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HIGHLIGHTS

- A sawdust mixture feedstock-based biorefinery producing bioethanol was developed
- The model was based our experimental database published in bioresource technology
- The plant converts 70,088 tons/year of biomass into 11,400 tons/year of ethanol
- Pinch Analysis lead to 19.1 and 18.7 MW of hot and cold utility, respectively
- Lignin, furfural, and other chemical production might reduce overall process costs

Modeling and simulation of a sawdust mixture-based integrated biorefinery plant producing bioethanol

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7 Abstract

The design, modeling and simulation of an integrated biorefinery plant assumed to convert different forestry assortments such as sawdust or shavings (sawmill waste) into bioethanol as the main product, lignin as the most valuable by-product, pellets as solid residue, and other valuable byproducts, was carried out. The proposed cellulosic ethanol biorefinery plant was simulated with ProSimPlus. The model was based on an experimental database involving the physicochemical characterization of the raw material, an Organosolv pretreatment as the deconstruction method, and enzymatic analysis. The investigated plant size processed 70,088 tons of biomass/year, with a production capacity of 12,000 tons ethanol/year. Ethanol productivity reached 349 L/ton of dry feedstock. Considering water consumption, approximately 4.8 liters of water were needed to produce a liter of ethanol. Finally, the energy targeting through conventional Pinch Analysis lead to 19.1 MW and 18.7 MW of hot and cold utility energy demand for the entire process, respectively.

20 Keywords: Bioethanol; biorefinery modeling and simulation; biomass pretreatment;

21 enzymatic hydrolysis; integrated biorefinery

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1. Introduction

Nowadays, the transition from the petroleum economy towards biofuel economy is highly accepted on both the national and international levels (Mesfun et al., 2019). Consequently, biofuels, especially from the second-generation, have gained a huge interest in the view of the current environmental problems and oil dependence. Furthermore, lignocellulosic biomass is perceived as an attractive candidate for second-generation biofuel production because its price is estimated as being the lowest compared to starch-based feedstock currently used to produce certain biofuels, and also because it is non-competitive with agro-food cultures (Bryngemark, 2019; Chovau et al. 2013).

France is endowed with forestry that can potentially provide a sustainable source of lignocellulosic biomass for bioethanol production. According to the national forest inventory, the forested mainland in France covers 17.10⁶ ha. This corresponds to an afforestation rate of 29.7% of the territory close to the world rate and which is also increasing. It includes 136 species of trees (Rametsteiner et al., 2007). Therefore, the local wood processing industries generate a significant amount of multisource sawdust and other wastes, especially from softwood. However, if these multisource wastes were to be converted into biofuels, they could allow satisfying a wide part of energy demand, which is still mainly covered by petroleum products. Moreover, this will create a new opportunity for the forestry sector to contribute to the development of a reliable and sustainable national energy model that fits well with the energy transition policy and the fight against climate change (Sarks et al., 2014).

Sawdust from the sawmill industry is a low-cost industrial residue that contains a significant amount of carbohydrates with the potential to be a raw substrate for bioethanol production in a biorefinery plant. Its use could promote local valorization of wood waste with a view of setting up a forest biorefinery. Its chemical structure is mainly constituted of cellulose, hemicellulose, and lignin, which makes it recalcitrant to deconstruct, thereby limiting enzyme

ability to convert cellulose and hemicelluloses into sugars (Mupondwa et al., 2017). Hence, in order to make sugars available for bioconversion, four key steps are needed. First, the *pretreatment process* is compulsory to overcome the barrier that lignin constituted in the substrate. Thus, this step allows the destruction of the sawdust matrix to make the cellulose more accessible to the enzymes. Afterward, the pretreated solid is either *chemically* or *enzymatically hydrolyzed* to transform cellulose and hemicelluloses into sugars. Third, *fermentation* is performed on the rich sugar hydrolysate from the previous step to transform the latter into ethanol, and finally, *distillation* allows the separation of ethanol from the fermentation broth.

The pretreatment stage has been identified as the real technological and economic barrier to the development of lignocellulosic-based bioprocesses. Efficient pretreatment step is, therefore, essential to fractionate lignocellulosic structures for subsequent chemical transformations. An efficient pretreatment process must be able to reduce the crystallinity of the cellulose within a reasonable time, improve the accessible area for the extraction of desirable components, and increase the hydrolysis rate after pretreatment (Agbor et al., 2011; Chin et al., 2020).

Organosolv pretreatment is a promising pretreatment for lignocellulosic materials. The concept of this process was derived from paper industry as an alternative to Kraft pulping and sulfite process, overcomes several inconveniences, such as severe water and air pollution (Bajpai, 2018; Tribot et al., 2019; Zhou et al., 2018). It is based on the extraction of lignin and hemicelluloses from wood materials using organic solvents with or without a catalyst (Zhang et al., 2016). However, the use of a catalyst (mineral acids, bases, or organic acids) allows to lower the pretreatment temperature (Tribot et al., 2019). The optimal temperature and exposure time are also interrelated. In general, a shorter exposure time requires a higher temperature and vice versa (Chin et al., 2020). Commonly used organic solvents in

Organosolv pretreatment are ethanol, methanol, acetone, or a mixture of water and organic solvent at temperatures ranging from 100 to 250 °C applied for a specific time (30–150 min). Low-boiling alcohols, such as methanol and ethanol, appear to be the most suitable organic liquids for use in Organosolv processes due to their low cost and easy recovery (Brosse et al., 2019; Zhao et al., 2009). Finally, ethanol is by far safer and preferred to methanol because of its low toxicity (Borand and Karaosmanoğlu, 2018; Zhao et al., 2009).

