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Vanillin production from lignin: Rigorous process simulation results for ethyl acetate versus aliphatic-alcohol-specific process designs

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ABSTRACT

Energy hotspots for the production of vanillin from Kraft lignin are identified and process improvements are proposed and rigorously simulated. The hotspots identified and addressed are related to the flowrate of methanol used as solvent and recycled in the process. Several alternative process designs containing fewer distillation columns and able to reduce the overall energy consumption are proposed. Recycling aqueous methanol, a distillation column is not required and the overall energy consumption is halved compared to the available literature (i.e. 42 %). In addition, based on a literature review and the screening of suitable solvents used for the liquid-liquid extraction of vanillin from the main product stream, the use of aliphatic alcohols such as hexanol is proposed as an optimal and underexplored solution. Their physicochemical properties allow for the elimination of the acidification step that takes place during the feed preparation stage at the beginning of the process. In this way, the process design can be simplified further. Two distillation columns are not required and the overall energy consumption of the process is reduced to 23% compared to previous studies. The proposed Kraft-lignin-based vanillin production process improvements contribute to the development and competitiveness enhancement of biomass-based vanillin production processes, which are currently in need of further refinement compared to the more mature petrochemical-based processes, but at the same time have the potential to be more sustainable, cleaner and energetically efficient.

1. Introduction

There exist both technological, environmental and economic pressures for finding alternative sourcing materials that come from biomass feedstock processing in order to replace petrochemical sources. The idea is similar to the biorefinery concept, transforming each feedstock component into many useful products. The availability of these bio-based chemicals is a reality at industrial level, but there are still many technical issues related to their production. Finding a solution to these problems is necessary before developing well established, greener processes, that can have an impact in the economy.

The currently available bio-based compounds include aliphatic or cycloaliphatic molecules, generally derived from starch, cellulose or triglycerides. Many of them, mainly the aromatic ones, are still obtained from petroleum. Additionally, a price increase of aromatics has been recently registered due to their reduced availability, caused by lower yields in the petroleum processing processes. This explains the current need for identifying aromatic building blocks derived from biomass.

In this context, there are three principal categories of phenolic compounds obtainable from renewable resources: lignins, tannins and cashew nutshell liquid. However, the yearly production volume of cashew nutshell liquid can be insufficient to turn it into a reliable renewable source. This is not an issue for lignin and tannins, which are extracted from wood. Depending on plant design and method of extraction employed, the major difficulties derive from their intrinsic chemical complexity, and also from their difficult processing and the challenges involved in achieving the desired purities. As a consequence of all these issues, guaranteeing these products' consistency along time can be a great challenge.

In the meantime, while great efforts are involved in identifying solutions to all these problems, a more viable strategy is operating with molecular compounds obtained by the depolymerization of these feedstocks, among which the depolymerization of lignin is at present intensively researched (Mota et al., 2016). Lignin valorization is a pivotal point to take into consideration in order to increase the efficiency and sustainability of biorefineries (Poveda-Giraldo et al., 2021). The most important lignin-derived monomers are 4-alkylphenols, 4-hydroxybenzaldehydes, 4-hydroxybenzoic acids, and

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4-hydroxycinnamic acids/esters which are upgradable into drop-in chemicals and new polymer building blocks.

At industrial level, the monoaromatic phenol currently obtained in highest quantities from lignin via depolymerization is vanillin. This compound is widely used as a building block in the food, pharmaceutical and chemical industries. Currently, it is one of the few molecular phenolic compounds industrially derived from biomass even though most of its production is still obtained from non-renewable petrochemical sources. Vanillin derived from biotechnological processes has the advantage that it is considered a natural product but a more efficient processing is required (Martău et al., 2021). The slow but unavoidable decrease in worldwide petroleum availability will generate a continuously growing demand that, in conjunction with supply problems and higher prices, will result in uncertain consequences both for the chemical industry and for society as a whole.

The annual production of vanillin is around 20,000 t, out of which only 15% is obtained from lignin (lignosulfonates) (Fache et al., 2016). Nowadays petrochemical processes are more mature, but technologies based on biomass compound extraction have a greater potential for process improvement and intensification, with clear advantages especially in areas such as environmental sustainability and being, overall, greener processes. From a Life Cycle Analysis perspective, production of vanillin from Kraft Lignin compared to crude oil has a lower environmental impact across all categories; decreasing acidification potential by 6.8 and toxic inhalation potential by 1.3 times and producing neutral CO_2 emissions (McCallum et al., 2021).

The sulfite pulping process is currently the only lignin source for vanillin production, even though this process only provides around 10% of the total amount if lignins extracted worldwide (Fache et al., 2016). Lignins derived from the Kraft process, which represent more than 90% of the global production (Rodrigues Pinto et al., 2012), are mainly burnt for generating the energy necessary to run the pulping processes. Approximately 50 Mt of lignin are produced annually worldwide, of which 98%–99% is incinerated to produce steam (Demuner et al., 2019). At the same time, there is a constant interest depicted in the literature in researching the depolymerization of the different types of lignins, such as the ones derived from the Kraft process. Other sources of lignin vary depending on local availability, e.g. bamboo (McCallum et al., 2021), eucalyptus (Poveda-Giraldo and Cardona Alzate, 2021) and marigold residues (Poveda-Giraldo and Cardona Alzate, 2021) etc.

The biorefinery paradigm that views lignins as high value-added aromatic building blocks is consistent with this approach, and opposed to considering them only as a cheap source of fuel for energy generation (Yadav, 2020). In this context, the present study is focused on studying the viability of Kraft-derived lignins as a source for vanillin extraction, obtained in alkaline and oxidative operating conditions.

The first stage towards producing lignin-derived vanillin is the treatment of an aqueous solution of lignin with oxidative agents operating at basic pH's, high pressures and high temperatures. The subsequent stage involves the depolymerization of the obtained material, leading to a complex and heterogeneous blend of lignins. At this point, the great challenge to deal with is the determination of the reaction mechanism that takes place, due to its high complexity (Fache et al., 2016). This alkaline oxidative process and the influence of fine-tuning some of the most common production parameters have been reviewed elsewhere (Mota et al., 2016) and research was conducted in order to increase the achievable conversion (Liu et al., 2020).

Most experimental studies identified in the literature were conducted in batch reactors (Araújo et al., 2010) but, for industrial applications, the study of continuous modes of operation is more interesting (Oliveira et al., 2019) due to the necessity of treating large volumes of liquor in the pulp industry, which is the original source of Kraft lignin. At the same time, a continuous operating mode is easier to control, automatize and better overall for obtaining homogeneous and consistent batches of the final product. This usually translates into lower capital investments and operating costs.

Consequently, the present work focuses on continuous reactor design and process simulation using Kraft lignin as the starting point. As discussed in the following sections, the present study focuses on vanillin recovery during the downstream processing stages and the recovery of the solvents employed. Vanillin production from Kraft lignin is a well established discussion topic in the literature. It is also well known that most of the process costs are due to the energy consumption from the reboilers of the distillation columns (used for solvent recovery). However, to our knowledge, solvent recovery has not been extensively addressed yet in the available literature in order to increase process efficiency.

