Solvent Screening and Process Simulation for Vanillin Production from Lignin

Alexandra Elena Plesu Popescu, Jonathan Torralba, Jordi Bonet-Ruiz*, Joan Llorens

University of Barcelona, Faculty of Chemistry, Department of Chemical Engineering and Analytical Chemistry, c/ Martí i Franquès 1, 6th Floor, 08028 Barcelona, Spain
bonet@ub.edu

Vanillin is an important building block for the chemical, pharmaceutical and food industries, with potential to become a key intermediate for bio-polymers. Vanillin nowadays is mostly produced from non-renewable petro-based resources as raw materials. A plausible process design to recover vanillin from an acidic oxidation of Kraft lignin in an hydroalcoholic mixture is available from recent literature, but it has yet to be improved before becoming a competitive one capable of substituting the petrochemical route. The alcohol used in the reaction is methanol. Following the reaction step, the process requires a flash drum and five distillation columns, most of the energy consumption being due to methanol recovery and recycle for which three distillation columns are employed. The first aim of the present study is to simulate and quantify the energetic costs and environmental impact of the proposed process design, while studying possible improvements to the principal energetic hotspots identified in the literature.Through rigorous simulations, it is shown that this base case design can be improved and the train of distillation columns simplified. Through the use of alternative designs, one of the distillation columns used to separate methanol from water coming from the vapour phase of the flash drum can be eliminated. An energy consumption of only 43 % relative to the base case scenario is achieved this way. The second aim of this work is to perform simulations of suitable solvents used for liquid-liquid extraction of vanillin from the main stream, taking into account both the energetic efficiency and the environmental impact of each one, and to classify them accordingly. Specific emphasis is put on the study of the performance of aliphatic alcohols such as hexanol, as their physicochemical properties allow for the elimination of the acidification operation in the pre-reactor feed preparation stage. This is important because it avoids the technological problems related to lignoacid precipitation that follows an acidification step and has the potential to reduce energy consumption greatly, as fewer columns would be needed. Rigorous simulations show that an energetic consumption reduction of 78 % relative to the base case design is achieved when using hexanol as the solvent in an aliphatic-alcohol-specific process design, improving the energy efficiency of both the currently used industrial methods and the commonly studied alternatives based on non-aliphatic alcohol solvents.

1. Introduction

Vanillin is a chemical compound used as a building block in a variety of industries, including the chemical, pharmaceutical and food industries. At the same time, it is currently one of the only molecular phenolic compounds produced on an industrial scale from biomass. It also functions as an aromatic monomer for various synthesis processes. Because all of this, it has the potential to become a key intermediate compound for the synthesis of bio-based polymers. Petro-based resources are the current raw materials of choice for the production of organic chemicals and polymers such as vanillin. This situation, though, is not a sustainable one because of the nonrenewable nature of the resources employed. Around 20,000 t/y of vanillin are produced, with 15 % of it coming from lignin. Industrially, only lignin from the sulfite pulping process is used for vanillin production, despite the fact that this kind of lignin accounts for only around 10 % of the total lignins extracted (Fache et al., 2016). Kraft lignins, which are the vast majority of lignins, are usually burned for energy in the pulping process. An ever increasing amount of research is, however, investigating the depolymerization and

possible use of all kinds of lignins, such as the ones coming from the Kraft process. This is consistent with the biorefinery approach that considers lignins as a source of medium-to-high added value aromatic building blocks instead of fuel for energy generation. The need for alternative solutions to the petrochemical sourcing of vanillin coming from the processing of the biomass feedstock is both a technological and economic priority.