In the present work, a computer model able to simulate the conversion of second-generation sawdust feedstock to the bioethanol process is developed. Possible applications already documented refer to actual demonstration factories currently in operation or under construction in the European Union (Gnansounou and Dauriat, 2010). Such a tool is devoted to apprehending the main steps of the process, focusing on key aspects from the perspective of engineering thermodynamics. It provides a useful tool for the preliminary analysis of various plant configurations, allowing a potential reduction of costs for the plant. Mass and energy balances are modeled to allow a comparison between various technological solutions. This tool also notably makes it possible to assess the potential recovery of waste streams from the main process, in particular about lignin-rich residues. An Organosolv process based on ethanol/water mixtures as the solvent was selected to fractionate sawdust feedstock into its main components. Alio et al. (2019) investigated for the first time the fractionation of sawmill mixed feedstock of four softwood species using a microwave-assisted Organosolv pretreatment. Subsequently to this study, hydrolysis and fermentation steps of a pretreated feedstock were carried out (Abdou Alio et al., 2020). The ProSimPlus simulator is a powerful tool to carry out process simulation which is able to model the bioethanol production plant using lignocellulosic waste feed, such as sawdust or other residues. The chemical composition of sawdust and other streams of the process measured experimentally in previous works was used as the starting point in the simulation of the biorefinery to produce lignocellulosic

bioethanol using ProSimPlus as a process simulation software. The design of the plant
included not only the Organosolv pretreatment, the enzymatic hydrolysis, and the
fermentation steps, but also focused on distillation for ethanol recovery, water-saving, and
energy integration. Lignin is recovered as a co-product for further use in added-value
biocomposite materials (Tribot et al., 2019).

According to Rodrigues Gurgel da Silva et al. (2018), only a few researchers have turned their
attention to investigate the synthesis, design, and process simulation of a large-scale
Organosolv plant. Thus, the originality and the main objective of this paper is to fill this gap
and develop a detailed process using the theoretical concepts and the experimental results
(yields and compositions) from previous investigations (Abdou Alio et al., 2020; Alio et al.,
2019) as a starting point to develop simulation of mass and energy balances based of an
Organosolv pretreatment.

13 2. Materials and methods

The ethanol biorefinery process design in this study is adapted from previous works by NREL (National Renewable Energy Laboratory) according to Humbird et al. (2011) in order to include an Organosolv instead of a dilute-acid pretreatment. Thus all the data summarized in **Table 1** were collected from the technical investigation of the feedstock for all bioethanol processes step (Abdou Alio et al., 2020; Alio et al., 2019). As said earlier, these data were used as the starting point for the modeling and simulation activities in this assessment to obtain ethanol and other chemicals from the sawdust material.

As major assumptions made for this analysis, a typical large-scale production plant is
considered: the amount of waste collected by the company is 200 tons/day; the moisture
content of which is estimated at 40%, which gives 120 tons of dry biomass processed per day.

It is also considered an operating period of 350 days per year which is the equivalent of 8410 hours/year (96% process uptime).

2.1. Modeling and simulation

The simulation of ethanol production from lignocellulosic biomass was carried out using ProSimPlusTM3.6. ProSimPlus is a French powerful software for running a multiphase process developed by PROSIM S.A. (Labège, France), including reliable thermodynamic data and comprehensive databases. For the current research, the NRTL (non-random two-liquid) property thermodynamic models were mainly used in the simulations. Ideal Gas was used for the simulation of combustion gases and NBS/NRC steam tables model was used in the simulation of water utilities. Components from ProSimPlus data banks were used whenever possible. The components and the properties which were not available in the software databases were obtained from the NREL data banks for production from lignocellulosic biomass and added in the model. Consequently, the BIODFMS3 physical properties database published by NREL was implemented and used in this study (Aden et al., 2002). As mentioned earlier, the simulations considered the setup of a plant processing 200 tons of feedstock per day.

17 2.2. Process model overview

The conventional NREL process model comprises nine following areas: feed handling, pretreatment and conditioning, enzymatic hydrolysis and fermentation, cellulase enzyme production, product recovery, wastewater treatment, storage, combustor, boiler and turbogenerator, and utilities.

In this study, only eight areas were studied, as shown in Fig. 1: commercial enzymes were
used without local production. Simulation of water treatment is simplified to implement water

recycling. The process produces bioethanol and lignin, while the solid residues in addition to fresh bark to provide the hot utilities of the process; solvent and water are recycled. The process model description is summarized below.