1.1. *Downstream processing*

On technical grounds alone, the isolation of each of the compounds produced during lignin depolymerization is not currently an economically viable proposition. The focus has been mainly directed towards the extraction of vanillin and syringaldehyde, two of the subproducts considered with higher value by industry (Silva et al., 2009). As the final mixture obtained is very complex, extensive literature is available that aims at tackling the problem of difficult downstream processing of the alkaline oxidative lignin depolymerization reaction (e.g. Silva et al. (2009)). The two major problems identified at this stage are related to the acidification of the mixture and the removal of the residual lignin. A review of the currently available processes and their respective theoretical merits can be found on (Camera-Roda et al., 2019).

1.2. *Solvent selection for the extraction step*

Ethyl acetate is widely used for the downstream processing stages due to the high vanillin recovery rate achieved. However, its use requires a large quantity of water for complete methanol removal from the products' mixture, which is a prerequisite for the subsequent extraction step. To bypass this drawback and increase the overall process efficiency, several improved alternative designs are described in the literature (e.g. Silva et al. (2009)). Recent studies have highlighted the need to find a better industrial solvent than ethyl acetate for the liquid extraction of vanillin (Khwanjaisakun et al., 2020).

The use of benzene was proposed by Wongtanyawat et al. (2018) but this chemical compound also has many disadvantages, among which its high toxicity is highlighted. This benzene-based process was rigorously simulated and its performance assessed using energy efficiency and environmental impact metrics. The energy consumption of both processes proved to be very similar but, even if benzene is a possible option to be considered, its high toxicity and phase-separation difficulties are issues that have to be taken into consideration (Kaygorodov et al., 2010). In that work, the possibility of employing other solvents for vanillin extraction was not investigated.

Kaygorodov et al. (2010), after analyzing the characteristics of typical industrial extraction solvents for vanillin (Table 1), proposed using aliphatic alcohols C_6–C_8 instead of benzene and other conventional extracting agents. These compounds present the distinct advantage that they can be used in weakly alkaline media, which is important because it implies that the acidification step of the reactor stream would not be necessary, and the number of distillation columns could be reduced. This would greatly reduce the energy consumption requirements of the overall process, and could help avoiding the technological problems related to lignoacid precipitation after the acidification step. Unfortunately, the available literature is mostly qualitative-based and the only numerical values provided when comparing solvent performance are their distribution coefficients. These coefficients represent the solvent recovery achieved, but they do not determine the cost of an extraction step. In order to obtain a quantitative heuristic for process design evaluation, the Distillation Sequence Efficiency method was found suitable (Bonet-Ruiz et al., 2017).

In summary, vanillin is currently an important chemical building

Table 1
Characteristics of commonly used solvents for vanillin extraction [based on Wongtanyawat et al. (2018)].

Extractant	Highlighted properties	Distribution Coefficient (D)
Hexane	High extraction selectivity properties but very low distribution coefficient	0.2
Toluene	Moderate toxicity issues and low distribution coefficient	4.1
Benzene	Industrially used solvent with significant toxicity issues and some phase-separation-related difficulties	6.3
Octanol	High distribution coefficient value but low selectivity	20.5
Chloroform	High distribution coefficient value and quick phase separation properties	26.5
Butanol	High distribution coefficient value but with the distinct problem of being soluble in water	27
Butyl acetate	High distribution coefficient value but low extraction selectivity. It also presents some stripping difficulties	28.2
Octylamine	High extraction selectivity and good distribution ratio, but some stripping difficulties	Up to 600

block mainly produced by mature industrial petrochemical processes. A cleaner and more sustainable production process can be designed when using Kraft lignin as the source material, but these process designs must still be improved in order to become more competitive. In this work, using the methods exposed by Plesu Popescu et al. (2020), the Kraft-lignin-based vanillin extraction process proposed by Wongtanyawat et al. (2018) is improved upon by modifying the methanol recycling step and by choosing the optimal solvent to extract the vanillin with. The present study expands and provides rigorous simulation results for the proposed alternative process designs.

2. Materials and methods

2.1. Problem definition and base case design

AspenPlus v10.0 (AspenPlus, 2021) is used for performing the simulations. Wongtanyawat et al. (2018) proposed process, which improves the previous one proposed by Schorr et al. (2014), is selected as the base case scenario and simulated. The process is economically viable with a return on investment of 14% assuming a plant lifetime of 10 years and interest rate of 10% (Abdelaziz et al., 2020). Vu et al. (2021) reviewed novel advances on process design and expanded the limits of the economic study performed, taking into consideration both the alkali regeneration and waste lignin combustion to partially satisfy the steam requirements. Production costs are related mainly to hot and cold utilities (61%), followed by Kraft lignin sourcing costs (27%). After heat integration, hot and cold utilities represent half of the total production costs (53%). The scope of the simulations performed relative to the whole process design can be seen in Fig. 1. This work focuses on analyzing and finding solutions to the unit operations present in the region shown inside the dashed lines.

As can be seen, the starting raw materials are Kraft lignin, methanol, water, sulfuric acid and air. Vanillin is the main product, and methyl vanillate is recovered as a byproduct. When using non-aliphatic alcohols as solvents, methanol and water are necessary in the acidic feed mixture. Sulfuric acid's function is to decompose Kraft lignin's lignocellulosic structure, while air provides the necessary oxygen for the oxidation reaction. The solvents assessed for the liquid-liquid extraction step are ethyl acetate and the ones described in Table 1, including aliphatic

