Energy Rev.*, vol. 15, no. 9, pp. 5194–5201, 2011.
- [48] J. C. F. Macedo, “Thermal and environmental analysis of the primary sludge from pulp and paper making in biomass boiler on the grid [In Portuguese],” Doctoral dissertation, Federal University of Itajubá, 2006.
- [49] D. Gavrilescu, “Energy from biomass in pulp and paper mills,” *Env. Eng. Manag.* vol. 7, no. 5, pp. 537–546, 2008.
- [50] M. Theis, B. J. Skrifvars, M. Zevenhoven, M. Hupa, and H. Tran, “Fouling tendency of ash resulting from burning mixtures of biofuels. Part 2: Deposit chemistry,” *Fuel*, vol. 85, no. 14–15, pp. 1992–2001, 2006.
- [51] A. T. Harris, S. Riddlestone, Z. Bell, and P. R. Hartwell, “Towards zero emission pulp and paper production : the BioRegional MiniMill,” vol. 16, no. 2008, 2010.
- [52] “Oil Fuel Properties.” Available: <http://www.globalcombustion.com/oil-fuel-properties/>. [Accessed: 20-Dec-2018].
- [53] A. Demirbas, “Theoretical heating values and impacts of pure compounds and fuels,” *Energy Sources, Part A Recover. Util. Environ. Eff.*, vol. 28, no. 5, pp. 459–467, 2006.
- [54] F. Abdollahi-Demneh, M. A. Moosavian, M. R. Omidkhan, and H. Bahmanyar, “Calculating exergy in flowsheeting simulators: A HYSYS implementation,” *Energy*, vol. 36, no. 8, pp. 5320–5327, 2011.
- [55] B. Kalitventzeff, F. Maréchal, and H. Closon, “Better solutions for process sustainability through better insight in process energy integration,” *Appl. Therm. Eng.*, vol. 21, no. 13–14, pp. 1349–1368, 2001.
- [56] A. Ingham, “Reducing the Carbon Intensity of Methanol for Use as a Transport Fuel,” *Johnson Matthey Technol. Rev.*, vol. 61, no. 4, pp. 297–307, 2017.
- [57] ASPENTECH, “Aspen Plus V8.8.” Aspen technology Inc., Bedford, United States, 2015.
- [58] F. Yoo, M., Lessard, L, Kermani, M., Maréchal, “OSMOSE Lua: A Unified Approach to Energy Systems Integration with Life Cycle Assessment,” in *12th International conference PSE 2015 and 25th International conference ESCAPE 2015*.
- [59] F. Maréchal and B. Kalitventzeff, “Process integration: Selection of the optimal utility system,” *Comput. chm. Engng*, vol. 22, no. 98, pp. 149–156, 1998.
- [60] S. Florez-Orrego, D., Oliveira Jr, “Comparative Exergy and Technoeconomic Assessment of Fossil and Biomass-Based Routes for Hydrogen and Ammonia Production,” in *International*

Conference on Contemporary Problems of Thermal Engineering - CPOTE 2018.

- [61] “Excel Calculation_for_Wood_Fuel_Parameters_16_EN KLIMAActiv.” Austrian Energy Agency, Vienna.
- [62] D. Flórez-Orrego, J. A. M. Silva, and S. De Oliveira, “Renewable and non-renewable exergy cost and specific CO₂ emission of electricity generation: The Brazilian case,” *Energy Convers. Manag.*, vol. 85, pp. 619–629, 2014.
- [63] D. Flórez-Orrego, J. A. M. da Silva, H. Velásquez, and S. de Oliveira, “Renewable and non-renewable exergy costs and CO₂ emissions in the production of fuels for Brazilian transportation sector,” *Energy*, vol. 88, pp. 18–36, 2015.
- [64] M. H. Börjesson and E. O. Ahlgren, “Pulp and Paper Industry - Energy Technology System Analysis Program - ETSAP,” *IEA ETSAP - Technol. Br. 107 - May 2015*, pp. 1–9, 2015.
- [65] Akbari, M., Oyedun, A., Kumar, A. Ammonia production from black liquor gasification and cogasification with pulp and waste sludges: A techno-economic assessment. *Energy*, v. 151, p. 133-143, 2018.
- [66] Andersson, J., Lundgren, J. Techno-economic analysis of ammonia production via integrated biomass gasification. *Applied Energy*, v. 130, p. 484-490, 2014
- [67] IEA Bioenergy. Black Liquor Gasification - Summary and Conclusions from the IEA Bioenergy ExCo54 Workshop. International Energy Agency BIOENERGY: ExCo:2007:03. Whakarewarewa, Rotorua, New Zeland. 2007.