2.2.1. Part 0: feedstock handling

The feedstock was collected and supplied from different surrounding sawmill industries as sawdust; hence, comminution was not included explicitly in this study. The transportation distance (between 50 and 100 km) of sawdust was estimated based on land patterns in France.

8 2.2.2. Part 1: Organosolv pretreatment

9 Sawdust mixture was stored in a sufficient amount to ensure the continuous operation of the 10 biorefinery. The feedstock was transported by a conveyor to a mixer (M101) where an 11 ethanol/water mixture (60:40 v/v) was added to the reactor in a solid-to-solvent ratio of 1:16 12 (w/v) (Fig. 2). As a catalyst, sulfuric acid was added in a total of 0.25% (w/w) to dry wood 13 sawdust matter. The mixture was sent to the pretreatment reactor (R101). The reactor 14 operated at 175 °C and 14 bars of pressure with a total residence time of 60 min. Once the 15 reaction is done, the pressure was reduced to atmospheric.

16 2.2.3. Part 2: Lignin and solvent recovery

The flashed reactor effluent was then separated in gas-liquid separator **S201** (Fig. 3). The evaporated solvent was sent to the solvent recovery columns and the pretreated mixture was filtered by passing through **S202** solid-liquid separator to obtain a solid-rich pulp (PULP), and another liquid-rich stream (Liq.) called black liquor. The wet solid fraction was mainly constituted of cellulose, while the liquid fraction contained dissolved hemicelluloses, lignin, and the remaining solvent. The solid stream was sent to a two-stage washing step (**M201** et **M202**), where a mixture of ethanol/water with the same concentration as in the reaction stage

was used, first, for cleaning the fibers and to recover some of the solvent and the remaining lignin. The resulting washing effluent was mixed with the liquid-rich stream, which can be treated to recover by-products (Organosolv lignin, furfural, HMF (5-hydroxyl-

methylfurfural)), and solvent. The second stage of the washing process was performed with water in a solid/water ratio of 1:2 to remove the remaining solvent present in the solid-rich stream. After the washing process, the pulp was sent to the mixing tank reactor (R301) for enzymatic hydrolysis (part 3).

The total effluent streams composed of washing solvent, water, and a by-product as degraded cellulose (glucose), hemicellulose (xylose) and lignin were sent to the mixing tank (M203) so that all the by-products and solvent can further be recovered (Fig. 3). First, sulfuric acid was added to the mixing tank to allow the precipitation of lignin which will later be separated by filtration S204. This lignin is called Organosolv lignin. The liquid stream was treated with two distillation columns. The first distillation column (C201) was used to separate the solvent from the fermentable sugars (xylose and glucose) that were afterward sent to the fermentation reactor (R302). After, the first distillation, the sugars-free stream (C018) was sent to a second column (C202) where the ethanol at the top column was distilled to be recycled and re-used at the pretreatment step. The water stream (C022) at the bottom of the column was forwarded to the water treatment and recycling part (Part 6). This area allows reducing the fresh makeup solvent required.

2.2.4. Part 3: enzymatic hydrolysis and fermentation

Several studies used separate hydrolysis and fermentation processes in their analysis. It was decided to use a similar setup in this study (Fig. 4), but data for modeling and simulation were modified, accounting for the raw materials from the Organosolv process applied to sawdust

and for the experimental results of fermentation and hydrolysis assays (Abdou Alio et al., 2020).

2.2.4.1. Enzymatic hydrolysis

The hydrolysis of the pulp stream can be performed by enzymes or acids (diluted or concentrated) catalysis. For bioethanol production using lignocellulosic materials, the enzymatic hydrolysis was demonstrated to be the most promising way for converting cellulose and hemicelluloses into simple sugars. Thus, the washed solid-rich was subjected to hydrolysis under a specific substrate charge. More specifically, the solid-rich stream reached the R301 reactor (Fig.4) where it was diluted to a solid content of 10% (w/w) in a 50 mM buffer (pH 5). The enzyme used was Cellic® Ctec2 (A/S, Bagsvaerd, Denmark) with a total enzyme amount of 18.42 g per kg of the slurry. The enzymatic hydrolysis occurred at 50 °C in R301 for 12 days. This step requires the use of several reactors in parallel for enzymatic hydrolysis to ensure continuous production.

14 2.2.4.2. Fermentation

Several microorganisms, such as bacteria, fungi, and yeast can ferment sugars to bioethanol. The most employed microorganism in fermenting carbohydrates from lignocellulosic is the yeast Saccharomyces cerevisiae, due to its high tolerance and robustness to inhibitory compounds. Consequently, after 12 days of hydrolysis, the stream from the enzymatic hydrolysis was further cooled up to 30 °C, mixed with the sugars recovered from C201, and sent to the fermentation reactors (R302), where Saccharomyces cerevisiae strain was added to the hydrolysate (Fig. 4). The fermentation took place in a 24 h time and had an initial inoculum level of 10% volume. Subsequently to the fermentation, the beer broth was sent to a beer well for separation and further ethanol purification.