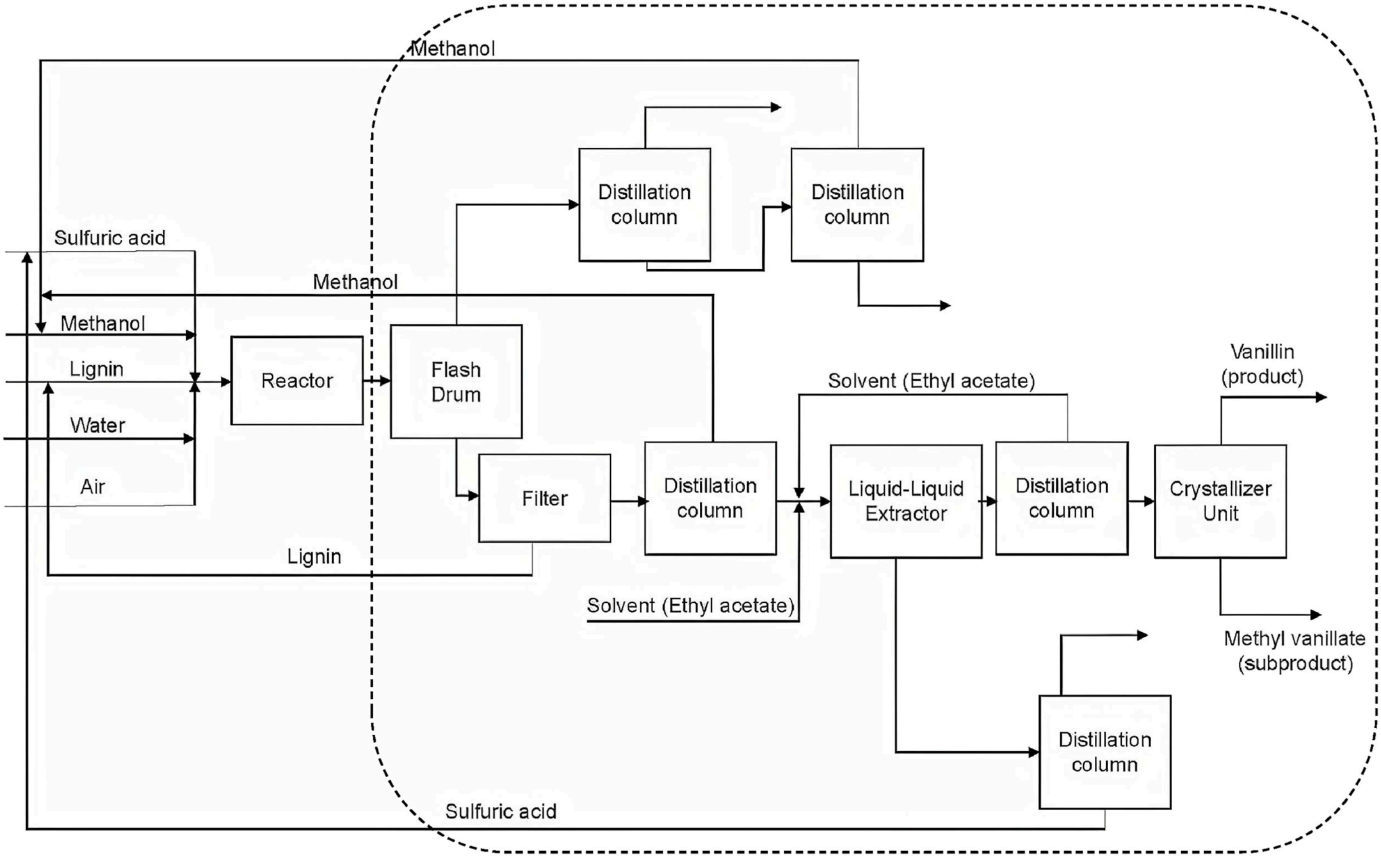

Fig. 1. *Unit operations under study in the simulations performed in the present work, in the context of a typical vanillin production process (based on Wongtanyawat et al. (2018)).*

alcohols C_6–C_8.

Vanillin production is set at a design specification of 10 kg/h (99.5% commercial grade product purity), as this value is representative for approximately 0.5% of global petrochemically-sourced vanillin production. A temperature of 210 °C and a pressure of 48 bar are specified for the bioreactor output stream, as per data described in the literature (Wongtanyawat et al., 2018). The pressure afterwards is set to 1 bar for the remaining stages of the process.

The physico-chemical properties of methyl vanillate are estimated using the molecule editor module of AspenPlus v10.0 (AspenPlus, 2021). NRTL is the thermodynamic model of choice. UNIFAC component property estimation method is used to estimate missing parameters. ELECNRTL model is used for the crystallizer block, in order to estimate electrolyte properties.

2.2. *Base case design implementation*

The input feed data provided for the process simulation is the reactor outlet stream described by Wongtanyawat et al. (2018) (Table 2). The output streams of the process include the final product (vanillin) and the by-product (methyl vanillate), which are separated during the final purification step by crystallization. The overall process flowsheet diagram is illustrated in Fig. 2.

As can been seen in Fig. 2, the simulated process includes several separation stages, represented by: a flash drum (FLASH), on one side followed by two distillation columns achieving the separation of liquid compounds from the gaseous ones (DIST-2 and DIST-3); on the other side followed by a filter for separating the unconverted lignin from the products' mixture (FILTER), a third distillation column for methanol recovery and recirculation back to the first stage of the process (DISTIL-1), and an extraction unit in which the separation of sulfuric acid is performed (LL-EXT); the recovery of sulfuric acid is then performed in another distillation column (DIST-5), followed by a distillation column which allows the recovery of the solvent (DIST-4), and ending in a last purification step of the final product in a crystallizer unit.

Initially, process simulations are performed using simplified block models (SEP and SEP2) to ensure the fulfillment of mass balances in the overall system, followed by rigorous simulations which are set up using Radfrac models for the distillation columns. Heater blocks are used to calculate the temperature of the different streams. For the final purification step, a crystallizer unit operation is set up, operating at a temperature of 5 °C and a pressure of 1 bar, as described in the literature (Wongtanyawat et al., 2018). The vanillin recovery objective is established to be fulfilled by implementing a design specification of 99.5% recovery. The base case scenario solvent used is the most common one in industry: ethyl acetate.

As previously mentioned, after the evaluation of the results obtained via the simplified models, rigorous models are implemented for the study of the distillation columns using Radfrac blocks. In each distillation column, 5 degrees of freedom must be fulfilled, which are set by the following variables: number of stages, distillate flowrate, reflux ratio, feed stage and pressure. Using sensitivity analysis, the influence of the reflux ratio is studied and parameters optimized for each column. Energetic costs and CO_2 emissions are also assessed during the simulations.

Table 2
Feed composition at the start of the process (bioreactor outlet stream composition) [based on Wongtanyawat et al. (2018)].

Feed Stream Composition	Mass flow (kg/h)
Methyl vanillate	2.03
Nitrogen oxide	0.85
Vanillin	10.00
Sulfur Dioxide	18.52
Sulfuric acid	35.39
Kraft lignin	61.01
Dimethyl Ether	139.11
Carbon dioxide	266.24
WaterH_2O	1721.43
Methanol	5750.42
Air	23,608.74

2.3. *Alternative process simulation*

According to Wongtanyawat et al. (2018), among the main energy consuming unit operations are: the liquid-liquid extraction unit and the subsequent distillation column for solvent recovery; the distillation columns in charge of the liquid mixture separation from gases and of methanol recirculation to the system (RAD1 and RAD2 in Fig. 2). The second section is considered the most consuming energetic hotspot of the process.

After initial simplified model assessments are performed on a number of process designs, two alternatives for this section are selected for a more detailed study (Figs. 3 and 4). Alternative one (Fig. 3) allows the optimization of the distillation column RAD1 in order to present an adequate water/methanol ratio in its output stream composition (B-DIST1). As a consequence of this, the second distillation column RAD2 proves to be unnecessary, and a big reduction in energy consumption can be achieved. The constant ratio of methanol/water in the reactor feed is the only condition that needs to be maintained.

Alternative two (Fig. 4) proposes the withdrawal of a side stream in the first phase separation column (RAD1) aiming at reducing the amount of water recirculated to the reaction step (SIDE stream). In case that an excess of water which cannot be reduced via parameter fine-tuning is detected in the recycling stream of Alternative 1, this one is a viable solution, as it also eliminates the need for a second distillation column.

A third alternative is also proposed based on the use of aliphatic alcohols, once this family of solvents has been proven to be viable options through rigorous simulations (Fig. 5). Distillation column 3 becomes redundant when using a process design which does not depend on the use of methanol for reaching a certain acidity (Wongtanyawat et al., 2018). The role of distillation column 1 also becomes simpler, as then it achieves the separation of gases in the distillate stream while water is recirculated through its bottoms stream. In summary, an intensified, simpler, more compact and energy efficient process is obtainable this way.

2.4. *Alternative process evaluation method*

At this point, a short-cut method is necessary for performance assessment of each alternative process design under study. For a process involving distillation columns, Pleşu et al. (2015) proposed a simple shortcut method (DSE, Distillate Sequence Efficiency).