The first step in the lignin-based process for vanillin production consists of treating an aqueous solution of lignin with oxidants at alkaline pH, at high temperature and pressure. The base lignin is depolymerized, yielding a complex and heterogeneous mix of lignins. This complexity makes the establishment of a reaction mechanism very challenging (Borges da Silva et al., 2010). A way for the isolation of each of these compounds is not currently possible nor economically viable. The efforts have been mainly directed toward the extraction of the more interesting subproducts: vanillin and syringaldehyde (Mota et al., 2016). In-situ recovery of vanillin from a bioreactor is also being investigated (Camera-Roda et al., 2019). From an industrial point of view, the use of Kraft lignin as a lignin source is attractive because more than 90 % of the total lignins produced worldwide come from this route (Pinto et al., 2012). The downstream separation in such a process normally uses ethyl acetate as solvent because it shows a high percentage recovery of vanillin product. Kaygorodov et al. (2010) reviewed the advantages and disadvantages of known vanillin extraction solvents and proposed the use of aliphatic alcohols C6-C8 over benzene and other common extractants. They affirm that these alcohols can be used in weakly alkaline media. This is important because it implies that reaction solution streams of lignin oxidation can be used without their acidification. This would eliminate the problems related to lignoacid precipitation following an acidification operation and improve the overall energy efficiency of the process, because fewer columns would be needed. Another advantage of the use of these alcohols would be that they are practically insoluble in water, which is good as the solvent lost in the raffinate from the extraction column is a metric for the solvent environmental impact.

The present study aims are, then twofold. First step is to perform rigorous mathematical simulations of a recent Kraft lignin-based vanillin extraction process (Wongtanyawat et al., 2018) to quantify relevant energetic and environmental impact parameters of the proposed process design. At the same time,to analyze and propose possible improvements to the principal energetic hotspots identified in the literature. Second, to perform a solvent screening procedure for liquid-liquid extraction of vanillin with special emphasis on aliphatic alcohols and to propose a greener and more energy efficient process design based on the special physicochemical properties of these alcohols.

2. Materials and methods

The simulations were performed using AspenPlus 10.0. A base case scenario was simulated (Figure 1a) based on recent literature (Wongtanyawat et al., 2018). The simulated phase separation section includes a flash drum (FLASH) and two distillation columns (DIST-2 & DIST-3) used to separate the gaseous components from liquid ones. It also includes a filter which separates the mixed products from the unconverted lignin (FILTER), a second column for the recovery and recirculation of methanol (DISTIL-1) and a liquid-liquid extraction unit which separates the sulfuric acid from the products (LL-EXT). A column for solvent recovery (DIST-4) prior to product purification in a crystallizer (5 ºC, 1 bar) and another for sulfuric acid recovery (DIST-5) follows. The simulations are performed first in simplified models like SEP and SEP2 and later in rigorous models (Radfrac). The thermodynamic model used is the NRTL, estimating the missing parameters by UNIFAC. The physico-chemical missing properties of methyl vanillate were estimated using AspenPlus. The columns have 5 degrees of freedom fulfilled by the following variables: reflux ratio, number of stages, feed stage, distillate flowrate and pressure. To optimize the distillation columns, the reflux ratio influence is studied using a sensitivity analysis.

The raw materials used for vanillin production are Kraft lignin, methanol, water, sulfuric acid and air. The main product obtained is vanillin while methyl vanillate is a byproduct. Methanol and water are required in the acidic feed mixture when non-aliphatic alcohols are used as solvents. Sulfuric acid's function is to break down the lignocellulosic structure of Kraft lignin. Oxigen comes from the oxidation reaction in the form of air. Ethyl acetate and the solvents listed in Table 1, as well as aliphatic alcohols C6-C8 are used as solvents for the liquid-liquid extraction step, and a simulation is run for each and every one of them to asess their performance. A calculation basis of 10 kg/h (99.5 % commercial grade product purity) vanillin production is selected for implementation (approximately 0.5 % of global vanillin production worldwide from the petrochemical route). A reaction temperature and pressure of 210 ºC and 48 bar are selected, based on existing data (Wongtanyawat et al., 2018). The pressure for the whole process afterwards is set at 1 bar.

The DSE (Distillate Sequence Efficiency) method (Plesu et al., 2015) is used as a fast and reliable short-cut for process efficiency evaluation. Because of its speed, it allows for a high throughput type screening of alternative process proposals. The method assumes that the distillation columns are heat engines producing separation instead of work. The only data required is the process output flow rates (Wi), the crude feed flow rate to the

process (Fc) and boiling point temperatures in order to calculate the condenser and reboiler temperatures and determine the Carnott efficiency of each column.

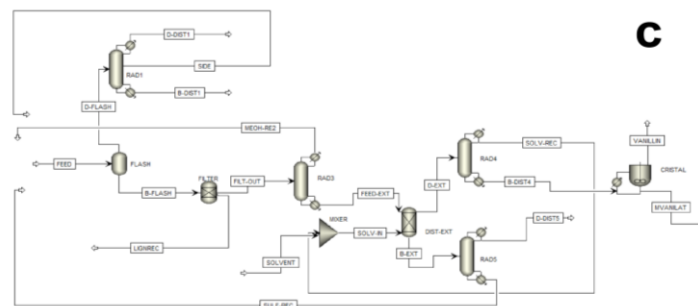Case 1: Flowsheet and DSE equation for base case process design
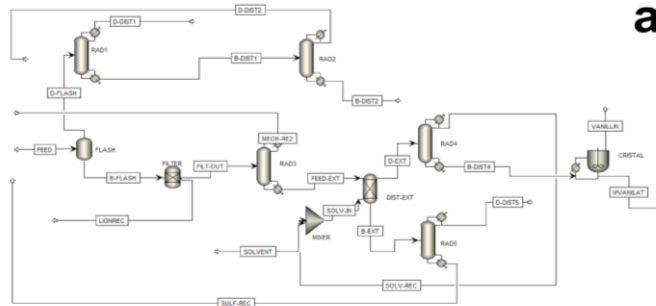
$$DSE_{base} = \frac{D - DIST_1}{FEED_1} * \eta_1 + \frac{B - DIST_2}{FEED_1} + \frac{D - DIST_2}{FEED_1} * (\eta_2 - 1) + \frac{MEOH - RE_2}{FEED_1} * (\eta_3 - 1)$$

$$+ \frac{D - DIST_5}{FEED_1} * (\eta_5) + \frac{B - DIST_4}{FEED_1} + \frac{SOLV - REC_\square}{FEED_1} * (\eta_4 - 1)$$

Case 2: Flowsheet and DSE equation for Alternative Process 1
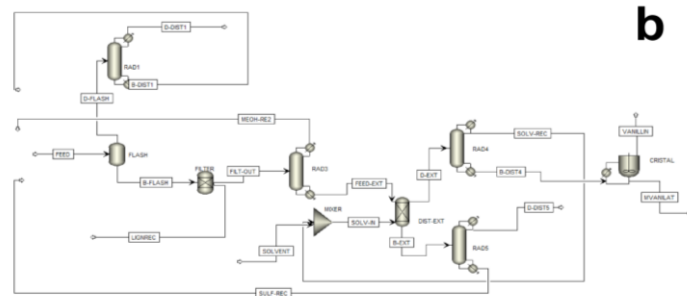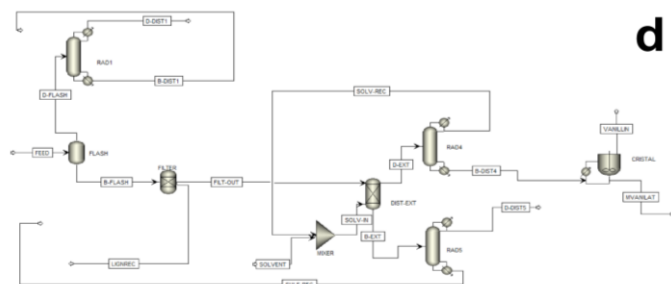

$$DSE_2 = \frac{D - DIST_1}{FEED_1} * \eta_1 + \frac{MEOH - RE_2}{FEED_1} * (\eta_3 - 1) + \frac{D - DIST_5}{FEED_1} * (\eta_5) + \frac{B - DIST_4}{FEED_1} + \frac{SOLV - REC_\square}{FEED_1} * (\eta_4 - 1)$$

Case 3: Flowsheet and DSE equation for Alternative Process 2

$$DSE_3 = \frac{D - DIST_1}{FEED_1} * \eta_1, + \frac{B - DIST_1}{FEED_1} + \frac{SIDE}{FEED_1} * (\eta_{SIDE} - 1) + \frac{MEOH - RE_2}{FEED_1} * (\eta_3 - 1) + \frac{D - DIST_5}{FEED_1} * (\eta_5)$$

Case 4: Flowsheet and DSE equation for simplified process design when using aliphatic alcohols as solvents

$$DSE_4 = \frac{D - DIST_1}{FEED_1} * \eta_1 + \frac{D - DIST_5}{FEED_1} * (\eta_5) + \frac{B - DIST_4}{FEED_1} + \frac{SOLV - REC}{FEED_1} * (\eta_4 - 1)$$

Figure 1: Flowsheet diagrams and DSE equations (efficiency). A: Base Case; B: Process Design 1; C: Process Design 2; D: Process Design 3.

For estimating the efficiency of a liquid-liquid extraction unit, Eq(1) is used. For rapid evaluation of solvent alternatives in the early design stage of a process, two methods are selected based on Bonet et al. (2015):

minimum flow rate calculation and percentage of solvent lost in raffinate. In order to perform a complete assessment of possible solvents, not only energy usage metrics are
evaluated but also each solvent potential environmental impact (PEI) and waste production. The Aqueous Toxicity Parameter (ATP, Eq(2)) and PEI values are estimated using the waste reduction algorithm (EPA, 2011), while the LC50 [mg/L] values are obtained using the TEST software, which uses the Fathead Minnow method.

$$F_{L-L} = \frac{^w solute_{out}}{^w solute_{in}}$$

(1)

$$ATP = \frac{w_{makeup\ solvent}}{LC50}$$

(2)

2.1 Alternative process simulation and evaluation

There are two principal hotspots that are energetically demanding in the existing processes (Wongtanyawat et al., 2018) which can be seen in (Figure 1a). The first one is the liquid-liquid extraction unit plus its subsequent solvent recovery distillation column. The second is the downstream separation columns that separate the gases from the liquid mixture and recirculate the methanol to the system. Two alternative process designs are proposed. Alternative one (Figure 1b) involves the fine tuning and optimization of column RAD1 to have an acceptable output stream (B-DIST1) in terms of composition (especially the water/methanol ratio) as to make the second column present in the base case design (RAD2) not necessary. Alternative two (Figure 1c) involves the implementation of a side stream in the first phase separation column (RAD1) in order to reduce the amount of water recirculating into the reaction step (SIDE stream).

3. Results and discussion

A solvent classification is presented (Table 1) which takes into account both resource efficiency related parameters, like solvent flow rate and the presence of solvent in the waste stream (equal to the solvent lost in the raffinate), and the intrinsic toxicity of the extraction operation (Tables 1 & 2). The algorithm for rating each solvent calculates the minimum flow rate needed for each one plus the solvent lost and multiplies the resulting quantity by their ATP value.

Table 1: Solvent viability classification based on resource requirements and environmental hazards

Classification (resources & environmental impact)	Solvent	Minimum solvent flow rate [kg/h]	Solvent lost in raffinate [kg/h]	Aqueous Toxicity Parameter (ATP/kg)	Fathead minnow LC50 (96 h) [mg/L]
1	Dichloromethane	37.53	4.13	0.12	319.93
2	Hexanol	38.17	1.60	0.33	117.07
3	Ethyl Acetate	60.65	17.34	0.26	230.18
4	Chloroform	61.02	2.47	0.63	96.14
5	Heptanol	47.08	0.47	1.30	36.17
6	Benzene	47.54	0.91	1.70	28.04
7	Toluene	63.01	0.32	1.84	34.24
8	Buthyl Acetate	61.58	1.68	3.42	17.99
9	Octanol	57.51	0.29	4.26	13.51
10	Octylamine	54.99	1.36	10.60	5.19
11	Hexane	68.14	0.02	27.26	2.5

Table 2: Potential Environmental Index values for top solvents.

Classification	Solvent	Total PEI index [PEI/h]	PEI ATP [PEI/h]
1	Dichloromethane	0.576	0.003
2	Hexanol	0.324	0.001
3	Ethyl Acetate	1.255	0.006
4	Chloroform	0.318	0.002
5	Heptanol	0.094	0.001

The premise proposed in the Introduction, that aliphatic alcohols C6-C8 could be good solutions as extractive vanillin agents in a liquid-liquid extraction operation is validated for hexanol and heptanol, while it isn't the case for octanol. Under the current classification criteria, heptanol is better than benzene (a commonly used industrial solvent), and hexanol is the best candidate if chlorinated compounds are discarded. The minimum solvent flow rate requirements for hexanol are lower than the requirements for the next best extractive agent (ethyl acetate), while presenting a close ATP value to it. The use of hexanol seems to be not only a viable option but one of the best possible alternatives for vanillin extraction for the currently standard process design.

Given that the acidification step needed for most solvents in the pre-reactor feed preparation stage is unnecessary when using aliphatic alcohols (Kaygorodov et al., 2010), the selection of hexanol as solvent could help simplify the overall process design. If methanol is not required to create a solution of certain acidity (Wongtanyawat et al., 2018), distillation column 3 can be removed, while distillation column 1 only needs to separate gases in its distillate stream and recirculate water through its bottom stream. Overall, a more compact, intensified, simpler and less energy consuming process is feasible. The proposed process design when hexanol is used as solvent is shown in Figure 1d. The DSE efficiency value obtained for this design (case 4) is the highest among the tested possibilities, i.e. 37.4 %, followed by alternative process 1 (Table 3).

Table 3: DSE comparison chart (including case 4 as an aliphatic-alcohols-exclusive process design option)

Case	Description	DSE [%]
1	Base case (5 columns)	15.6
2	Alternative 1 (4 columns)	27.0
3	Alternative 2 (4 cols. + side stream)	20.7
4	Hexanol (3 columns – No MeOH recovery step needed)	37.4

Through rigorous (Radfrac) simulations, the energy consumption for all simulated process designs is presented in Table 4. It can be seen that the reboilers of the aliphatic-alcohol-especific design (case 4) consume much less energy that even alternative process 1. This is because, contrary to the other design options, the high mass flow rate of methanol (575 kg methanol/kg of vanillin produced) is not present, so the overall global mass flow rate recycled that needs phase separation is much lower in this scenario.

Table 4: Energetic comparison chart between different process designs

Case	Energy consumed in reboilers [MW]	Difference between Consumed (reboilers) / available (condensers) energy [MW]
1. Base case (5 columns)	16.87	-3.21
2.Alternative 1 (4 columns)	7.00	-3.26
3.Alternative 2 (4 cols. + side stream)	7.31	-3.34
*4.*Alt. 3: aliphatic alcohols (3 cols.)	3.77	-1.95

Alternative 3 (case 4) relative energy consumption is only 22 % that of the base case design, while alternative 1 (case 2) is 41 % and alternative 2 (case 3) consumes 43 %. These results agree with the classification obtained using the shortcut DSE method.

Recent studies have highlighted the need to find a better solvent for the liquid extraction of vanillin than the commonly used ethyl acetate (Khwanjaisakun et al., 2020). This is a key requirement for increasing the competitiveness and viability of vanillin production from Kraft lignin. In the present study we propose hexanol as a promising alternative backed by rigorous quantitative mathematical models. It presents the added benefit of being an aliphatic alcohol that allows for a more integrated, compact design with only 3 distillation columns and an overall higher energetic efficiency than the industrial processes that use solvents pertaining to other chemical families.

4. Conclusions

In this study, we performed rigorous simulations of a recently proposed Kraft-lignin-based vanillin extraction process and quantified relevant energy efficiency and environmental impact parameters while at the same time proposing process design alternatives. The efficiency of the base case design analyzed is intrinsically low, while

the proposed alternatives achieved better performance results. Alternative 1's DSE value is 73 % higher than that of the base case scenario. Alternative 2´s value is 32 % higher. Alternative 1 only consumes 41 % of the reboiler energy that the whole base case process design needs. Alternative 2 consumes a similar 43 %. A third process design alternative based on the use of aliphatic alcohols as solvents is proposed and it achieved the highest DSE efficiency among all considered options, obtaining a value 239 % higher than the one attained by the base case scenario. The global heat duty of this process design distillation columns is only 22 % relative to the value obtained by the base case design.

A solvent screening for the vanillin liquid-liquid extraction step was also performed taking into consideration the resource intensivity of each solvent as well as their raffinate solubility and related toxicity parameters. These parameters were used in conjunction to achieve a comprehensive metric for solvent classification. Aliphatic alcohols C_6-C_8 proved to be viable solvents to achieve the liquid-liquid extraction step desired separations, but only hexanol and heptanol are considered good solvents. Hexanol achieved the best results in the proposed solvent classification. The models tell us that it is less resource dependent and with a similar toxicity than the industrially used ethyl acetate. It also performs better than the industrially used benzene.

The results, as proven by rigorous mathematical models, have shed light on the possibility of designing a sustainable Kraft-lignin-based vanillin extraction process that consumes up to 78 % less energy than the most commonly used ones, while using a greener and less toxic solvent for the liquid-liquid extraction step. Overall, 15 different processes have been analyzed and simulated, including 11 preselected solvent candidates plus 4 different process designs. The suggestions made in the present work may be worthy of further analysis for possible future industrial implementation.

Acknowledgements

References

Bonet J., Plesu V., Pleşu A.,Tuluc A., Iancu P.,Tohaneanu M., Llorens J., 2015, Fast Solvent Screening for Counter-Current Liquid–Liquid Extraction Columns, Clean Technologies and Environmental Policy, 17, 1227–1238.

Borges da Silva E., Zabkova M., Araújo J.D., Cateto C.A., Barreiro M.F., Belgacem M.N., Rodrigues A.E., 2009, An Integrated Process to Produce Vanillin and Lignin-Based Polyurethanes from Kraft Lignin, Chemical Engineering Research and Design, 87(9), 1276-1292.

Camera-Roda G., Loddo V., Palmisano L., Parrino F., 2019, Green synthesis of vanillin: Pervaporation and dialysis for process intensification in a membrane reactor, Chemical Engineering Transactions, 75, 1-6.

EPA (United States Environmental Protection Agency), Environmental Optimization Using the WAste Reduction Algorithm (WAR) <cfpub.epa.gov/si/si_public_record_report.cfm?Lab=NRMRL&dirEntryId=238300> accessed 30.03.2020.

Fache M., Boutevin B., Caillol S., 2016, Vanillin Production from Lignin and Its Use as a Renewable Chemical, ACS Sustainable Chemistry & Engineering, 4(1), 35-46.

Kaygorodov K.L., Chelbina Y.V., Tarabanko V.E., Tarabanko N.V., 2010, Extraction of Vanillin by Aliphatic Alcohols, Journal of Siberian Federal University. Chemistry, 3(3), 228-233.

Khwanjaisakun N., Amornraksa S., Simasatitkul L., Charoensuppanimit P., Assabumrungrat S., 2020, Techno-economic analysis of vanillin production from Kraft lignin: Feasibility study of lignin valorization, Bioresource Technology, 299, 122559.

Mota I., Pinto P., Loureiro J., Rodrigues A., 2016, Recovery of Vanillin and Syringaldehyde from Lignin Oxidation: A Review of Separation and Purification Processes, Separation & Purification Reviews, 45(3), 227-259.

Plesu V., Bonet Ruiz A.E., Bonet J., Llorens J., Iancu P., 2015, Shortcut assessment of alternative distillation sequence schemes for process intensification, Computers & Chemical Engineering, 83, 58-71.

Wongtanyawat N., Lusanandana P., Khwanjaisakun N., Kongpanna P., Phromprasit J., Simasatitkul L., Amornraksa S., Assabumrungrat S., 2018, Comparison of Different Kraft Lignin-Based Vanillin Production Processes, Computers & Chemical Engineering, 117, 159-170.