2.2.5. Part 4: Ethanol recovery

After fermentation was finished, the fermentation broth consisted of ethanol, a variety of undesired co-products, and a large portion of water. Therefore, there are several technologies convenient for ethanol purification, such as pervaporation, multiple column distillation, liquid-liquid extraction, and so on, that use the differences in the physical and chemical properties of ethanol from unwanted products as the driving force for separation. Depending on the product that needs to be recovered and the composition of the mixture, an appropriate separation technology must be chosen. Hence, in this study, ethanol recovery was carried out in a multi-column separator (Fig. 5) similar to the one proposed by Aden et al. (2002). First, the fermentation broth was sent to a flash process to remove the main part of the carbon dioxide present in the flow (C047), and the resulting flow stream was sent to the mixer (M401). From this mixer, the broth was directed to the first distillation column (C401) where three streams were separated. The overhead stream was rich in carbon dioxide and contained about 13% (w/w) ethanol. This flow could be mixed with the fermentation vent and sent to a vent scrubber (C402), where water was added in a counter-current configuration to recover ethanol present in the vapor phase. The effluent from the scrubber was returned to the beer well. The bottom product of the distillation column contained the unreacted and dissolved solids, which can be dried and burnt for energy production (Part 6). Finally, an intermediate withdrawal containing 42% (w/w) ethanol, i.e. 99.5% of the total ethanol from the R302 effluent, was sent to the rectification column (C403). It was then purified to the nearest azeotropic point, and then, sent to the molecular sieves to decrease residual water. Two streams left the molecular sieves: ethanol at 99.5% (w/w), and lower concentration ethanol (72%) that could be returned to the distillation column. The rectification column bottom containing less than 0.1% (w/w) ethanol was sent to water recycling.

2.2.6. Parts 5, 6 and 7

The residual solids and dissolved sugars from the beer bottom were concentrated through a triple-effect evaporator as proposed by Aden et al. (2002). Solids were removed after the first effect and concentrated syrup was recovered after the third effect; both were mixed and sent to a combustion chamber at a moisture content of 51%.

Part 6 was dedicated to water treatment. Main assumptions are total removal of organic dissolved matter and 1.0% of entering water is not recycled. The current publication provides a supplementary figure that shows the generalized flowsheet (**supplementary data 1**)

Finally, part 7 provided the hot utilities of the process by burning the unreacted solids and sugars concentrated in Part 5. Another wood waste fresh bark was also burnt in the combustion chamber to meet energy requirements. Additional 200 t/d of fresh bark, whose composition is given in Table 1, were necessary to produce 900 t/d of steam at 60 bars and 478 °C. This steam was used in a Rankine cycle at four levels of pressure respectively 60, 10, 2, and 0.125 bars. The cycle was simulated with three turbines to produce electricity and two withdrawals at intermediate pressures of 10 and 2 bars, respectively, to provide hot utilities to the process (supplementary data 2).

17 2.3. Key technical parameters

The key technical parameters used in ProSimPlus simulations were obtained from Alio et al. (2020) and Alio et al. (2019), as mentioned earlier. In the pretreatment stage, most of the hemicelluloses are degraded into xylose and furfural, and the crystalline structure of most of the cellulose is broken down, increasing enzyme accessibility to the cellulose for hydrolysis step before the fermentation step. Enzymatic hydrolysis includes cellulose and hemicellulose conversion into sugars. Fermentation of C5 and C6 sugars are also considered. **Table 2** summarizes the data needed to simulate the process.

2.4. Heat integration

The ProSimPlus simulation showed that hot and cold external utilities were required to meet the needs of ethanol production utilities. Since external utilities are expensive and require large quantities, the ability to integrate heat between processes was investigated using process pinch technology. In this article, an integrated ProSimPlus module was used to apply process pinch analysis. Pinch Analysis established a hot and cold composite curve from the available hot and cold streams in the flow diagram. Later, the two composite curves built from the hot and cold streams were compared with each other at a minimum approach temperature to determine the possible amount of heat exchange (integration) between the hot and cold flows. This integration of heat between processes reduced the external hot and cold energy requirements of a production circuit. In this work, the minimum approach temperature ΔT_{min} of 10 °C was used for the pinch analysis. Hot effluents of the process were integrated in the calculations by cooling down to a temperature of 25 °C. Phase change was linearized for the calculations in the pinch module.

3. Results and discussion

This process model was set up to assess the viability of a second-generation ethanol production process, which uses a mixture of sawmill waste of softwood as the feedstock, biomass widely available in Auvergne-Rhône-Alpes region (France) as a forest residue or from dedicated short-rotation forestry. An efficient conversion process of the cellulosic and hemicellulosic biomass into liquid ethanol, combined with a valorization of the lignin content, would allow an energy conversion that would meet the ever-growing energy demand. The simulation considered the scale-up of the laboratory and pilot-scale systems used to estimate the data to produce significant results in terms of mass and energy balances for the design and

the development of new industrial perspectives. However, the results presented in this section will focus first on mass balances.