The theoretical basis of the method is to apply an infinite/infinite analysis (Bonet et al., 2007) to determine process feasibility and stream parameters. DSE is a fast assessment method useful to rank the possible different distillation column configurations from an energy efficiency point of view. It is based on heuristics assuming that the distillation columns are heat engines producing separation instead of work, operating between a hot source (the reboiler) and a cold source (the condenser), while reducing entropy variation instead of producing mechanical work. The efficiency of each stream is calculated taking into consideration the Carnot efficiencies of the columns involved (Eq. (1)). The method has been extended to include in its calculations: the effect of recycle streams by Bonet et al. (2017), assuming that the efficiency of a recycle stream is −1; extractor solvent screening by Bonet-Ruiz et al. (2017).

$$DSE = \sum^{i} \frac{W_i}{F_C} \cdot \prod_{C} \eta_{iC} \tag{1}$$

W_i is the flow rate of each one of the streams collected from the process or recycle streams, F_c is the crude feed flow rate (the input

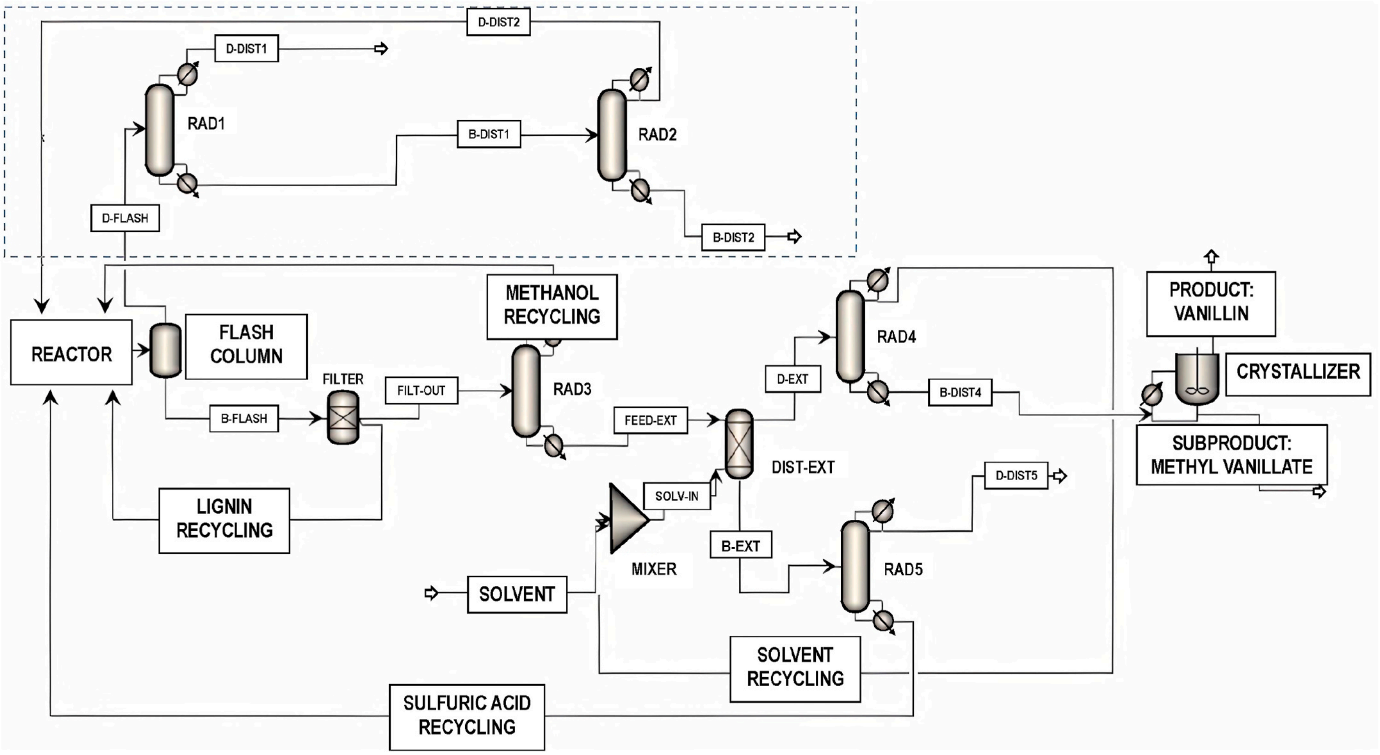

Fig. 2. Base case scenario process design.

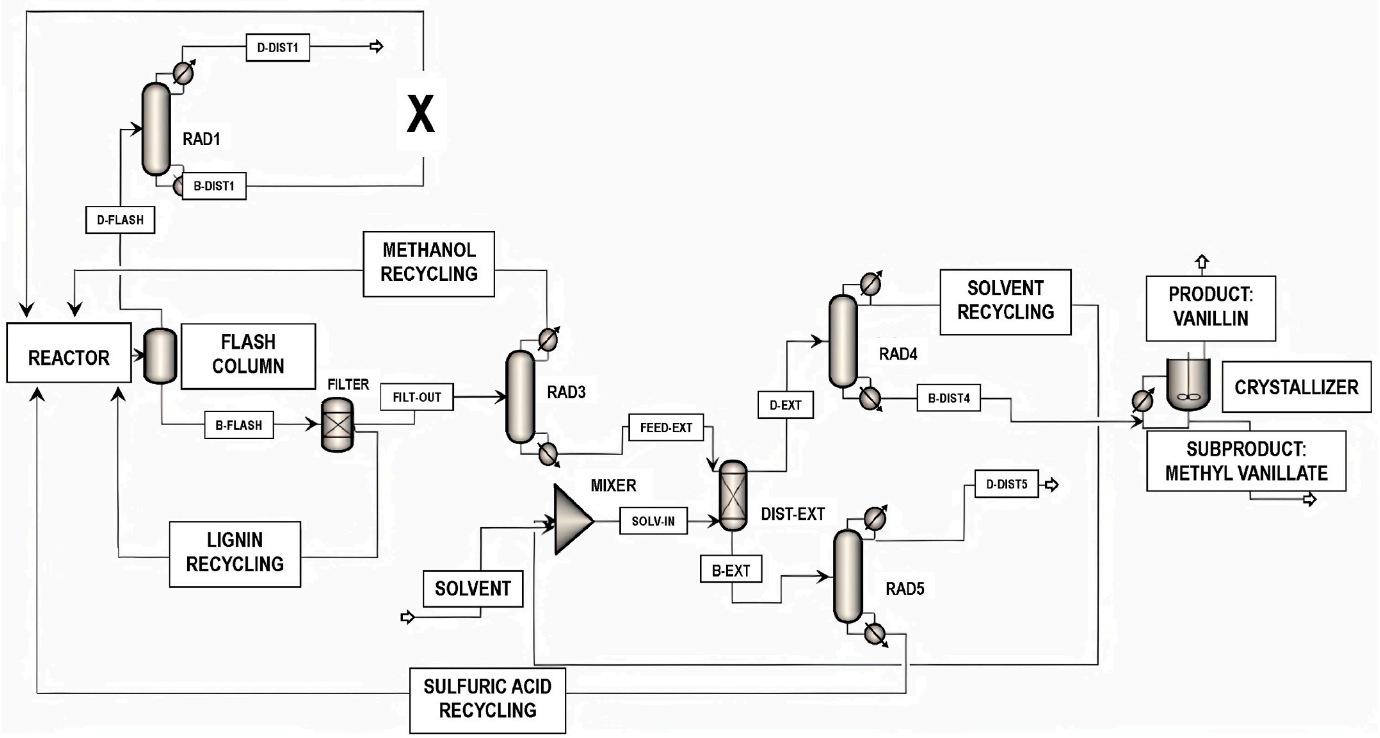

Fig. 3. Process design focused on aqueous methanol recycling.

stream of the process) and η_{ic} the Carnot efficiency of each distillation column. To calculate this last parameter, the boiling points of the relevant streams are needed.