3.1. Ethanol production mass balance

The analysis of the ethanol production simulation process from lignocellulosic residues is turned towards process productivity. In this case, from the initial 200 tons of sawdust feedstock per day, simulations showed that the product stream from Organosolv pretreatment yielded 33.11 tons of ethanol per day (1380.2 kg of ethanol/h), as shown in the C063 stream (Table 3). The ratio between ethanol production expressed in liters and the mass of dry biomass consumed expressed in tons is, therefore, 349 L/ton. In detail, almost all the glucose was consumed during the fermentation. This was mainly obtained in the enzymatic hydrolysis step. In the pretreatment step, only a small fraction of cellulose was converted into glucose. In this sense, the cellulose conversion was limited to 16.2%. In the enzymatic hydrolysis, the conversion of cellulose into glucose reached 80%. However, it arises that 35% of the hemicellulose of the raw materials remained unconverted in the process, probably due to the lack of efficiency of S. cerevisiae for converting xylose into ethanol. It must be mentioned that the combination of columns C201 and C202 allowed to remove the furfural from the sugars produced in the pretreatment reactor (0.7 t/d of furfural in stream C011 and 0 in stream C046). Consequently, the conversion into ethanol could be raised by recycling those sugars (stream C044 and C046) into the fermenter R303 without any risks of inhibition.

The results thus highlighted an ethanol production of approximately 11,600 tons of ethanol/year with a biomass feed of 42,052 tons of dry biomass per year, which is in the common range found for this kind of process. For example, for the same quantity of dry feedstock, Porzio et al. (2012) obtained less than 10,000 tons of ethanol/year by using a twostage dilute acid steam explosion pretreatment and a productivity of only 303–316 L/t dry

biomass. The results also outperform the simulations of the diluted acid process reported by Rodrigues Gurgel da Silva et al. (2018). Conversely, based on an Organosolv process modeling on the same feedstock quantity, their simulations yielded a higher ethanol production of 11,922 tons of ethanol/year. But this ethanol amount was achieved because the authors considered a high conversion of both xylan and cellulose into convertible sugars, thus into ethanol. First, it must be pointed out that the present work uses a mixture of softwood species as the feedstock, contrary to the literature which always deals with a unique wood specie. This drawback was partially counterbalanced by a higher ethanol concentration achieved in the fermentation in the present study (12.7 % w/w) than in Rodrigues Gurgel da Silva et al. (2018)'s case (11.1% w/w), which highlights the effectiveness of our pretreatment. In addition, C5 fermentation was not favored in this work, as stated above, so that ethanol production could still be enhanced by fermenting xylose in the residue (**C057**) so that ethanol productivity could outperform the literature in this case.

Finally, **Table 4** illustrates these statements by displaying a detailed comparison of ethanol
concentration in the fermenter, and ethanol productivity values with the literature.

3.2. Water mass balance

Water consumption in the biochemical conversion process is generally considered high
compared to a thermochemical pathway process or even a petroleum-based fuel process, in
terms of a liter of water used per liter of fuel produced (L/L).

The overall water balance according to the simulation results indicate the water consumption. Additional water enters the process via the raw material and raw chemicals, both as free water, and "potential" water, i.e. the burning product of lignin and unconverted sugars. Also, water is utilized in the hydrolysis reactions. Based on actual make-up water flow, the current design needed water consumption of 8417 kg/h versus 8760 kg/h from Humbird et al. (2011) for a plant that has the same feedstock throughput, using an acid-based pretreatment.

 Conversely, 8332 kg of water/h were consumed according to Rodrigues Gurgel da Silva et al. (2018) flowsheet design using an Organosolv pretreatment under the same feedstock throughput. However, based on the detailed ethanol yield from the ProSimPlus simulation, the water consumption in the design, about 4.8 liters of water used per liter of ethanol, was nearly the same as that obtained in the Organosolv simulations of the literature and far lower than in the NREL study (7.65 L/L) or with diluted acid pretreatments (**Table 4**). The key advantage of the Organosolv pretreatment, as already emphasized by the literature, is that it saves water in comparison to conventional acid or steam explosion processes. In order to be economically feasible, the overall process needed to recover as much as possible the solvent (water and ethanol) used in the process. Based on the simulation data gathered in **Table 3**, up to 99.9% of the ethanol and 99% of the water that were used initially were recycled. But the recovery increased the whole process energy demand.

13 3.3. Energy balance

All hot and cold process streams extracted from a flowsheet model of the studied case design were listed in **Table 5**. By summing all thermal loads of all cold and hot flows, the maximum hot and cold utility requirements of the studied case were obtained. Thus, the hot and cold utilities demand represented 19.1 and 18.7 MW, respectively. Among this demand, distillation columns were the most important part of the energy consumption respectively 65% for boilers and 71% for condensers. The energy per ethanol produced was 27.4 kWh per kg of ethanol.