Following the methodology explained in Pleşu et al. (2015) and the descriptive notation for the streams shown in Fig. 2, the following DSE equations (Figs. 2–5) are obtained for the different design alternatives proposed. Fig. 2 shows the process diagram from Fig. 1 that is implemented and simulated (Aspen Plus® v10.0) (AspenPlus, 2021). Distillation columns are solved using the Radfrac rigorous model (Rad). The streams are named following the block where they are connected. For

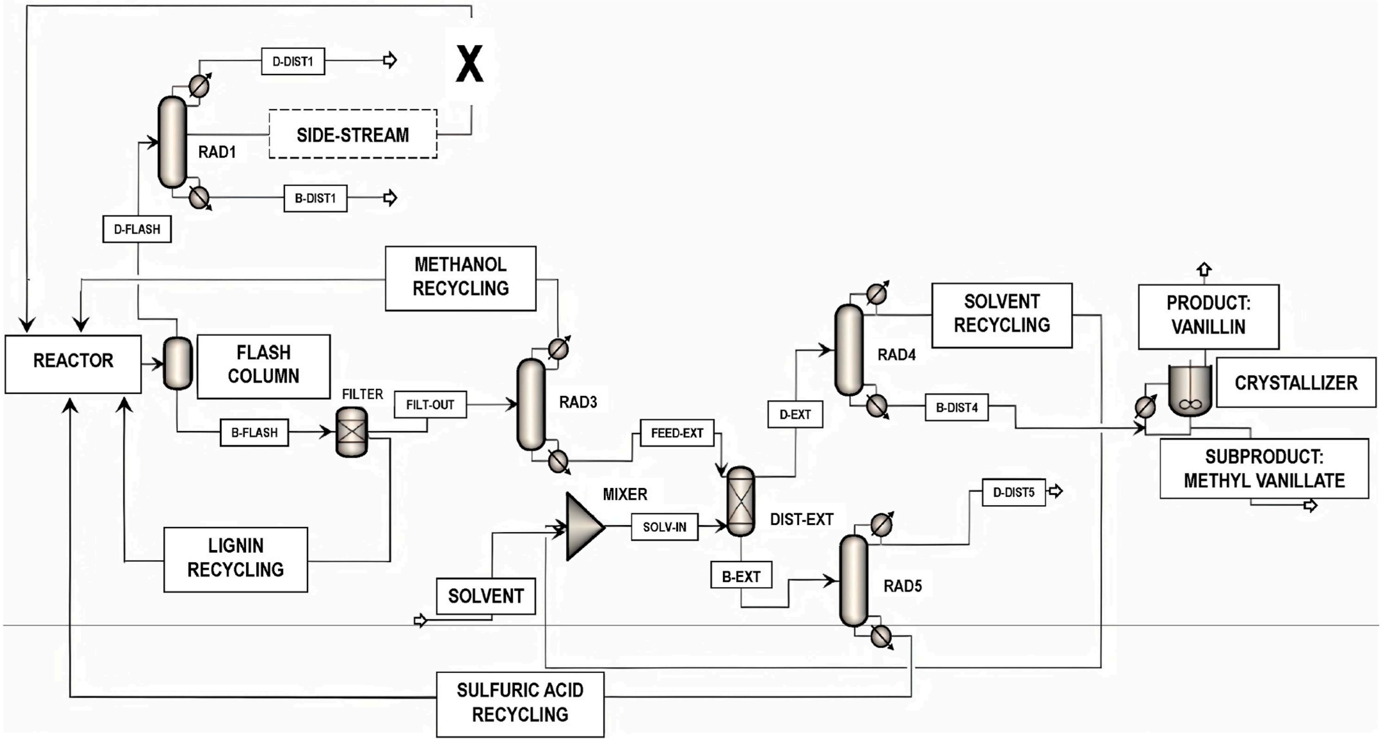

Fig. 4. Process design focused on methanol recovery via distillation column side stream.

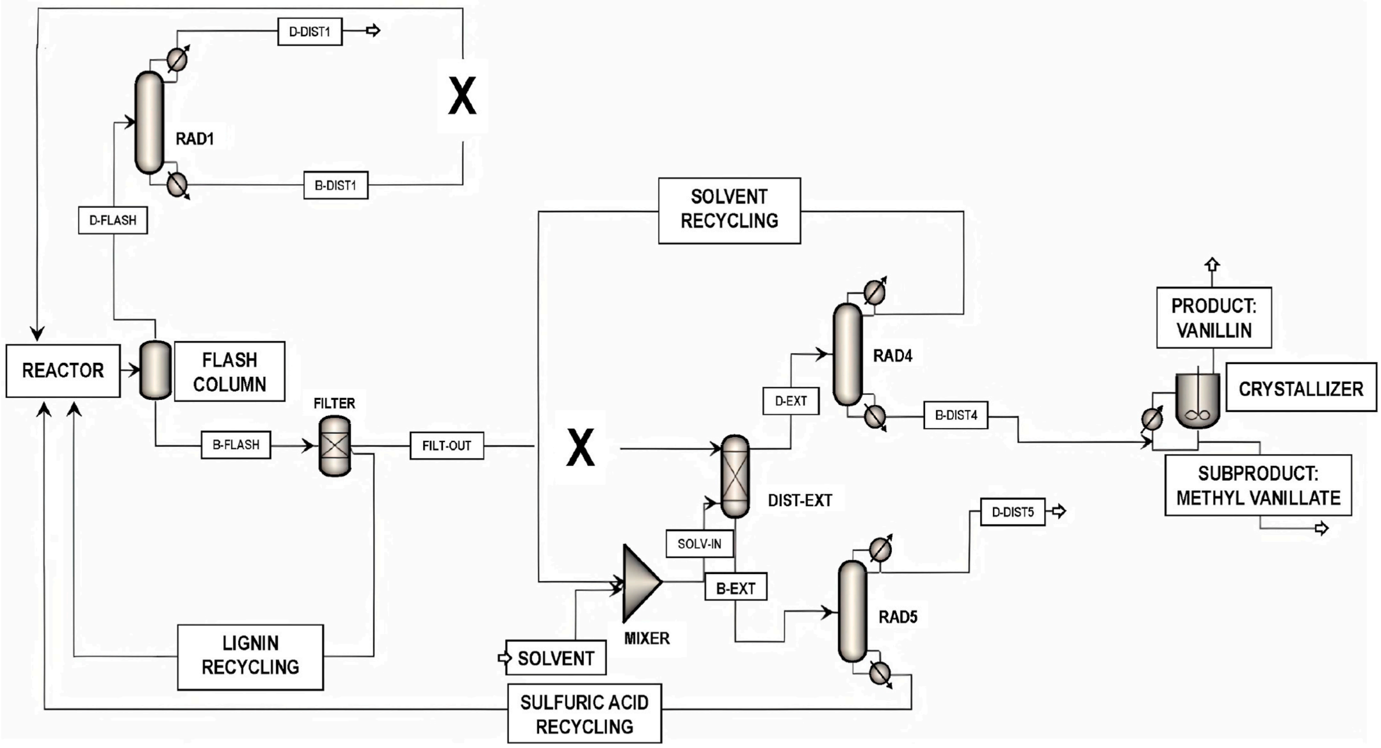

Fig. 5. Process design specific for aliphatic alcohol solvents.

instance, a D indicates that a stream is collected at the distillate and a B that it is collected at the bottoms. The letters after the dash indicates the corresponding block (e.g. DIST1 names the output stream of distillation column 1 (RAD1)). The flow rate of each stream in Eq. (1) (Wi) is indicated in Eqs. (2)–(5) by using directly the name of the corresponding stream from the process scheme. The Carnot efficiency of each distillation column in Eq. (1) (η_{iC}) is indicated in Eqs. (2)–(5) by relating it to its corresponding column number (e.g. the Carnot efficiency of the first distillation column (RAD1) is indicated as η_1).

A dashed square indicates a high energy consumption hotspot, marking it as a key region to work on in order to increase the efficiency of the overall design and obtain a cleaner technology. The reactor is followed by a flash unit intended to concentrate the lighter compounds of the mixture in the D-Flash stream. This stream is rich in methanol, a raw material required in the reaction step. Two distillation columns separate the lighter and heavier compounds relative to methanol. A first distillation column (RAD1) separates the lightest compounds (D-DIST1 stream). A second distillation column (RAD2) separates the water (B-DIST2 stream) and methanol (D-DIST2 stream), that is recycled back to the reactor.

$$\mathrm{DSE}_{base} = \frac{D-DIST_1}{FEED_1}\cdot\eta_1 + \frac{B-DIST_2}{FEED_1} + \frac{D-DIST_2}{FEED_1}\cdot(\eta_2-1) + \frac{MEOH-RE_2}{FEED_1}\cdot(\eta_3-1) + \frac{D-DIST_5}{FEED_1}\cdot(\eta_5) + \frac{B-DIST_4}{FEED_1} + \frac{SOLV-REC}{FEED_1}\cdot(\eta_4-1) \tag{2}$$

As the reactor also requires water, in this work, this last methanol-water separation step is not considered essential and the column previously dedicated to this task can be eliminated (as represented in Fig. 3). According to the DSE value obtained for the base case scenario (Eq. (2)), in this case, the second term corresponding to the water stream (B-DIST2) does not impact negatively the overall process efficiency, but implies an unnecessary waste of resources. The third term, in contrast, reduces the overall process efficiency by obtaining always a negative value (due to a Carnot efficiency value smaller than 1 in the second column, which is always penalized by the presence of a recycling stream). Both terms are removed from Eq. (3).

Implementing a side stream with a rich methanol content in the first column (Fig. 4) is another option to effectively remove the column used to separate water from methanol. This process presupposes a process intensification step where both previously employed columns are merged into a single, more efficient, one. Another aspect with the potential to increase noticeably the overall design efficiency is the optimal solvent selection for the liquid-liquid extraction step. When aliphatic alcohols are used as solvents, column RAD3 for methanol recycling is not needed (Fig. 5).

$$\mathrm{DSE}_1 = \frac{D-DIST_1}{FEED_1}\cdot\eta_1 + \frac{MEOH-RE_2}{FEED_1}\cdot(\eta_3-1) + \frac{D-DIST_5}{FEED_1}\cdot(\eta_5) + \frac{B-DIST_4}{FEED_1} + \frac{SOLV-REC}{FEED_1}\cdot(\eta_4-1) \tag{3}$$

$$\mathrm{DSE}_2 = \frac{D-DIST_1}{FEED_1}\cdot\boldsymbol{\eta}_{1'} + \frac{B-DIST_1}{FEED_1} + \frac{SIDE}{FEED_1}\cdot(\eta_{SIDE}-1) + \frac{MEOH-RE_2}{FEED_1}\cdot(\eta_3-1) + \frac{D-DIST_5}{FEED_1}\cdot\cdot(\eta_5) + \frac{B-DIST_4}{FEED_1} + \frac{SOLV-REC}{FEED_1}\cdot(\eta_4-1) \tag{4}$$

$$\mathrm{DSE}_{aliphatic} = \frac{D-DIST_1}{FEED_1}\cdot\eta_1 + \frac{D-DIST_5}{FEED_1}\cdot(\eta_5) + \frac{B-DIST_4}{FEED_1} + \frac{SOLV-REC}{FEED_1}\cdot(\eta_4-1) \tag{5}$$

The solvents listed in Table 1 are tested during a solvent screening process for their evaluation as possible candidates for industrial application in the liquid-liquid extraction step. For this purpose, the minimum solvent flow rate calculation (Bonet et al., 2014) and the solvent suitability screening (Bonet et al., 2015) methods were selected and applied.

In addition to energy consumption metrics, to perform a thorough assessment of the candidate solvents, the Potential Environmental Impact (PEI) of each solvent is also evaluated.

The Aqueous Toxicity Parameter (ATP) is estimated as follows (Eq. (6)):

$$ATP = \frac{w_{makeup\ solvent}}{LC_{50}},\ where\ LC_{50}\left[\frac{mg}{L}\right] : Fathead\ Minnow\ method \tag{6}$$

Following the rule of thumb, a low solubility in the raffinate and a low PEI value are features of a viable and promising solvent.

PEI value is determined by applying the Waste Reduction algorithm (WAR-EPA, 2016), and LC_{50} values are obtained using TEST software, both being developed and available from the Environmental Protection Agency (EPA, USA).

3. Results and discussion

3.1. Solvent screening

The solvent ranking obtained (Table 3) takes into consideration both resource efficiency results (e.g., amount of solvent present in the waste stream, solvent flowrate), and environmental/toxicological metrics.

According to the results shown in Table 3, the solvents that needs a lower flowrate to achieve the required vanillin separation are dichloromethane, hexanol and heptanol. These last two compounds, being aliphatic alcohols, have the advantages described in the Introduction and could be used to simplify the process.

Benzene and octylamine do not require high flow rates but present toxicity related problems. The most commonly used extraction agent, ethyl acetate, is shown to require a flow rate almost 60% higher than hexanol. Ethyl acetate is also highly soluble in the raffinate and great quantities of solvent are lost in the waste stream. Because of this, a much higher flow rate is needed compared to the solvents which achieved better results in the classification.

Comparing dichloromethane with hexanol, which are the ones that require a lower solvent flow rate, the first one presents a much higher solubility in the raffinate, meaning that a higher quantity would be present in the waste stream. This has obvious consequences for waste treatment and contamination assesment. Heptanol (third place), also achieves the required 99.5% separation of vanillin but needs a higher flow rate. However, it has the distinct advantage that its solubility in the raffinate is one third that of hexanol.

Dichloromethane is the compound that shows the lowest toxicity,

Table 3

Solvent ranking based on resource efficiency and environmental impact metrics.

Rank	Solvent/Extractant	Minimum solvent flow rate [kg/h]	Solvent lost in raffinate [kg/h]	ATP (Aqueous Toxicity Parameter)	PEI index [PEI/h]	PEI ATP [PEI/h]
1	**Dichloro-methane**	37.53	4.13	0.12	0.576	0.003
2	**Hexanol**	38.17	1.60	0.33	0.324	0.001
3	**Ethyl Acetate**	60.65	17.34	0.26	1.255	0.006
4	**Chloroform**	61.02	2.47	0.63	0.318	0.002
5	**Heptanol**	47.08	0.47	1.30	0.094	0.001
6	**Benzene**	47.54	0.91	1.70	–	–
7	**Toluene**	63.01	0.32	1.84	–	–
8	**Buthyl Acetate**	61.58	1.68	3.42	–	–
9	**Octanol**	57.51	0.29	4.26	–	–
10	**Octylamine**	54.99	1.36	10.60	–	–
11	**Hexane**	68.14	0.02	27.26	–	–

Table 4

DSE and energy consumption comparison.

Case	Description	DSE [%]	Reboilers energy consumption [MW]
1	**Base case scenario**[a]	15.6	*16.87*
2	**Alternative design 1**[b]	27.0	*7.00*
3	**Alternative design 2**[c]	20.7	*7.31*
4	**Hexanol**[d] **(aliphatic-alcohol-exclusive design)**	37.4	*3.77*

[a] 5 distillation columns.

[b] 4 distillation columns.

[c] 4 distillation columns + 1 side stream.

[d] 3 distillation columns – No methanol recovery step necessary.

followed by ethyl acetate and hexanol. It can also be seen that heptanol presents 3.9 times higher ATP value, despite its lower solubility in the raffinate compared to hexanol. Hexane presents an extremely low solubility but an extremely high toxicity.

Hexanol, heptanol and octanol (all aliphatic alcohols) achieved different positions in the present ranking. When considering toxicity metrics, hexanol obtained the second best overall results, while heptanol ranked fifth and octanol ninth. The preceeding classification shows a correlation with the chain length of these compounds, which significantly affects their viability.

Summarizing, hexanol and heptanol confirm the assumption mentioned in the Introduction that the use of aliphatic alcohols C_6–C_8 represent a viable and underexplored solution as extractive vanillin agents. This is not the case with octanol. Heptanol achieved better results than benzene, a common industrial solvent, while hexanol became the best candidate when chlorinated compounds are avoided. When using hexanol, the minimum solvent flow rate needed is lower than the one for ethyl acetate (the second most promising candidate), while the toxicity metric (ATP value) remains similar. Hexanol seems a viable (and according to the assessed metrics, one of the best) solvent to use in the current industrial vanillin extraction processes.

3.2. Alternative process evaluation

Once the Carnot efficiencies are calculated, the DSE values are assessed for each scenario (Table 4). It can be seen that the ranking obtained by the shortcut DSE method is in agreement with the reboiler duty results determined by rigorous simulations.

The base case scenario obtained the lowest efficiency (15.6%) and the highest energy consumption (16.87%) metrics. Case 4 obtained the highest efficiency (37.4%) and presented the overall lowest energy consumption. Case 3 (side-stream recovery of methanol) obtained better results than base case scenario but consumes a similar amount of energy than case 2 (aqueous methanol recycling step).

The proposed design alternatives, energetically speaking, greatly improve the efficiency of the base case scenario used as reference. According to the DSE values calculated, the energy efficiency of Alternative 1 is 73% higher than the one obtained by the base case scenario, while Alternative 2 shows a value 32% higher. The aliphatic-alcohol-specific design option presents the overall highest efficiency, obtaining an efficiency value 38% higher than the one achieved by Alternative 1.

3.3. Composition profile analysis

The composition profiles of the relevant streams were analyzed (Supplementary Material) to determine if the composition of the recirculating streams coming from the different processes proposed are acceptable or if water presence is too high.

Base case design recirculates 99.9% of methanol, with the process stream achieving a much lower H_2O/MeOH ratio (0.006) compared to the one of the feed stream (29.9). The assumed advantage of this design is the reduction of the recirculated water to almost zero.

The present work questions the desirability of this assumption. The hypothesis behind the proposed alternatives is that water presence in the recirculating stream is not a major issue, as water is already present in the feed stream. If a proper ratio water/methanol is achived and maintained, the water purge from the system does not seem necessary (as shown in the composition profiles of Supplementary Material). More so, it does not seem optimal nor resource effective to continually add water to the feed only to totally remove it by an extra distillation column during the first separation stage.

According to Table 5A, Alternative 1 presents a relatively simpler composition profile than Alternative 2, which has a more complex design. Its main advantage is the complete elimination of the gases, but generally presents only slight improvements compared to Alternative 2, considering that the B-Dist1 stream recirculates almost all the water and 99.76% of the methanol present in the feed. The main difference between Alternatives 1 and 2 is the almost 100% water recirculation achieved by Alternative 1, which may be a desirable or undesirable scenario depending on the acidification conditions needed for this two-compound mixture. Alternative 1 achieves a H_2O/MeOH ratio of 27.2 compared to the 29.9 in the feed stream.

Since hexanol, an aliphatic alcohol, eliminates the need of using methanol as an extra acidification agent, it allows for a more intensified process design (Fig. 6B) consisting of only 3 distillation columns and providing an overall higher energetic efficiency (Table 4). In this way, the reboilers of the aliphatic-alcohol-specific design consume much less energy than the ones of Alternative 1.

Compared to the base case process design, the relative energy consumption of Alternative 3 represents only 22% of the base case consumption, while for Alternative 1 it is 41% and for Alternative 2, 43%. The cause of the higher energy efficiency of Alternative 3 is that it is the only design that does not need methanol. This way, 575 kg methanol/kg of vanillin produced (see Tables 2 and 6) are no longer present in the system. This reduces the total amount of mass that needs phase

Table 5

Stream composition of the rigorous simulations for A: Alternative Design 1 (ethyl acetate used as solvent) and B: aliphatic alcohol specific process design (hexanol used as solvent).

Stream Name	B-DIST1	B-DIST4	B-EXT	B-FLASH	D-DIST1	D-DIST5	D-EXT	D-FLASH	REACTOR	FEED-EXT	FILT-OUT	LIGNIN REC.	METHANOL REC.	SOLVENT REC.	SOLVENT	H_2SO_4 REC.
Mass Flow [kg/h]	7141.6	18.5	216.7	427.7	24,044.5	191.5	73.1	31,186.1	31,613.7	229.2	366.7	61.0	137.5	54.6	60.6	25.2
LIGNIN	0	0	0	0.143	0	0	0	0	0.002	0	0	1	0	0	0	0
H_2SO_4	0	0.438	0.109	0.083	0	0	0.160	0	0.001	0.154	0.096	0	0	0.065	0	0.941
N_2	0	0	0.001	0.001	0.982	0	0	0.757	0.747	0	0.001	0	0.002	0	0	0
METHANOL	0.785	0	0	0	0	0	0	0	0	0	0.354	0	1	0.000	0	0
WATER	0.215	0	0.805	0.442	0	0.903	0.100	0.049	0.054	0.793	0.516	0	0.054	0.135	0	0.002
VANILLIN	0	0.462	0	0.023	0	0	0.136	0	0	0.044	0.027	0	0	0.025	0	0
ETHYL VANILLATE	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
DME	0	0	0	0	0.006	0	0	0.004	0.004	0	0	0	0	0	0	0
CO_2	0	0	0	0	0.011	0	0	0.009	0.008	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SO_2	0	0	0	0	0.001	0	0	0.001	0.001	0	0	0	0	0	0	0
ETHYL ACETATE	0	0	0.085	0	0	0.097	0.576	0	0	0	0	0	0	0.772	1	0
MET.VANILLATE	0	0.100	0	0.005	0	0	0.028	0	0	0.009	0.006	0	0	0.003	0	0