This energy demand is consistent with the data from the literature (Table 4). For an Organosolv process, Rodrigues Gurgel da Silva et al. (2018) found 18.7 and 15.0 MW as utility requirements and 23.9 kWh per kg of ethanol. The difference between their simulations and this work is the simulation of part 5 which is the evaporation of the solids and syrup that requires hot and cold utilities. Without part 5, the energy falls to 24.0 kWh/kg of ethanol. On

the other hand, the acid diluted process is much less energy-intensive (13.2 kWh/kg of ethanol). The origin of the rather high energy demand of the whole process can be identified in the solvent recycling unit. This counterbalances the higher ethanol productivity and water efficiency of the Organosolv process. In particular, ethanol as the solvent must be recycled and an important amount of water is required in the pretreatment process to dilute ethanol and to cause lignin precipitation. The water terminates in the solvent recycling system, which requires the highest energy input.

3.4. Pinch Analysis and further heat integration

Based on the data of Table 5, the next step in the Pinch Analysis is to determine energy
targets. The energy targets represent the minimum amount of utilities required to meet the
process flow requirements (Ghannadzadeh and Sadeqzadeh, 2017). As mentioned in section
2.4, this was done by plotting composite cold (blue) and hot (red) process curves, as shown in
Fig.6a.

The hot and cold composite curves give an idea of the heat availability and heat demand in the process, respectively. The pinch temperature was evaluated at 90.2 °C. According to **Fig. 6a**, the potential of heat recovery is not very high on this process as the overlay between hot and cold composite curves is rather partial. Maximum energy recovery (MER) was estimated at 2.7 MW. Consequently, the hot and cold utilities demand could be reduced from 19.1 and 18.7 MW to respectively 16.4 and 16.0 MW which would represent less than 15.0 % of heat integration on the process. There are two main reasons for this poor heat recovery potential:

(*i*) the flash after the pretreatment reactor (R101) does not allow to use a hot stream at 175 °C
that is why the hot composite curve for Fig. 6a does not reach 175 °C that would raise the MER.
The evaporated solvent after the valve V101 represents nonetheless a heat integration because
it reduces the energy demand of column C201 by vaporizing the feed of column.

(ii) the level of temperature (pressure range) on the distillation columns (**C201**, **C202**, **C401**, and **C403**) does not allow the heat transfer between condensers and boilers although enthalpy fluxes of condensers are higher than the boilers' one.

The grand composite curve confirms that heat recovery in the process is limited. Only small pockets of self-sufficient process to process heat transfer can be seen in Fig. 6b in the cooling area: between 90 and 86 °C, between 73 and 57 °C for example. The residual cooling necessity (15.9 MW) was obtained thanks to water from 12 to 25 °C with a volumetric flow rate of 25375 m^{3}/d . Concerning the hot utilities, two levels of pressure steam were selected: 10 bars high pressure (HP) steam at a condensing temperature of 179.9 °C for temperatures higher than 106.9 °C and 2 bars low pressure (LP) steam at a condensing temperature of 120.2 °C for temperatures between 106.9 °C and the pinch temperature. The unreacted sugars and solids could only partially generate required steam that is why available fresh bark was added to match hot energy requirements. The HP and LP hot utilities steam represented in Fig. 6b were those produced by the Rankine cycle of part 7. 175 t/d and 470 t/d of HP and LP steam, respectively, were withdrawn for heat transfer on the process. The condensed vapors were then used to preheat water before the cycle boiler. The Rankine cycle could also produce 6887 kW of electricity, but $10265 \text{ m}^3/\text{d}$ of freshwater was also needed for the cycle condenser.

18 3.5. Effect of co-product markets in production cost

According to **Table 3**, it can be noticed that the amount of unreacted **Residue** in the production stream **C057** of 21 tons/day which corresponds to 7,344 tons/year is mainly composed of 58% lignin, 32% cellulose, 8% hemicellulose, and 1.7% others. In the present simulations, these unreacted solids were further burned in a perspective of cogeneration, increasing the capacity of heat integration for the process. In another perspective, this solid residue can be used as pellets, but this would increase external energy demand. Furthermore, the potentiality for selling by-products, which are transformed into value-added by-products in the ethanol production plant, also has the prospective for reducing production costs. Outstandingly, expenses occurred in treating industrial effluents to avoid serious pollution problems. For example, Organosolv lignin (18.96 tons/day which represents 6,644 tons of lignin/year) can be purified and transformed into marketable products, i.e. powder lignin that helps balance the economics of the overall production process. Potential applications have been reviewed by Tribot et al. (2019). This will result in cost savings that come either from reduced waste handling costs or from the generation of revenue from the sale of by-products. The consequence is that the economic analysis of the Organosolv process is still difficult to assess, as it strongly depends on the co-products.

4. Conclusion

Process simulations demonstrate that an ethanol/water Organosolv pretreatment could be successfully applied to a mixture of softwood species in a forest biorefinery. An ethanol productivity of 349 L/ton of dry biomass is achieved. The biorefinery design enhances water and ethanol savings (4.8 L/L ethanol, and 99% recovery, respectively), at the expense of energy requirements (10.9 and 8.6 kWh/L ethanol for hot and cold utilities, respectively). The plant converts 70,088 tons/year biomass into 11,400 tons/year ethanol. A better understanding of the process was achieved, but further research on the valorization of co-products must help balance the economics of the overall process.

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	1	Figure captions
1 2 3 4	2	Fig. 1: Simplified bioethanol production hierarchy block diagram
5 6 7	3	Fig. 2: Simulation flowsheet of the Organosolv pretreatment
8 9 10	4	Fig. 3: Simulation flowsheet for lignin and solvent recovery
11 12 13 14	5	Fig. 4: Simulation flowsheet for hydrolysis and fermentation steps
15 16 17	6	Fig. 5: Simulation flowsheet of the setup for ethanol separation and purification
18 19 20	7	Fig. 6: Pinch Analysis results curves of the biorefinery: a) composite curves representing hot and
21 22	8	cold streams with ΔT_{min} =10 °C; b) grand composite curve with hot and cold utilities simulated
23 24 25	9	for the process
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Table captions

2 Table 1: Main process data for simulation of ethanol production from wood waste

 Table 2:
 Key technical parameters

 Table 3: Process streams mass balance in tons/d of the flowsheet

Table 4: Comparison of process data between the present studied case and one from the
literature (Rodrigues Gurgel da Silva et al., 2018) for an alternative Organosolv and a diluted
acid pretreatment

Table 3: Hot and cold streams data of the process including all the different process 9 sections(supply temperature T_{in} ; target temperature T_{out} ; heat energy Q; heat capacity $F \cdot C_p$)













Features	Values
Feedstock:	
Sawdust	Cellulose 44.3% \pm 0.5% (dry wt.), hemicellulose 25.6% \pm 0.2% (dry wt.),
Composition	lignin 26% ± 3% (dry wt.)
Moisture content	40%
Bark	Cellulose 28.3% \pm 1.2 % (dry wt.), hemicellulose 13.0% \pm 0.8% (dry wt.),
Composition	lignin 52% ± 4.2% (dry wt.)
Moisture content	20%

Reactors:

Τ	Pretreatment	Enzymatic	Ethanol by			
Type	Organosolv	Hydrolysis	Fermentation			
0.1	Ethanol/water	N 7 4	XX 7 4			
Solvent	(60:40)	Water	water			
Catalvat	U SO	Cellulase and	Saccharomyces			
Catalyst	$H_2 SO_4$	hemicellulase	cerevisiae			
Contraction	0.250/	18.42 g	10% of fermentation			
Concentration	0.25%	per kg of slurry	volume			
Temperature	175 °C	50 °C	30 °C			
Pressure	13.8 atm	1 atm	1 atm			
Residence time	60 min	12 days	24 h			
рН	-	5	5			

Separations:

Solvent recovery	Concentration C201	Rectification C202
Number of stages	15	40
Stage efficiency	57%	57%
Feed stage	2	25
Reflux ratio	0.03	1.0
Condenser	Total	Total
Pressure	1.0 atm	1.0 atm

Ethanol recovery	Concentration C401	Rectification C403			
Number of stages	32	60			
Stage efficiency	48%	57%			
Feed stage	2	40			
Reflux ratio	3.0	3.2			
Condenser	Partial	Partial			
Pressure	2.1 atm	1.9 atm			
Additional	Withdrawal stage 8	Feed stage 20			
Scrubber	Absorption column C402 (5 stages,	1.0 atm, non-isothermal)			
Ethanol Pressure swing adsorption molecular sieves C404 (95.0 °C, dehydration					

Table 1:

Technical parameters		Yield
Pretreatment	Cellulose to glucose	16.5%
	Hemicellulose to xylose	81%
	Lignin removal	45.8%
	Ash	0%
	Extractives	100%
Enzymatic hydrolysis	Cellulose to glucose	80%
	Hemicellulose to xylose	60%
Fermentation	Glucose to ethanol	99%
	Xylose to ethanol	64%