Stream Name	B-DIST1	B-DIST4	B-EXT	B-FLASH	D-DIST1	D-DIST5	D-EXT	D-FLASH	REACTOR	FILT-OUT	LIGNIN REC.	SOLVENT REC.	SOLVENT	H_2SO_4 REC.
Mass Flows [kg/h]	1502.3	25.9	228.3	327.8	24,033.2	204.7	103.5	25,535.5	25,863.3	266.8	61.0	77.5	65.0	23.6
LIGNIN	0	0	0	0.186	0	0	0	0	0.002	0	1	0	0	0
H_2SO_4	0	0.547	0.091	0.108	0	0	0.141	0	0.001	0.133	0	0.005	0	0.880
N_2	0	0	0.001	0.001	0.982	0.001	0.001	0.924	0.913	0.001	0	0.002	0	0
WATER	1	0	0.900	0.668	0	0.991	0.129	0.059	0.067	0.821	0	0.173	0	0.120
VANILLIN	0	0.376	0	0.030	0	0	0.096	0	0	0.037	0	0.003	0	0
DME	0	0	0	0	0.006	0	0	0.005	0.005	0	0	0	0	0
CO_2	0	0	0	0	0.011	0	0	0.010	0.010	0	0	0	0	0
SO_2	0	0	0.001	0	0.001	0	0	0.001	0.001	0	0	0	0	0
HEXANOL	0	0	0.007	0	0	0.008	0.612	0	0	0	0	0.817	1	0
METHYL VANILLATE	0	0.077	0	0.006	0	0	0.020	0.001	0	0.008	0	0	0	

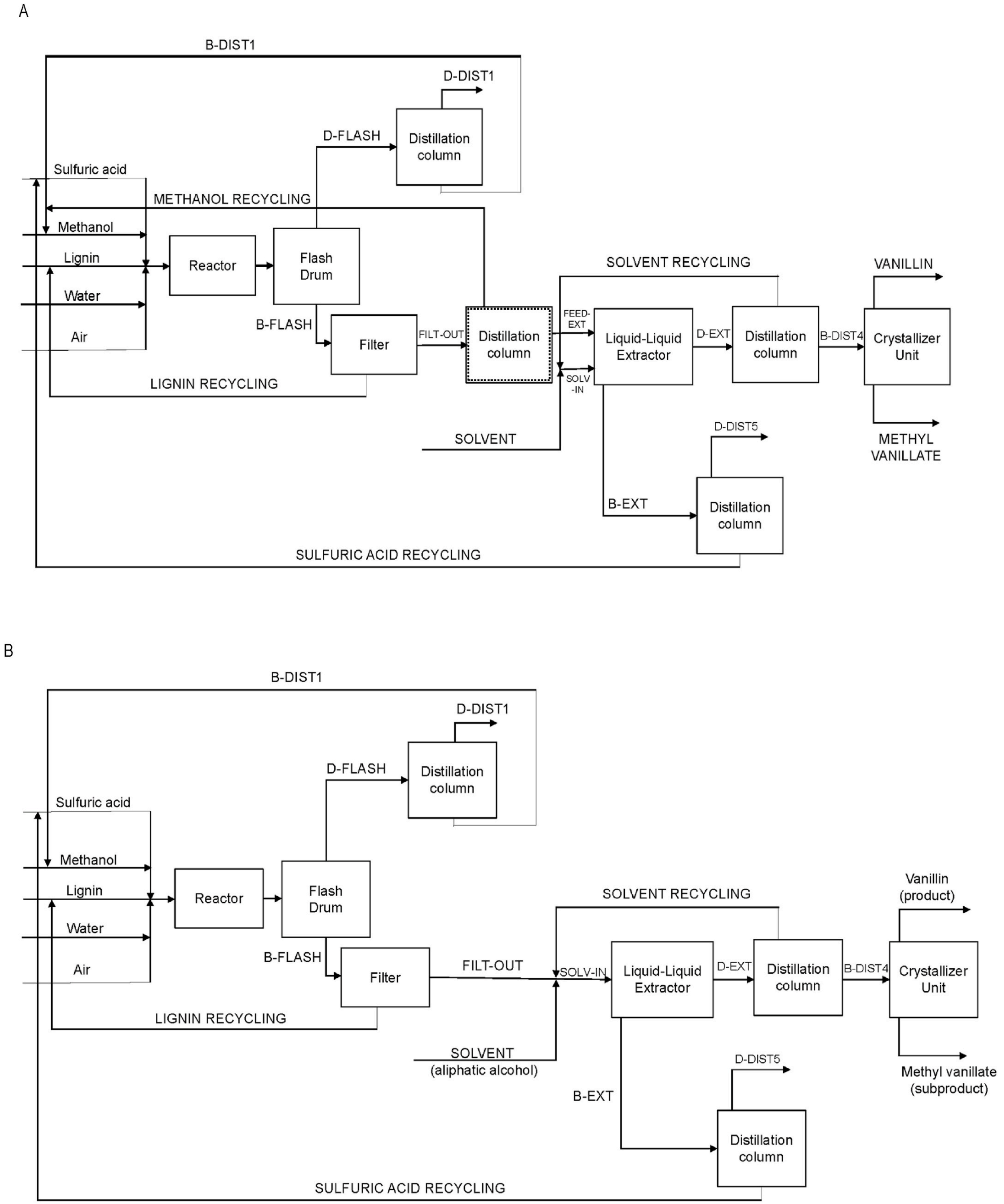

Fig. 6. Process Flow Diagrams. A: alternative solvent 1; B: aliphatic-alcohol-specific design. Dashed line: distillation column used in A that is. not necessary on B.

Table 6
Optimized distillation column parameters for base case scenario and the two most energy efficient process designs proposed.

	Base Case Scenario					Alternative Design 1					Aliphatic-Alcohol-Specific Design				
Distillation column no. (RAD)	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
Feed stage	2	7	5	5	4	4	–	5	5	4	3	–	–	5	4
Number of stages	4	12	10	10	8	8	–	10	10	8	4	–	–	10	8

separation.

Finally, in Table 6, a summary of the distillation columns present in the two best alternatives explored in the present work and how they compare to the ones needed for the base case scenario can be seen. Presented there are the optimal feeding stage for each column, optimized through sensibility analysis, and the number of stages needed for each column in order to achieve the desired separations. In each column, the distillate stream is collected from the first stage and the bottom stream from the last stage. Alternative Design 1 needs one less column than base case design while the aliphatic-alcohol-specific option removes two of them. Alternative 1 adds more stages in column one in order to substitute the second column, but this is not the case for the hexanol-based design, which is still able to maintain the use of only four stages in the first column.

Overall, after analyzing all the metrics obtained, it is shown that, when possible, the use of alphatic alcohols and more specifically of hexanol is preferrable to the other alternatives studied.

4. Conclusions

The rigorous simulation results shown in the present work highlight that simple process modifications, such as including an aqueous methanol recycling stream as an extra inlet for the reactor instead of a pure methanol one as per current standard designs, can reduce greatly the energy consumption of the overall process (up to a 40% decrease as per current simulations) and the total number of distillation columns needed.

Another key aspect that needs further investigation is the solvent selected to extract the vanillin. Nowadays, ethyl acetate is the most commonly used solvent. In the present study, this solvent is compared with many others already proposed in the literature. Hexanol is proposed as a good candidate to substitute ethyl acetate, compared to which it presents unique advantages such as reduced toxicity values. The use of aliphatic alcohols as solvents opens the possibility of designing processes that only need three distillation columns, while obtaining relative energy consumption values of only 22% those achieved by the base case design.

In summary, the recycling of aqueous methanol is a simple and recommended measure that can be easily implemented in order to improve current industrial vanillin production processes, while further research on the use of aliphatic alcohols (e.g. hexanol) as solvents when Kraft lignin is used as source material is deemed worthy of consideration for further process improvement and optimization. Recommended future work also includes the empirical verification, via pilot plant operation, of the rigorous simulations performed in the present work.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.clet.2021.100133.

Conflicts of Interest

The authors declare no conflict of interest.

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