C024	Water Treat.	157.7	ı	·	ı	ı	ı	ı						I			157.7	25.0	1.0		
C063	Ethanol	0.2	ı	33.1	ı	ı	ı	ı	I	ı	ı	ı	ı	ı	ı	ı	33.3	92.1	1.7	•	
C058	C403	49.6	0.0	33.1	I	ı	0.0	0.0	I	0.0	0.0	I	0.0	I	0.5	0.0	83.2	112.1	1.9	1 0	
C057	Residue	224.5	I	0.0	0.0	0.5	11.2	6.7	1.7	12.2	I	0.5	1.2	0.4	5.0	0.8	267.0	123.4	2.1		
C055	C401	274.1	0.5	33.2	0.0	0.5	11.2	6.7	1.7	12.2	0.0	0.5	1.2	0.4	5.5	0.8	350.8	100.0	2.1	0.0	
C047	R302	232.1	31.6	33.1	0.0	0.5	11.2	6.7	1.7	12.2	0.0	0.5	1.2	0.4	5.5	0.8	339.9	45.3	1.0	0 1	
C046	M302	232.1	I	I	0.0	50.0	31.9	6.7	1.7	12.2	0.0	0.5	1.2	0.4	ı	0.8	339.9	30.0	1.0		
C044	R301	107.7	I	I	ī	41.4	5.8	6.7	1.7	12.2	0.0	0.5	1.2	ļ	I	0.8	177.8	50.0	1.0	T	
C020	E202	56.7	I	I	0.0	8.6	26.2	0.0	I	0.0	0.0	I	I	ļ	I	0.0	91.4	30.0	1.0	ı	
C101	Org. lignin		ı	ı	0.7	ı	ı	ı	I	18.9	ı	ı	ı	I	ı	ı	19.6	48.5	1.0	P	
C015	Liq	169.7	I	74.1	0.7	8.6	26.2	ı	I	18.9	0.4	ı	ı	I	ı	ı	298.6	48.5	1.0	I	
C016	Pulp		I	ı	ı	I	I	44.4	6.8	12.2	0.0	ı	ı	ı	I	0.8	64.1	33.2	1.0		
C011	R101	136.0	I	180.0	0.5	8.6	26.2	44.4	6.8	31.1	0.7	I	I	I	I	0.8	435.0	174.6	13.8	0.4	-
C009	E101	139.5	I	180.0	0.5	I	I	53.2	30.7	31.1	0.0	ı	ı	ı	I	ı	435.0	175.0	13.8	0.4	-
C006	Fresh sawdust	76.7	ı	ı	ı	I	I	53.2	30.7	31.1	ı	ı	ı	ı	ı	ı	191.7	25.0	1.0	,	
	Streams	Water	Carbon dioxide	Ethanol	Sulfuric acid	Glucose	Xylose	Cellulose	Hemicellulose	Lignin	Furfural	Cellobiose	Enzyme	S. cerevisiae	Acetic acid	HMF	Total flow (t/d)	T (°C)	P (atm)	Vap. fraction	(m/m)

	Studied case ^a	Organosolv ^b	Diluted acid ^b
Ethanol productivity (kg/h)	1380.2	1417.2	1271.7
Ethanol concentration (% w/w)	12.7	11.1	5.4
Hot utilities (MW)	19.1	18.7	11.7
Cold utilities (MW)	18.7	15.0	5.1
Total energy (MW)	37.8	33.7	16.8
Energy (kWh)/kg of ethanol	27.4	23.9	13.2
Water consumption (kg/h)	8417.0	8332.2	22090
Ethanol/water ratio (L/L)	4.8	4.7	19.0
Ethanol/dry biomass ratio (L/t)	349	358	232

^a Results obtained for 120 tons of dry biomass per day of sawmill mixed feedstock

^b Results obtained from 2124 tons of dry biomass of spruce feedstock per day have been normalized based on 120 tons of dry biomass per day

Streams	Physical status	$F \cdot C_n (kW/°C)$	Tin (°C)	T _{out} (°C)	O (kW)
Bo Column C201	Lia	2995.0	100 5	102.0	4236.7
Bo. Column C201	Liq	14 221 5	00.5	00.0	5831.3
C024		14 521.5	99.J 56 A	<i>33.3</i>	20.7
C034	Liq	2.9	36.4	/0.0	39.7
C008	Liq	29.1	25.7	175.0	4341.5
Bo. Column C403	Liq	8 701.1	119.0	119.1	438.0
C042	Liq	6.4	26.3	50.0	151.0
C054	Liq	15.3	45.5	100.0	833.7
Bo. Column C401	Liq	4 836.4	123.0	123.4	1925.4
C065	Liq-Vap	4 327.6	101.1	101.4	1340.0
Cond. Column C201	Liq-Vap	768.50	90.6	81.0	- 7323.9
Cond. Column C202	Liq-Vap	55 146.0	78.4	78.2	- 5710.1
C022	Liq	7.7	99.9	25.0	- 579.4
C032	Liq	6.6	78.2	25.0	- 351.1
C013	Liq	6.1	90.8	70.0	- 126.8
C101	Liq	0.3	58.8	25.0	- 9.8
C019	Liq	3.3	101.9	30.0	- 237.9
Cond. Column C403	Liq-Vap	224 760.0	95.2	95.2	- 1537.9
C063	Liq	1.1	95.2	25.0	- 75.9
C060	Liq	2.4	119.10	25.0	- 227.1
C044	Liq	6.6	50.0	30.0	-131.9
Cond. Column C401	Liq-Vap	0.5	102.7	60.4	- 20.0
C068	Liq	8.8	101.4	87.0	- 126.0
C074	Liq	3.0	100.1	25.0	- 223.6
C083	Vap	1096.7	62.00	60.4	- 1719.5
C090	Liq	3.1	60.5	25.0	- 109.0
C081	Liq	3.0	86.4	25.0	- 180.0

Supplementary data 1

Click here to access/download Supplementary Interactive Plot Data (CSV) Supplementary 1.xlsx Supplementary data 2

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CRediT authorship contribution statement

Maarouf Abdou Alio: Conceptualization, Methodology, Software. Formal analysis, Writing
original draft. Agnès Pons: Supervision, Conceptualization, Project administration, Writing
review & editing. Alain Marcati: Software, Methodology, Formal analysis. Christophe
Vial: Software, Methodology, Conceptualization, Supervision, Writing - review & editing,
Project administration.

Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: