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RESEARCH ARTICLE

REVISED Innovative vanillin yielding from lignin: process modelling and assessment

[version 2; peer review: 1 approved, 3 approved with reservations]

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Abstract

In this work, we present the modelling of a novel process to promote vanillin production from lignin using PODIC®. The model includes the PODIC® production, lignin depolymerisation, and final product separation. Furthermore, a complete assessment of the proposed process in terms of economic and environmental performance was carried out. Regarding the economic evaluation, a comprehensive study was done leading to high investment (13.76 €/kg lignin) and operational (5.16 €/kg lignin) costs. The main reasons for the elevated costs were identified and alternative process configurations were evaluated. Despite this, the main result was that the proposed process is challenging to commercialize. An environmental analysis of the environmental impacts generated by the overall production process of vanillin and phenolic compounds was carried out considering energy consumption, human health, greenhouse gas emissions, water consumption and human toxicity. Electricity consumption of the PODIC® reactor was identified as the hotspot of the system. The CO2 emissions were also compared with the *Borregaard* process and found to be similar.

Keywords

Lignin; Vanillin; Electrochemical; Depolymerisation; TEA; LCA; Model

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REVISED **Amendments from Version 1**

The new version includes the changes suggested by the reviewers. In this sense, the introduction section was expanded with the current state of lignin depolymerisation options and a better description of the LIBERATE process. Moreover, the source of the experimental data used to calibrate the model and the activities done to scale up the process were also included. Finally, the whole text was reviewed to improve the discussion of the results. No new data/conclusions were added.

Any further responses from the reviewers can be found at the end of the article

Introduction

Vanillin is a versatile compound with a plethora of feasible applications in different industries like (1) the food industry (as flavouring), (2) the cosmetic industry (as fragrance), (3) the chemical industry (as an antifoaming agent), and (4) pharmaceutical industry (as odour-masking agent)[1]. The foreseen global production in 2024 is expected to be close to 60,000 t (a growth of 8% from 2019)[2].

There are several routes to produce synthetic vanillin, but the most prominent option is the petroleum-based route, specifically from guaiacol (80% of the world's supply)[3–5] while natural vanillin accounts for just 1% of the total market[6]. The rest is mainly obtained by a bio-based pathway through oxidative depolymerisation of lignin/lignosulfonates[7]. *Borregaard* (Norway) is the main active vanillin producer from lignosulfonates, operating for the last 20 years using this approach[3]. *Borregaard* obtains vanillin inside a multiproduct biorefinery with spruce wood as feedstock. Focusing on the vanillin process, it is fed by the liquor generated as waste during the sulphite process of wood pulp. Lignin depolymerisation into vanillin consists of oxidant treatments at alkaline conditions, high temperatures and high pressures. The first stage generates concentrated lignosulfonates using ultrafiltration, precipitation, and evaporation. After the reaction phase, the product mixture is separated by liquid-liquid extraction. During the depolymerisation of lignin, a heterogeneous mixture of compounds is produced, containing aldehydes, acids and phenolics, among other byproducts. High-purity vanillin can be obtained when this mixture is treated by a sequence of separation and purification stages. Furthermore, to promote vanillin production, copper-based catalysts are used[8] although it also means high complexity in the reaction stage since it implies a three-phase reactor.

The previous process focused on lignosulfonates but Kraft-lignin valorisation can be performed by a similar approach, which is highly interesting since its production is larger and more cost-efficient than the one for lignosulfonates[3,9]. Valorisation by acidic oxidation seems to be also feasible, but the development of this approach is still ongoing with a low TRL[10]. Indeed, different works have been published in the literature dealing with lignin depolymerisation by alternative technologies like biological, microwave-assisted, pressurized fluids, ionic liquids, electrochemical, or deep eutectic solvent depolymerisation[11–14]. Among them, the electrochemical pathway is especially relevant since it only requires electricity to drive the depolymerisation reaction. Thus, it avoids the need for severe operational conditions and/or harmful chemicals, also enhancing the direct integration options with renewable energy, which potentially increases the sustainability of the lignin depolymerization. For this reason, the electrochemical pathway was deeply studied following two different approaches, via an ex-cell[14–16] oxidiser and direct[17–21] electro-depolymerisation. An ex-cell produced oxidizer has the advantage of being used as a platform chemical of which the properties can be customized individually. For lignin depolymerization, this oxidizer can be mixed with lignin for pre-oxidation, which will be followed by a thermal treatment. Here, the lignin can be dissolved in a sodium hydroxide solution or used directly as a powder. The latter option has a decisive economic and environmental advantage, as it does not require the use of sodium hydroxide.

Although high selectivity is one of the main aims, a complex mixture is the usual product from any lignin depolymerisation reaction. Thus, vanillin production from biomass or lignin requires several purification steps due to the formation of a complex mixture of organics during depolymerization, which compromises profitability. Indeed, several studies have been performed with the objective to optimise the downstream separation, involving the use of membrane-based units and ion exchange recovery systems[22,23]. Nevertheless, it is not obvious if these modifications would be enough to ensure a positive cash flow for the operation. Therefore, improvements in the conversion steps are required to increase the vanillin yield. Furthermore, a profitable conversion of biomass requires the production of multiple products based on all three main compounds of woody biomass cellulose, hemicellulose and lignin, like in *Borregaard's* case. Finally, profitability will be more complex in the case of Kraft-lignin as the vanillin yield is lower than the one found for lignosulfonates[24].

For these reasons, a completely new ex-cell approach was proposed in the H2020 project LIBERATE (grant agreement No 820735). The aim is to develop a solution that uses a liquid-phase oxidant, avoiding three-phase depolymerisation reactors. This oxidant will be electrochemically produced and, therefore, reducing the need for harmful chemicals while focusing the energy consumption on green electricity and increasing its sustainability. The selected oxidiser was sodium peroxodicarbonate, Na_2CO_6, PODIC® since it also promotes vanillin production[14–26]. Moreover, focusing on Kraft-lignin, the proposed process considered two different approaches. The first one followed a conventional operational way, where lignin is firstly dissolved in NaOH before being mixed with the PODIC® solution, which is produced from sodium carbonate and electricity in an electrochemical reactor. Further, the mixture is fed into a thermal reactor to perform the depolymerisation. The second approach explores a more innovative option where the lignin powder is directly dissolved into the PODIC® solution. This way, the use of external NaOH is prevented,

being substituted by a cheaper chemical (sodium carbonate) and electricity that can be obtained from renewable energy sources. This alternative was developed as a solution to the negative economic performance of the first approach since it highly reduced the dilution and the need for external NaOH. Nevertheless, although the second LIBERATE solution was promising, it required a deep assessment in terms of economic and environmental performance, which is the main aim of the research gathered in this work. So, a comprehensive calibrated process model of the solution is presented, followed by a complete Techno-Economic Analysis (TEA) and Life Cycle Assessment (LCA). Further, the potential benefits in environmental impact terms can be considered by avoiding the current state of the art for lignin processing, which is combustion as biomass[27]. This would reduce CO_2 emissions, extracting value-added products from the lignin.

Proposed solution

Experimental background

The work displayed in this paper focuses on the modelling and the evaluation of the solution developed inside the LIBERATE project. Thus, no detail about the experiments performed will be provided. However, the experimental base can be found in the work of *Zirbes et al.*[14], where it is demonstrated that vanillin yields up to 6.2% are feasible from lignin thermal oxidation (at 180 °C) using Na_2CO_6 as an oxidiser.

On the other hand, the LIBERATE experimental activities did not only focus on the lab scale but also a pilot was developed[28], obtaining similar yields in both scales (up to 8%). Thus, it was demonstrated that the technology could be used at different scales without significant losses in the yields.

Developed process

The process consists of three main sections: 1) a PODIC® reactor converting sodium carbonate to peroxodicarbonate and sodium hydroxide by applying an electric current over boron-doped electrodes, 2) a reactor section where PODIC® solution is mixed with solid lignin to oxidize and thermally depolymerize lignin and produce the phenolic aldehydes, phenolic acids and guaiacol, 3) a product separation sequence where vanillin and light phenols are separated by an adsorber system and subsequent membrane section where the eluate from the adsorber section containing mixed phenolics and partially converted lignin is dewatered. NaOH and sodium carbonate follows the water in the membrane section and is recirculated to the PODIC® reactor. Sodium carbonate is required to produce the PODIC®, and NaOH and CO_2 are side products of this reaction. Thus, by sparging the produced CO_2 during the decomposition in a downstream gas-liquid reactor also fed with the side the NaOH solution, the sodium carbonate can be regenerated ($CO_2(g) + 2\ NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O(l)$). For this reason, an alternative process with the addition of sodium carbonate regeneration was also established, which also includes the use of additional CO_2 to enhance the regeneration. A scheme of the process is given in Figure 1 (see Energy and mass balances from the process model in Annex 1 for a more detailed scheme).

The process was modelled in the COCO-simulator (https://www.cocosimulator.org/) and using the CAPE-OPEN *Python* unit operation add-on, both by *Amsterchem*. The *Python* unit operation add-on was used with custom program code to describe the membrane section. The flowsheet based on Figure 1 can be found in the provided COCO-simulator file. Note that this flowsheet includes process integration actions, like sodium carbonate regeneration and recirculation. Indeed, this process flowsheet was the result of different interactions focusing on minimising the main sustainability issues early detected: dilution and PODIC® production cost. The complete set of simulator input files and auxiliary codes are given at (https://doi.org/10.5281/zenodo.8424715)[1].

[1]Note that the user should put python-files and folders under "%APPDATA%\Python\Python311\site-packages" where one should adapt the "Python311" to match the python version used.

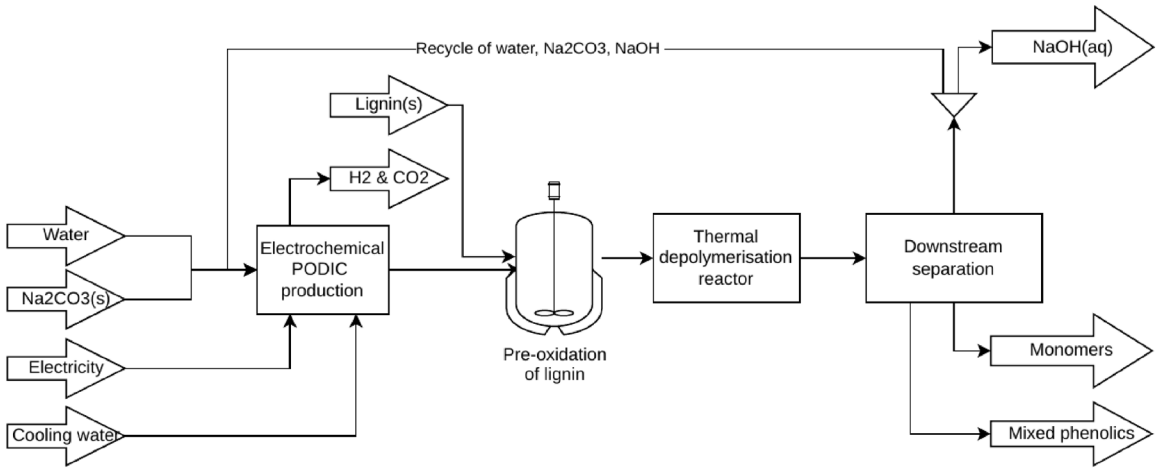

Figure 1. Process scheme.

PODIC® production pathway

As previously mentioned, the process concept developed inside the LIBERATE project to maximize vanillin production is based on the use of PODIC® (Na_2CO_6). Thus, the first step in the proposed solution is the production of the liquid oxidiser (PODIC®) to use in the thermal reactor. To do so, a preliminary electrochemical reactor (using a boron-doped anode and a stainless-steel cathode) is needed to perform its production from Na_2CO_3. More details can be found in the piloting work[28].

Thus, to include it in the assessment, its production from sodium carbonate had to be modelled. The net reaction from sodium carbonate to sodium peroxydicarbonate (PODIC®) is assumed to be:

$$2\ Na_2CO_3 + 2\ H_2O \rightarrow Na_2C_2O_6 + 2\ NaOH + H_2\ (g)$$

The PODIC® will also decompose during the operation, and a plausible mechanism for the decomposition is given by:

$$2\ Na_2C_2O_6 + 4\ H_2O \rightarrow 2\ H_2O_2 + 4\ NaHCO_3$$

With the peroxide eventually decomposing by:

$$2\ H_2O_2 \rightarrow 2H_2O + O_2(g)$$

So, the net overall reaction becomes:

$$2\ Na_2C_2O_6 + 2\ H_2O \rightarrow 4\ NaHCO_3 + O_2\ (g)$$

The formation of bicarbonate will affect the carbonate equilibrium in the electrolyte and may lead to the release of carbon dioxide if the electrolyte is saturated with CO_2 according to the following reactions:

$$NaHCO_3 + H_2O \rightleftarrows H_2CO_3 + NaOH$$

$$H_2CO_3 \rightarrow H_2O + CO_2(g)$$

Thus, based on the assumption of CO_2 saturation in the electrolyte, the overall reaction for PODIC® decomposition is formulated as:

$$2\ Na_2C_2O_6 + 2\ H_2O \rightarrow 4\ NaOH + 4\ CO_2 + O_2(g)$$

Lignin depolymerisation mechanism

In order to represent a possible varying lignin composition, the lignin was parameterized as the lignin monomers in their alcohol representation: p-coumary alcohol, coniferyl alcohol, and sinapyl alcohol. Of primary interest are the phenolic aldehydes, phenols and quinones that can be derived from these:

- Hydroxy-benzaldehyde, vanillin and syringaldehyde, acetovanillone, and acetosyringone
- Various phenols
- Ring-oxidated compounds of the above.

Thus, the reaction mechanism was based on simplified reactions (monomer to product + residue), defining the required stoichiometries to close the mass balance. Note, naturally this is a simplified description of the complex substrate, the reactions, and its product mixture, though it is a sufficiently accurate description with respect to the purpose of modelling the full process, utility systems, and separation system. The overall aim is to develop a simplified but closed mass balance for the main classes of products, the energy costs, and the sizing and definition of equipment. **The different reactions can be found in the developed flowsheet (available at https://doi.org/10.5281/zenodo.8424715), constituting the main output from this section.**

Kinetics and thermodynamics

For PODIC® production, the forward reaction rate to sodium peroxodicarbonate can be calculated by knowing the number of electrons transferred and, the current and an efficiency factor:

$$r_1 = I \cdot \eta / (v \cdot F)$$

Where I is the current, η is the current efficiency, ν is the charge count and F is the Faraday constant. The reverse reaction of sodium peroxodicarbonate decomposition can be represented by a standard Arrhenius expression and as a first-order reaction

$$r_2 = V \cdot A \cdot e^{(-Ea/RT)} \cdot C$$

where V is the reaction volume and C is the concentration of PODIC®, and the remaining expression is the classical Arrhenius equation.

The degradation reactions for lignin are modelled by specifying the degree of conversion. Since the temperature effect of the lignin degradation is negligible, the focus when defining the thermo-dynamic properties of the chosen components and the mixture of these is to get a proper description of the heat capacity and the vapor-liquid and liquid-liquid equilibrium for the main separation operations. The process includes an adsorption system using acetic acid and alcohols to strip the adsorbent and the thermodynamic description was chosen to be the Non-random Two-Liquid (NRTL)-model, using the Hayden O'Connel model for better describing the association effects in the gas phase caused by acids. The model parameters have been used as available in the *ChemSep* package database. Where the components were not already defined, parameters as given by NIST database have been used. Where no data was available in NIST the compounds have been given the correct gross molecular formula and otherwise been set to the same values as for vanillin.

Process assessment

Techno-Economic Assessment (TEA)

The process TEA was based on the process model described in the section Developed process, also assessing the two different working modes (with CO_2 supply for NaOH conversion and without the feeding of extra CO_2). The evaluated case is the same as the one used in the process model: a plant that treats 1,268 kg/h of lignin to produce vanillin, phenols, and partially depolymerized lignin.

Concerning the economic model, the bare module costing method[29] is used. This method estimates both capital (CAPEX)

and operational (OPEX) costs based on average values for the chemical industry. To evaluate the purchase price of equipment components, the methodology considers both direct and indirect costs, as well as contingencies and fees. Additionally, when there is limited information, the method also includes correlations based on industrial equipment to compute the base purchase cost in base conditions (common materials and near-ambient pressures) and its correction by correlation factors to incorporate the equipment material and operational conditions (mainly pressure and chemical resistance). These correlations are based on the main characteristics feature of the evaluated device. The assumptions to estimate these features are listed in ANNEX 1, where the equations to compute the CAPEX and the OPEX are also included. Furthermore, scale-up robustness was demonstrated (see section Experimental background) and numbering up and engineering constraints (like maximum device size in an industrial environment) were imposed for the electrochemical reactor to have a realistic evaluation. The investment cost for each involved device calculation can be also seen in ANNEX 1. To compute the OPEX contributions, energy and mass balances were needed. These balances were obtained from the process model and the information retrieved can be found in ANNEX 1.

Finally, once the CAPEX and OPEX are known, the process's economic performance can be evaluated by several economic indicators, mainly the Net Present Value (NPV), the Internal Return Rate (IRR), and the Return on Investment (ROI). A detailed description of them is done in ANNEX 1.

TEA tool

The TEA was performed by a tailored tool developed in *Python* that can be found at https://doi.org/10.5281/zenodo.8424715. This tool and the computed economic indicators are the main results of this section.

Life cycle analysis (LCA)

This study aimed to evaluate the environmental impact of the production process for vanillin and phenolic compounds, being these evaluations the main outcomes from this part. This calculation was carried out using *SimaPro 9.3.0.3* software, the *ReCiPe 2016* method (midpoint with hierarchical perspective), limiting the impact categories to be analyzed to 5 (energy consumption, human health, greenhouse gas emissions, water consumption and human toxicity) and secondary data obtained and adapted from Ecoinvent 3.8 database. The inventory is available at https://doi.org/10.5281/zenodo.8424715.

The study has a cradle-to-gate scope, the functional unit was defined as 1 kg of the desired product and the geographic and technological scope is the European one.

Life cycle analysis starts from the environmental impact associated with dry Kraft-lignin powder production[30,31]. For this environmental analysis, 3 subsystems were identified:

- Lignin Feed, using lignin derived from the Kraft process.
- PODIC® process considers the input of sodium carbonate and water, as well as the energy consumption of the reactor and the pumps (PODIC® and feed).
- Thermal Depolymerization + Separation: this subsystem considers the rest of the process.

Consumptions involved (varying between the case with CO_2, WCO_2, and without CO_2, $NoCO_2$), taking as an avoided product the production of low-concentration acetic acid. Also, for this subsystem a mass allocation was applied between the two products obtained: vanillin and phenolic compounds. More detailed information is provided in ANNEX 2.

Process CAPEX and OPEX

Analysis of the process with CO_2 supply

Capital cost (CAPEX)

The investment cost for each unit is listed in ANNEX 1, while the total CAPEX (once the corresponding multipliers to include piping, instrumentation, and other additional investment costs were included) was 145 M€, which is relatively high in comparison to the literature cases (see Table 3), with a distribution between the reaction and separation sections is close to 50%. A high CAPEX was not unexpected since the involved stream has a high dilution rate (water content >70 wt%). Indeed, the dilution effect is clear in the CAPEX of the adsorption process, which was nearly three times larger than the thermal reactor cost. Moreover, other devices contribute to the total CAPEX: the PODIC® reactor and the nanofiltration unit (NF). The power consumption of the PODIC® reactor is considerable (5.19 kWh/kg $_{PODIC®}$) for this process. Concerning NF, the high salt concentration leads to high osmotic pressures that mean low fluxes through the membrane, which implies large surfaces to treat the involved streams, increasing the total CAPEX.

Operational cost (OPEX)

The OPEX for this case can be seen in Table 1 and Figure 2, where it can be observed that the main contributor is the direct cost and, inside it, the raw materials, energy and maintenance have the main roles. As for raw materials breakdown, sodium carbonates account for 69%, while electricity and cooling are the main energy consumed (59% and 33%, respectively). In both cases, PODIC® production is the main reason for their consumption. Finally, maintenance implies circa 30% of the direct cost, which is explained by the high total CAPEX, which is principally due to the dilution and the investment required for the PODIC® production.

Analysis of the process without CO_2 supply

Capital cost (CAPEX)

The evaluation of the investment required for the case when CO_2 is not fed is presented in ANNEX 1. This approach was included to assess what happens if the permeate obtained from the NF is directly recirculated without an additional reactor to transform the NaOH into carbonate (NaOH reactor). Thus, it was expected to observe a reduction of the CAPEX that could compensate for the expected increase in the OPEX due to the extra carbonate to balance the one that would come from the NaOH. However, the total CAPEX for this approach without CO_2 supply was similar, even a little higher, to the one with CO_2 (146 vs 145 M€). This result was because recycling the NaOH implies larger streams at the steady state operation, increasing the size of the equipment, thus the CAPEX. Regarding cost distribution between reaction and

Table 1. Process OPEX when CO_2 is supplied.

Cost	OPEX, €/kg_{Lignin}	OPEX, %
Fixed	0.99	19.46
Direct	3.21	62.93
Indirect	0.96	18.71
Total	5.16	-
Direct OPEX breakdown	**OPEX, €/kg_{Lignin}**	**OPEX, %**
Labour	0.11	3.39
Energy	0.77	24.09
Raw material	1.00	31.25
Waste treatment	0.00	0.06
Maintenance	0.95	29.54
Patents	0.15	4.77
Membrane cleaning, smart grid, and H_2 recovery	0.22	6.90

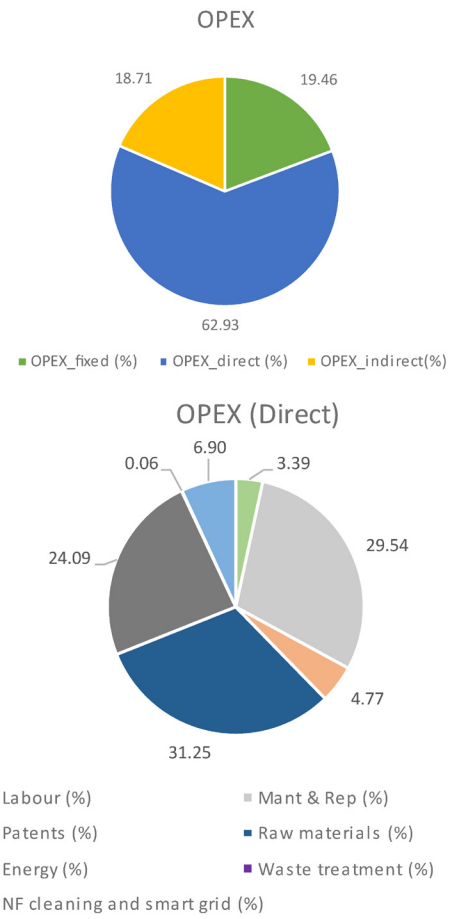

Figure 2. OPEX breakdown when CO_2 is supplied.

separation, both were again balanced. Finally, similarly to the previous case, the high costs are related to dilution, large PODIC® reactor and NF system.

Operational cost (OPEX)

The values related to the OPEX for this case are listed in Table 2 and Figure 3. As expected, the total OPEX was higher due to the need for more carbonate to produce PODIC®, also explaining the increase in the role of the raw materials in the direct OPEX (carbonate implies 80%). This increase in the raw materials requirements reduced the energy contribution up to 17% being the PODIC® reactor responsible for circa 64% of the total energy cost. Finally, maintenance contribution is still high due to the dilution.

Comparison with literature

Once the CAPEX and the OPEX were computed, a comparison with other processes (Cases 1–3) where lignin was transformed into vanillin was performed. Vanillin was selected as a reference since it is the key compound delivered by the process and the one with more information available in the literature. The three cases involve "conventional" approaches, where lignin is thermally degraded by the action of a catalyst, caustic conditions, and oxygen supply. However, while cases 1 and 3 are theoretical studies, case 2 is based on values from a real multiproduct biorefinery when the original raw material is woody biomass. More details can be found in ANNEX 1.

The contrast of all the considered cases in the deliverable can be seen in Table 3, where it can be checked that the best option for the evaluated process is when CO_2 is supplied. However, the costs for this option are still higher than the ones found in the literature (see ANNEXE 1 for details).

Table 2. Process OPEX when CO_2 is not supplied.

Cost	OPEX, €/kg_{Lignin}	OPEX, %
Fixed	1.00	16.15
Direct	4.13	66.56
Indirect	1.13	18.25
Total	6.27	-
Direct OPEX breakdown	**OPEX, €/kg_{Lignin}**	**OPEX, %**
Labour	0.11	2.63
Energy	0.71	17.09
Raw material	1.95	47.16
Waste treatment	0.00	0.05
Maintenance	0.96	23.19
Patents	0.19	4.51
NF cleaning and smart grid	0.22	5.36

Improvement options

As previously explained, the highest costs and, thus, profitability bottlenecks, are related to the high dilution in system[2] (in addition to PODIC® reactor and NF costs). For this reason, different process optimisation alternatives ("corrections" to these bottlenecks) were applied in the economic model[3] to evaluate how much the cost can be reduced. The corrections were:

a) Assume that the MF/NF is located before the adsorption to reduce the dilution in the separation train. The need for dilution in the thermal reactor to obtain high vanillin yields was experimentally confirmed inside the LIBERATE project. However, it has a detrimental effect on the downstream separation. In principle, water removal by membrane-based[4] operations could be performed upstream of the adsorption to avoid losing vanillin, but this could not be experimentally verified. Thus, the effect of this approach (assuming no vanillin losses and a final feasible water content of 35wt%) on the economics was verified by simulation.

b) Free electricity due to national grid green surplus. The process is powered using renewable energies. However, the evaluation involves realistic profiles, meaning that the renewable energy sources' production depends on the weather conditions and, so, they will not be able to produce all the energy required for every hour. Thus, despite having this connection to renewable energy sources, there are hours when energy from the grid is required. For this reason, it was assumed that only during these favourable periods there will be a surplus in the national grid resulting in free renewable energy.

c) Reduce the Thermal reactor residence time to 1 hour to be in line with the ones used as reference cases.

d) Better NF performance. The reported flux for the NF at the working salt concentration was 5 LMH. Nonetheless, this value was measured at a temperature lower than the real one considered in the process (40 °C vs 20 °C). Thus, the real flux could be better and, for this reason, a more optimistic flux of 10 LMH was imposed.

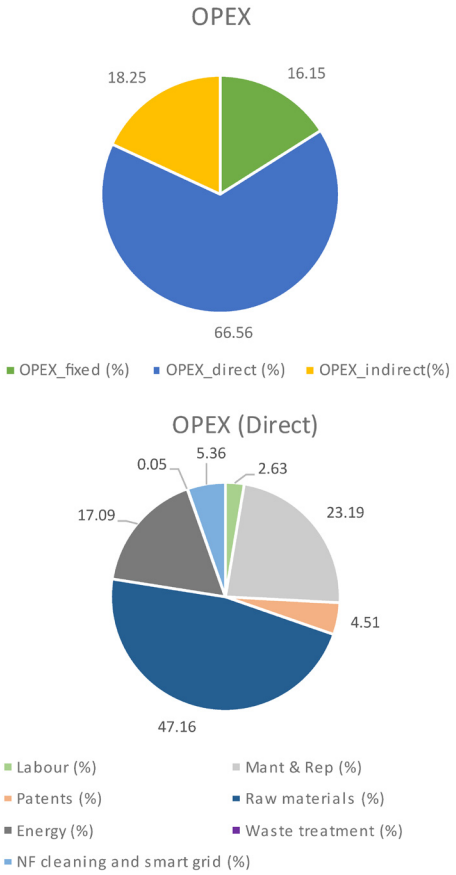

Figure 3. OPEX breakdown when CO_2 is not supplied.

The effect of applying all these corrections can be seen in Table 4 and Figure 4, even when all of these improvements

Table 3. CAPEX and OPEX in comparison to literature-based cases (see ANNEXE 1 for details).

Value	Process with CO_2 supply	Process without CO_2 supply	Case-1	Case-2	Case-3
CAPEX, €/kg$_{Vanillin}$	388.57	392.54	120.71	87.7	34.90
CAPEX, €/kg$_{Lignin}$	13.76	13.90	0.66	0.58	1.81
OPEX,€/kg$_{Vanillin}$	144.22	175.50	24.56	17.67	15.19
OPEX, €/kg$_{Lignin}$	5.16	6.27	0.13	0.12	0.79
(Vanillin) Yield, %	3.58	3.58	0.55	0.30	5.20

[2]The adsorption is fed with a stream with a water content >70 wt%

[3]The estimations come from "rough" simulations based on the economic tool

[4]Evaporation at an early stage was discarded to avoid an increase in the concentration of salts

Table 4. CAPEX and OPEX for different scenarios in comparison to literature-based cases.

Value	Process with CO_2 supply	a*	a&b*	a&b&c&d*	Case-1	Case-2	Case-3
CAPEX, €/kg$_{Vanillin}$	388.57	234.93	234.93	175.10	120.71	87.7	34.90
CAPEX, €/kg$_{Lignin}$	13.76	8.32	8.32	6.20	0.66	0.58	1.81
OPEX,€/kg$_{Vanillin}$	144.22	116.56	91.87	78.67	24.56	17.67	15.19
OPEX, €/kg$_{Lignin}$	5.16	4.13	3.25	2.78	0.13	0.12	0.79
(Vanillin) Yield, %	3.58	3.58	3.58	3.58	0.55	0.30	5.20

*Applied scenario(s) based on the corrections explained before.

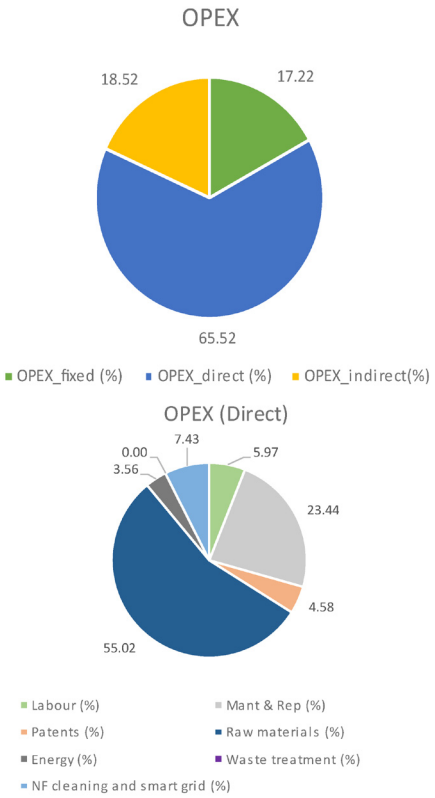

Figure 4. OPEX breakdown when scenarios a, b, c, and d are applied.

are considered, the process costs are closer but still above the ones found in the literature (see ANNEXE 1 for details). Furthermore, the main contribution to the OPEX is, still, the raw materials, where the carbonate required for PODIC® production implies 69% of the total direct OPEX. Similarly, PODIC® production represents 28% of the total CAPEX. Therefore, it is obvious that PODIC® is a bottleneck in reducing the process costs to approach the reference cases. Despite this, it is worth highlighting that reference cases 1 and 2 include assumptions not realistic for the operational conditions used in the evaluated process. And, if these assumptions are included in the economic model[5], the vanillin production cost for LIBERATE was: 42.5 €/kg$_{Vanillin}$ (CAPEX) and 23.2 €/kg$_{Vanillin}$ (OPEX), which is similar to those from the reference cases. To sum up, the evaluated process would lead to similar costs to those found in the literature once nearly an ideal performance is assumed (even with the high cost due to the PODIC® production). However, when a more realistic approach is followed, the costs are in the expected range, but with higher values. **Thus, further efforts would be required on the related chemistry to reduce PODIC® production costs. Similarly, reducing the dilution in the reaction would be another key factor in enhancing the economic performance**.

Economic indicators

The next step for the analysis consists of computing the economic indicators previously mentioned: Net Present Value (NPV), Internal Rate of Return (IRR), Return On Investment (ROI), and the payback period. This calculation was only done for the best one (the one where CO_2 is fed) since it is the most probable to imply positive incomes, also including the effect of the different corrections explained in the previous subsection (Table 5). Considering the results obtained, it can be concluded that the **process is not profitable even under ideal conditions due to the high dilution of the final products, which reduces the selling price**. Further up-grading costs will be imposed to achieve identical product specifications.

The presented calculations were performed with a Kraft-lignin price of 250 $/t and considering the price index of 2019 to compare with the literature. However, the current Kraft-lignin price should be higher (near 1,000 $/t)[32,33]. Further, an estimate using an updated index cost (near 820 for 2022)[34] should be evaluated. These re-evaluations and the following calculations will focus on the case without any correction since it represents the "real" process (Table 6).

Parametric analysis in terms of the economic indicators

A sensitivity analysis was performed considering a variation of ±20% in the CAPEX and OPEX contributors. However, since no positive incomes were obtained, only the NPV could be assessed (Figure 5). Focusing on the results, the main factor of

[5]Essentially, they are: (1) lignin content in the feed close to 10 wt%, (2) vanillin yield circa 10%, and (3) membrane fluxes of 200 MLH. Moreover, they include energy integration, an assumption similar to the scenario b (free electricity) considered in this work.

Table 5. Economic indicators for different scenarios.

Indicator	Process with CO_2 supply	a&b&c&d*	a&b&c&d* & ideal performance
NPV (€/kg_{Lignin})	-74	-36	-23
IRR (%)	-	-	-
ROI (%)	-	-	-
Payback period (y)	>30	>30	>30

*Applied scenario(s) (see Comparison with literature).

Table 6. Economic performance with a Kraft-lignin price of 1,000 $/t and an updated index cost.

Value	Process with CO_2 supply	Process with CO_2 supply- 1,000	Process with CO_2 supply -1,000-2022
CAPEX, €/$kg_{Vanillin}$	388.57	388.57	497.70
CAPEX, €/kg_{Lignin}	13.76	13.76	17.62
OPEX,€/$kg_{Vanillin}$	144.22	167.10	186.72
OPEX, €/kg_{Lignin}	5.16	5.91	6.61
NPV, €//$kg_{Vanillin}$	-74	-83	-98
(Vanillin) Yield, %	3.58	3.58	3.58

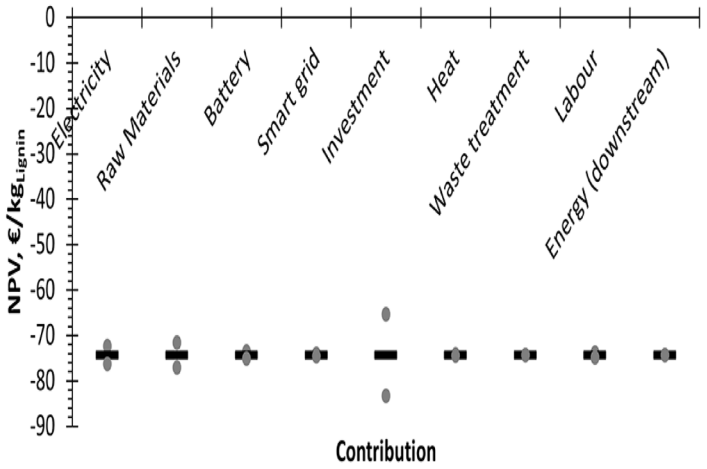

Figure 5. Parametric study of the NPV. Note that the bars refer to the base case, while the dot represents the scenarios with the ±20% changes.

cost is the investment cost, whereas raw materials and energy have a less pronounced role. This is in line with the result obtained in the OPEX breakdown for the considered case (Figure 2), where energy and raw materials had similar contributions to the direct OPEX.

Process minimum selling prices

Another important indicator of economic performance is the minimum selling price of products (vanillin, phenols, and partially degraded lignin). For a more realistic result, a lignin price of 1,000 $/t was used. An initial screening of five different scenarios was executed to try to explore if positive values are feasible including a change in the scale (the treated lignin flow was increased up to 50 times). Moreover, values for the vanillin selling price close to the maximum feasible value found in the literature (circa 25 $/kg, see ANNEX 1) were used. Similarly, the selling price for the phenols and the partially degraded lignin were set to values in line with the ones found

in the literature (see ANNEX 1)[6]. The results are listed in Table 7, concluding that **only when the scale-up of the process is performed, positive values can be obtained for a realistic evaluation of the process at "feasible" selling prices** (scenario (IV)). Note that all the set prices for this scenario are at high values and, for phenols and partially depolymerized lignin an average of the prices for pure compounds had to be used since lower values would mean a not profitable solution. Similarly, a vanillin selling price much lower than the maximum would also lead to an unprofitable situation. Thus, **the values used in scenario IV are the minimum selling prices.**

Environmental analysis of the process with and without CO_2

The analysis of the processes with CO_2 and without CO_2 was carried out, evaluating it in the environmental impact categories previously highlighted.

The impacts were determined for the 3 sub-systems referred to the generation of 1 kg of linked product. In the case of the PODIC® process, it was observed that the case without CO_2 generated a higher impact than that with CO_2 in 5 out of 6 impact categories analysed, being equivalent to that obtained with CO_2 in the impact category of fossil resources scarcity.

Being Lignin Feed subsystem an identical input in both case studies, in the case without CO_2 the impact of the PODIC® process generated a higher downstream impact on the production of vanillin and phenolic compounds than in the case study with CO_2. This is equivalent to an increase in the impact of vanillin production of 2 to 4 % in 4 of 5 environmental impact categories and a decrease of 3 % in case of fossil resource scarcity.

For the case of production of 1 kg of vanillin or phenolic compounds, the lowest environmental impact is for the case with CO_2, being 1.37 and 1.38 kg CO_2 eq respectively in the case of global warming, compared to 1.43 and 1.41 kg CO_2 eq obtained for the case without CO_2.

Evaluating both processes to produce 1 kg of vanillin (Figure 6), it was observed that the PODIC® process generated the highest environmental impact in 4 of 6 environmental impact categories analysed and the second highest impact in the two Human toxicity environmental impact categories behind wastewater, keeping the same impact ratios for the production of phenolic compounds.

Causes of the environmental impact

In both cases, it was found that **the electrical consumption of the PODIC® reactor has the largest impact**. In the case with CO_2, the largest impact of all categories assessed was due to this electrical consumption. However, in the case without CO_2, it was observed that the electricity consumption of the reactor had the second highest impact in the environmental impact associated with the water consumption category, after sodium carbonate (see Figure 7).

Comparison with the literature

The result obtained for the carbon footprint of producing 1 kg of vanillin was estimated at 1.37–1.43 kg CO_2 eq. This result is similar to the one reported by LCA on the Borregaard process (1.34 kg CO_2 eq./kg vanillin)[35] and significantly lower than the Kraft-lignin scenario analyzed by Wongtanyawat *et al.*: 137 kg CO_2 eq./kg vanillin[23].

Conclusions

The proposed process for vanillin production from lignin was successfully modelled and simulated using COCO-simulator, also including the most relevant kinetics and reaction mechanisms (e.g., PODIC® formation and degradation). Moreover, a complete techno-economic analysis of the proposed process to depolymerize lignin into added-value compounds (e.g., vanillin) was done. During this analysis, the main bottlenecks were identified, namely the high dilution rate and the production of a

[6]Note that the references are values per kilogram of a pure compound, while the process produced a diluted product. Thus, the selling price(s) used in Table 7 refers to this diluted product. For instance, a selling price for vanillin of 25 $/kg means the process output that contains vanillin (but also water and organics) is sold at this price.

Table 7. Initial screening of the minimum selling price(s).

Value	Process with CO_2 supply- 1,000				
	(I)	(II)	(III)	(IV)	(V)
Selling price, $/kg (VAN/PHEN/OLIG)*	7.6/0.76/0.3	25**/0.76/0.3	25**/0.76/0.3	25**/6.7/6.7	7.7/6.7/6.7
Scale (lignin flow), kg/h	1,268.54	1,268.54	50·1,268.54***	50·1,268.54***	50·1,268.54***
NPV, €/kg	-83	-77	-56	2.4	-4
IRR, %	-	-	-	4.13	-
ROI, %	-	-	-	28	-
Payback period, y	-	-	-	29	-

*It refers to the diluted product, not to the pure compound; **Value close to the one used in the references; ***Vanillin output: 18,636 t/y → Nearly 30% global production 2024[2]. VAN/PHEN/OLIG: Vanillin/Phenols/Partially depolymerized lignin

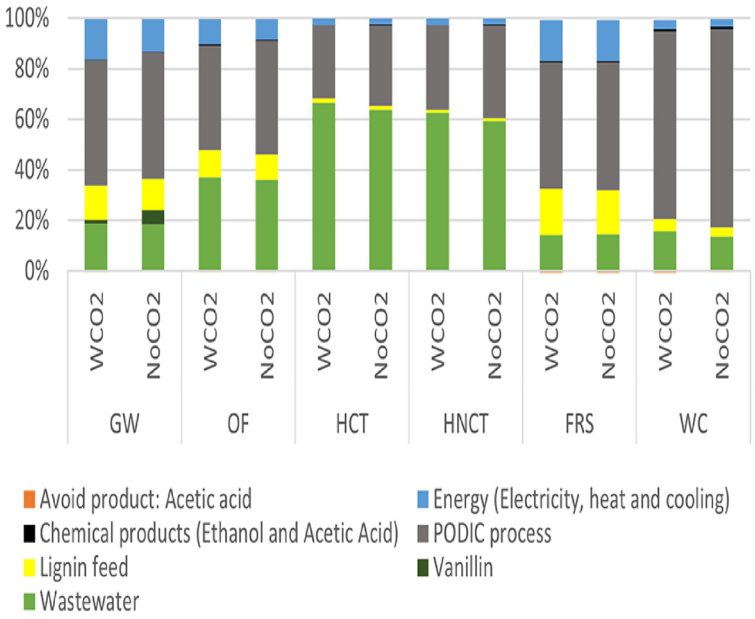

Figure 6. Relative environmental impact analysis of the vanillin production process.

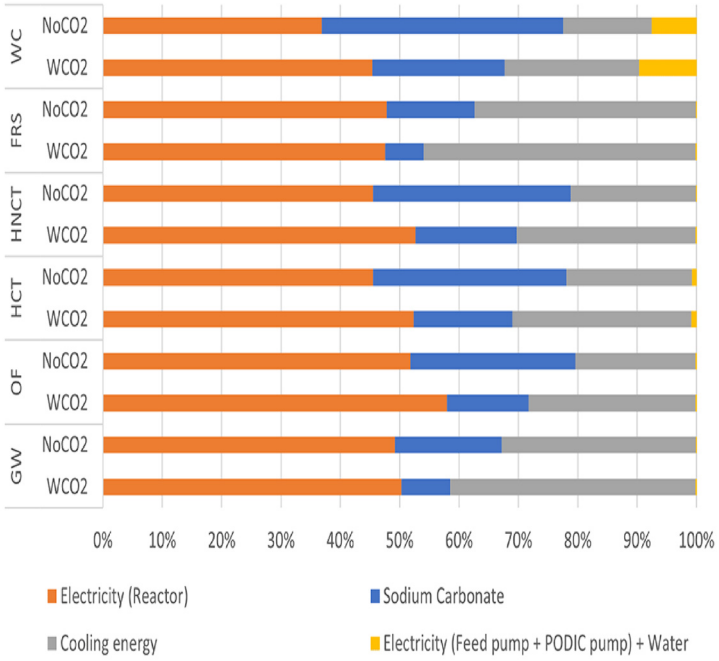

Figure 7. Relative environmental impact analysis of PODIC® production process.

chemical (PODIC®) to promote the conversion of lignin into vanillin. As an overall conclusion, it can be established that the process can be hardly profitable at the current conditions, even at a larger scale, due to the high costs (CAPEX and OPEX of 13.76 and 5.91 €/kg $_{Lignin}$, respectively).

Finally, based on the results of the environmental analysis, in both cases, the PODIC® process was the major factor; the highest environmental impact is due to the power consumption of the reactor, giving the option to further reduce this impact by switching to renewable energy-based electricity consumption. The CO_2 emissions evaluated were similar to those obtained by the *Borregaard* process, again empowering the need for additional improvements in the LIBERATE process to obtain a more sustainable solution.

Annexes

Annexe 1 can be found at https://doi.org/10.5281/zenodo.8424826, while Annexe 2 is available at https://doi.org/10.5281/zenodo.8424810.

Nomenclature

Acronyms

CAPEX: capital expenditure

IRR: internal rate of return

LCA: life cycle assessment

OPEX: operational expenditure

NPV: net present value

ROI: return on investment

TEA: techno-economic analysis

Symbols

A: pre-exponential factor, 1/s

C: concentration of PODIC®, mol/m^3

E_a: activation energy, J

F: Faraday constant, 96,485 s·A/mol

I: the current, A

r_1: PODIC® production rate, mol/s

r_2: PODIC® decomposition rate, mol/s

V: reaction volume, m^3

R: ideal gas constant, 8.31 J/(K·mol)

T: temperature, K

Greek letters

η: the current efficiency, dimensionless

ν: the charge count, dimensionless

Data availability

Zenodo: Files and inventory, https://doi.org/10.5281/zenodo.8424715

This project contains the following:

- LCA
- LCI.xlsx

Process model

- 230212 feedmode2 (1).zip
- Liberate.pcd

TEA

- Economics_SG.py
- Economics_Turton.py
- PV.xlsx
- P_w.xlsx
- TEA_2_nco2.py
- charge.py

Data are available under the terms of the Creative Commons Attribution 4.0 International license (CC-BY 4.0).

Acknowledgements

The work done in this paper was a collaboration done by researchers from three different institutions (IDENER, SINTEF and ENSO INNOVATION) inside the framework of the LIBERATE project. In this sense, the work here presented is the result of the interaction and efforts of all of them. However, it can be specified where each of them had a major contribution:

- Olaf Trygve Berglihn, Eloy Ottaviano, and Álvaro Cabeza were in charge of the process modelling, LCA, and, TEA, respectively. Furthermore, they were involved in the writing process and, so, they are marked as corresponding authors.
- Theresa Rücker and Torbjørn Pettersen were responsible for the experimental part, gathering and treating the data that were used in the model. Similarly, they collaborated on the technical analysis of the process bottlenecks.
- Abraham Aliko and Lucía Gálvez worked on the development of the *Python* files to perform the TEA.
- Bernd Wittgens and María López were in charge of the concept development and review of the whole work.

References

1. Pacek AW, Ding P, Garrett M, *et al.*: **Catalytic conversion of sodium lignosulfonate to vanillin: engineering aspects. Part 1. Effects of processing conditions on vanillin yield and selectivity.** *Ind Eng Chem Res.* 2013; **52**(25): 8361–8372.
Publisher Full Text
2. **Global vanilla and vanillin market trends, share, size, growth, opportunity and forecast report 2019–2024**. [cited 2023 Mar 1].
Reference Source
3. Fache M, Boutevin B, Caillol S: **Vanillin production from lignin and its use as a renewable chemical.** *ACS Sustain Chem Eng.* 2016; **4**(1): 35–46.
Publisher Full Text
4. Araújo JDP, Grande CA, Rodrigues AE: **Vanillin production from lignin**

oxidation in a batch reactor. *Chem Eng Res Des.* 2010; **88**(8): 1024–32.
Publisher Full Text

5. Ponnusamy VK, Nguyen DD, Dharmaraja J, *et al.*: **A review on lignin structure, pretreatments, fermentation reactions and biorefinery potential.** *Bioresour Technol.* 2019; **271**: 462–72.
PubMed Abstract | Publisher Full Text

6. Bomgardner MM: **Following many routes to naturally derived vanillin.** *Chem Eng News.* 2014; **92**(6): 14.
Reference Source

7. Wong SS, Shu R, Zhang J, *et al.*: **Downstream processing of lignin derived feedstock into end products.** *Chem Soc Rev.* 2020; **49**(15): 5510–60.
PubMed Abstract | Publisher Full Text

8. Tarabanko VE, Vigul DO, Kaygorodov KL, *et al.*: **Catalytic oxidation of flax shives into vanillin and pulp.** *Catalysts.* 2022; **12**(9): 1003.
Publisher Full Text

9. Zhang R, Maltari R, Guo M, *et al.*: **Facile synthesis of vanillin from fractionated Kraft lignin.** *Ind Crops Prod.* 2020; **145**: 112095.
Publisher Full Text

10. Wu Z, Hu L, Jiang Y, *et al.*: **Recent advances in the acid-catalyzed conversion of lignin.** *Biomass Conv Bioref.* 2023; **13**(1): 519–39.
Publisher Full Text

11. Roy R, Rahman MS, Amit TA, *et al.*: **Recent advances in lignin depolymerization techniques: a comparative overview of traditional and greener approaches.** *Biomass.* 2022; **2**(3): 130–154.
Publisher Full Text

12. Zhou N, Wass Thilakarathna WPD, *et al.*: **A review: depolymerization of lignin to generate high-value bio-products: opportunities, challenges, and prospects.** *Front Energy Res.* 2022; **9**: 758744.
Publisher Full Text

13. Sun Z, Fridrich B, De Santi A, *et al.*: **Bright side of lignin depolymerization: toward new platform chemicals.** *Chem Rev.* 2018; **118**(2): 614–678.
PubMed Abstract | Publisher Full Text | Free Full Text

14. Zirbes M, Graßl T, Neuber R, *et al.*: **Peroxodicarbonate as a green oxidizer for the selective degradation of Kraft lignin into vanillin.** *Angew Chem Int Ed Engl.* 2023; **62**(14): e202219217.
PubMed Abstract | Publisher Full Text

15. Klein J, Alt K, Waldvogel SR: **Selective degradation of lignosulfonate and lignin with periodate to 5-iodovanillin.** *Adv Sustain Syst.* 2022; **6**(4): 2100391.
Publisher Full Text

16. Arndt S, Weis D, Donsbach K, *et al.*: **The "Green" electrochemical synthesis of periodate.** *Angew Chem Int Ed Engl.* 2020; **59**(21): 8036–8041.
PubMed Abstract | Publisher Full Text | Free Full Text

17. Zhu H, Wang L, Chen Y, *et al.*: **Electrochemical depolymerization of lignin into renewable aromatic compounds in a non-diaphragm electrolytic cell.** *RSC Adv.* 2014; **4**: 29917–29924.
Publisher Full Text

18. González-Cobos J, Prévot MS, Vernoux P: **Electrolysis of lignin for production of chemicals and hydrogen.** *Curr Opin Electrochem.* 2023; **39**: 101255.
Publisher Full Text

19. Zirbes M, Quadri LL, Breiner M, *et al.*: **High-temperature electrolysis of Kraft lignin for selective vanillin formation.** *ACS Sustain Chem Eng.* 2020; **8**(19): 7300–7307.
Publisher Full Text

20. Zirbes M, Waldvogel SR: **Electro-conversion as sustainable method for the fine chemical production from the biopolymer lignin.** *Curr Opin Green Sustain Chem.* 2018; **14**: 19–25.
Publisher Full Text

21. Lindenbeck LM, Barra VC, Dahlhaus S, *et al.*: **Organic chemicals from wood: selective depolymerization and dearomatization of lignin via aqueous electrocatalysis.** *ChemSusChem.* 2024; **17**(9): e202301617.
PubMed Abstract | Publisher Full Text

22. Žabková M, da Silva EAB, Rodrigues AE: **Recovery of vanillin from lignin/vanillin mixture by using tubular ceramic ultrafiltration membranes.** *J Memb Sci.* 2007; **301**(1–2): 221–37.
Publisher Full Text

23. Wongtanyawat N, Lusanandana P, Khwanjaisakun N, *et al.*: **Comparison of different kraft lignin-based vanillin production processes.** *Comput Chem Eng.* 2018; **117**: 159–70.
Publisher Full Text

24. Pinto PCR, Costa CE, Rodrigues AE: **Oxidation of lignin from *Eucalyptus globulus* pulping liquors to produce syringaldehyde and vanillin.** *Ind Eng Chem Res.* 2013; **52**(12): 4421–8.
Publisher Full Text

25. **Process for the oxidation of carbon-containing organic compounds with electrochemically produced oxidizing agents and arrangement for carrying out the process**. November 12, 2018.
Reference Source

26. Seitz AK, Kohlpaintner PJ, van Lingen T, *et al.*: **Concentrated aqueous peroxodicarbonate: efficient electrosyn- thesis and use as oxidizer in epoxidations, *S*-, and *N*-oxidations.** *Angew Chem Int Ed Engl.* 2022; **61**(25): e202117563.
PubMed Abstract | Publisher Full Text | Free Full Text

27. Di Francesco D, Dahlstrand C, Löfstedt J, *et al.*: **Debottlenecking a pulp mill by producing biofuels from black liquor in three steps.** *ChemSusChem.* 2021; **14**(11): 2414–25.
PubMed Abstract | Publisher Full Text | Free Full Text

28. Rücker T, Pettersen T, Graute H, *et al.*: **Pilot scale electrolysis of peroxodicarbonate as an oxidizer for lignin valorization.** *ACS Sustain Chem Eng.* 2024; **12**(30): 11283–11296.
PubMed Abstract | Publisher Full Text | Free Full Text

29. Turton R, Shaeiwitz JA, Bhattacharyya D, *et al.*: **Analysis, synthesis, and design of chemical processes**.

30. Bernier E, Lavigne C, Robidoux PY: **Life cycle assessment of kraft lignin for polymer applications**.

31. Brinkmann T, Giner Santonja G, Schorcht F, *et al.*: **Best available techniques reference document for the production of chlor-alkali**. 2014; [cited 2021 Apr 27].
Publisher Full Text

32. Abdelaziz OY, Al-Rabiah AA, El-Halwagi MM, *et al.*: **Conceptual design of a Kraft lignin biorefinery for the production of valuable chemicals via oxidative depolymerization.** *ACS Sustain Chem Eng.* 2020; **8**(23): 8823–9.
Publisher Full Text

33. **Wholesale Kraft lignin for all your storage demands.** Alibaba.com. [cited 2023 Mar 1].
Reference Source

34. **Cost indices.** Towering Skills. [cited 2023 Mar 1].
Reference Source

35. Modahl IS, Brekke A, Raadal HL: **Life cycle assessment of cellulose, ethanol, lignin and vanillin from Borregaard, Sarpsborg**. 2009.
Reference Source

Open Peer Review

Current Peer Review Status: ? ✓ ? ?

Version 2

Reviewer Report 27 December 2024

https://doi.org/10.21956/openreseurope.20743.r49127

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✓ **Daochen Zhu**
Jiangsu University, Zhenjiang, China

The quality of the revised manuscript has been greatly improved, and I have no further objections. I suggest accepting it

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Biodegradation and high-value conversion of lignin

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard.

Version 1

Reviewer Report 29 February 2024

https://doi.org/10.21956/openreseurope.18075.r37851

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? **Yunxuan Wang**
[1] The University of Tennesse-Knoxville, Knoxville, Tennesse, USA
[2] The University of Tennesse-Knoxville, Knoxville, Tennesse, USA

The work " Innovative vanillin yielding from lignin: process modeling and assessment " demonstrated the economic and environmental evaluation of vanillin production from lignin using

the PODIC® catalyst. Results show that the proposed process is hard to commercialize, and the use of the proposed PODIC® led to the most significant environmental impact. The writing of the manuscript hindered the delivery of the study, as many sentences are not grammatically correct and have numerous typos. Overall, the manuscript should be accepted after addressing the issues listed below.

1. The manuscript needs spelling checking as there are numerous typos. For example, in the PODIC® production pathway section the authors wrote: “its production form sodium carbonate had to be modelled”.
2. Full name of an abbreviation should be given for TRL, NPV when they first appear in the context.
3. For Figure 6, the meanings of the bars and dots should be explained.
4. Many citations are missing from the manuscript. The authors made statements like “ones found in the literature” numerous times with no citation and no results from other studies.
5. In the Analysis of the process with CO_2 supply section, the authors claimed that 145 M is a relatively high cost. What does the “relatively” compare with?
6. In the Introduction, the authors claimed that the use of NaOH is prevented, however, in the study lignin is dissolved in sodium hydroxide, and the process is not NaOH-free.
7. Detailed experimental conditions are missing from the Developed process section.
8. In the Developed process section, the process for “sparging the produced CO_2 in the caustic solution” to regenerate sodium carbonate needs to be described in more detail.

Is the work clearly and accurately presented and does it cite the current literature?
Partly

Is the study design appropriate and does the work have academic merit?
Yes

Are sufficient details of methods and analysis provided to allow replication by others?
Partly

If applicable, is the statistical analysis and its interpretation appropriate?
I cannot comment. A qualified statistician is required.

Are all the source data underlying the results available to ensure full reproducibility?
No

Are the conclusions drawn adequately supported by the results?
Yes

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Biorefinery, Lignin valorization, green solvents

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.

Author Response 11 Dec 2024

Álvaro Cabeza Sánchez

We thank the comments and review done to improve the quality of our manuscript. We include the answers below:

- *The manuscript needs spelling checking as there are numerous typos. For example, in the PODIC® production pathway section the authors wrote: "its production form sodium carbonate had to be modelled".*
  Answer: The complete manuscript was reviewed to remove any typo

- *Full name of an abbreviation should be given for TRL, NPV when they first appear in the context.*
  Answer: The full name was provided and the text was checked to ensure that the definition was available before being used

- *For Figure 6, the meanings of the bars and dots should be explained.*
  Answer: Meanings added (the bars refers to the base case and the dot to de case where the 20% change was applied)

- *Many citations are missing from the manuscript. The authors made statements like "ones found in the literature" numerous times with no citation and no results from other studies.*
  Answer: These references are included in Annexe 1. This was clarified in the text.

- *In the Analysis of the process with CO_2 supply section, the authors claimed that 145 M is a relatively high cost. What does the "relatively" compare with?*
  Answer: The cost is "high" in comparison to the three reference cases. It was clarified in the text.

- *In the Introduction, the authors claimed that the use of NaOH is prevented, however, in the study lignin is dissolved in sodium hydroxide, and the process is not NaOH-free.*
  Answer: The description was clarified. The evaluated process focuses on the dissolution of the lignin in the PODIC stream, not in externally provided NaOH. In this way, the use of external NaOH is prevented. Indeed, NaOH is a byproduct of the PODIC production.

- *Detailed experimental conditions are missing from the Developed process section.*
  Answer: The manuscript is based on the evaluation of the simulated process and a detailed description of the experiments related was not agreed. However, the references to the papers with the experimental work description were included.

- *In the Developed process section, the process for "sparging the produced CO_2 in the caustic solution" to regenerate sodium carbonate needs to be described in more detail.*
  Answer: This step was clarified. Essentially, the idea is to regenerate the Na2CO3 using the produced NaOH and CO2 in the LIBERATE process in a gas-liquid reactor.

Competing Interests: No competing interests were disclosed.

Reviewer Report 26 February 2024

https://doi.org/10.21956/openreseurope.18075.r37861

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?

Zhi-Hua Liu
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Authors provided the modelling of a novel process to promote vanillin production from lignin, including the PODIC© production, lignin depolymerisation and final product separation. The manuscript should be revised to address following concerns.

1 The references should be updated in the manuscript.
2. Biosynthesis method of vanillin should also be introduced in the introduction.
3 More information about vanillin production should be introduced in the introduction section.
4 The electrochemical PODIC production process should be descripted more clear.
5 Figure 2 should be revised to clearly show the key information.
6 Please avoid abbreviations in the text and provide full names
7 The resolution of some images is too low.
8 More discussion about the results should be provided.
9 The key findings of the manuscript should be highlight in each section.

Is the work clearly and accurately presented and does it cite the current literature?
No

Is the study design appropriate and does the work have academic merit?
Yes

Are sufficient details of methods and analysis provided to allow replication by others?
Partly

If applicable, is the statistical analysis and its interpretation appropriate?
Partly

Are all the source data underlying the results available to ensure full reproducibility?
Yes

Are the conclusions drawn adequately supported by the results?

Yes

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Authors provided the modelling of a novel process to promote vanillin production from lignin, including the PODIC© production, lignin depolymerisation and final product separation. The manuscript should be revised to address following concerns. 1 the references should be updated in the manuscript2. biosynthesis method of vanillin should also be introduced in the introduction3 more information about vanillin production should be introduced in the introduction section4 The electrochemical PODIC production process should be descripted more clear5 Figure 2 should be revised to clearly show the key information6 please avoid abbreviations in the text and provide full names7 The resolution of some images is too low8 more discussion about the results should be provided9 the key findings of the manuscript should be highlight in each section

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.

Author Response 11 Dec 2024

Álvaro Cabeza Sánchez

We would like to acknowledge the review and the comments. Below, we explain how we have addressed them.

- *The references should be updated in the manuscript.* **Answer:** the introduction was reviewed and updated
- *Biosynthesis method of vanillin should also be introduced in the introduction.* **Answer:** references to different approaches (including biosynthesis) were included in the introduction
- *More information about vanillin production should be introduced in the introduction section.* **Answer:** additional references were included in the introduction
- *The electrochemical PODIC production process should be descripted more clear.* **Answer:** the description was detailed and references to the related experimental work were included
- *Figure 2 should be revised to clearly show the key information.* **Answer:** Figure 2 was removed since it is not easily understandable. It can be found in the flowsheet, where it can be used to perform the process simulation
- *Please avoid abbreviations in the text and provide full names.* **Answer:** The text was reviewed to ensure that the abbreviations are defined before their use and explained to make it easier the reading
- *The resolution of some images is too low.* **Answer:** Images with better quality were provided
- *More discussion about the results should be provided.* **Answer:** the discussion was reviewed for a better understanding.
- *The key findings of the manuscript should be highlight in each section.* **Answer:** the key

results were highlighted in bold

Competing Interests: No competing interests were disclosed.

Reviewer Report 20 February 2024

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This manuscript presents an innovative approach to producing vanillin from lignin, utilizing a novel process involving PODIC® for depolymerization. The work includes comprehensive process modeling, techno-economic analysis (TEA), and life cycle assessment (LCA). The present work are interesting, and some comments as follows:
1. The PODIC® method is interesting, but the introduction to this method is not detailed enough, and please provide a comparative analysis of why you chose this method instead of other depolymerization methods and whether it can provide more advantages. Providing more in-depth analysis and discussion, for example in terms of efficiency, yield, and environmental impact, can help strengthen the persuasiveness of this approach.
2. The economic evaluation provides a good introduction to the investment and operating costs of the process, and it is best to further discuss how to further reduce costs and improve competitiveness with chemically synthesized vanillin in the future.
3. This manuscript mainly provides conclusions based on process simulation and evaluation. If the results of small-scale production or experimental data at the laboratory level can be provided, it will provide strong support for the accuracy of model predictions.

Is the work clearly and accurately presented and does it cite the current literature?
Yes

Is the study design appropriate and does the work have academic merit?
Yes

Are sufficient details of methods and analysis provided to allow replication by others?
Yes

If applicable, is the statistical analysis and its interpretation appropriate?
Yes

Are all the source data underlying the results available to ensure full reproducibility?
Yes

Are the conclusions drawn adequately supported by the results?
Yes

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Biodegradation and high-value conversion of lignin

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.

Author Response 11 Dec 2024

Álvaro Cabeza Sánchez

First of all, we would like to acknowledge the review of our work. The changes and answers of the provided comments are detailed below:

Reviewer Comment:

- *The PODIC® method is interesting, but the introduction to this method is not detailed enough, and please provide a comparative analysis of why you chose this method instead of other depolymerization methods and whether it can provide more advantages. Providing more in-depth analysis and discussion, for example in terms of efficiency, yield, and environmental impact, can help strengthen the persuasiveness of this approach.*

Answer: The use of PODIC was justified by three main reasons:

1. It means moving from a gas-liquid scenario (thermal oxidation of lignin) to a monophase reactor where electrochemically produced PODIC® is used. Thus, mass transfer limitations would be avoided.
2. The base fact that PODIC® selectively oxidizes lignin into vanillin
3. It implies an electrochemical approach where only electrons are used as reagents and thus toxic and/or harmful reagents can be omitted/reduced

The manuscript focused on the evaluation of the economic and environmental performance of the optimal solution found in the LIBERATE-process at pilot scale (TRL6). For this reason, the obtained results were just compared with the literature in terms of cost and environmental impact. Other evaluations would require the use of experimental information that was not agreed to share in this document. However, the papers where the experimental data are available and discussed were included in the manuscript.

Reviewer Comment:

- *The economic evaluation provides a good introduction to the investment and operating costs of the process, and it is best to further discuss how to further reduce costs and improve competitiveness with chemically synthesized vanillin in the future.*

Answer: The process bottlenecks were identified (mainly dilution and the PODIC production) and feasible solutions were provided and evaluated. Moreover, process

optimisation was also done during the scale-up. All of them have been grouped inside a subsection named "Improvement options" for a better understanding of the discussion.

Reviewer Comment:

- *This manuscript mainly provides conclusions based on process simulation and evaluation. If the results of small-scale production or experimental data at the laboratory level can be provided, it will provide strong support for the accuracy of model predictions.*

Answer: The manuscript focuses on giving a view of the feasible performance at an industrial scale based on simulation. In this way, other researchers can get access to the overall aspects of the solution developed and the “current” economic and environmental perspectives. The experimental part is not in the scope and, indeed, it was not agreed to include it here since it was published by the developers in other papers. The references of these experimental papers were included.

Competing Interests: No competing interests were disclosed.

Reviewer Report 13 February 2024

https://doi.org/10.21956/openreseurope.18075.r37489

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Adam Slabon
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The manuscript of Sanchez et al reports the chemical process to obtain vanillin from lignin based on process modelling. The work is interesting for both academic and industrial researchers, but there are three issues.
1. there is no experimental proof that vanillin can be obtained in such high yield as required for the process after scale-up. The authors should take the low yield into account or provide experimental proof for the reactor concept. I do not ask for building the reactor, but the difficulties for scale-up regarding yield should be discussed.
2. the references omit the major developments in the field of electrochemical lignin depolymerization. For instance, using carbonate electrolytes have been recently reported to be efficient solvent systems ref[1]. There are several more recent advancements in the field. The introduction is short and could be extended.
3. What about the stability of the electrodes during long-term electrolysis? Nearly all published articles just focus on relatively short time frames. However, for many catalyst systems the leaching of the electrode provides many problems.

References

1. Lindenbeck LM, Barra VC, Dahlhaus S, Brand S, et al.: Organic Chemicals from Wood: Selective Depolymerization and Dearomatization of Lignin via Aqueous Electrocatalysis.*ChemSusChem*. 2024. e202301617 PubMed Abstract | Publisher Full Text

Is the work clearly and accurately presented and does it cite the current literature?
No

Is the study design appropriate and does the work have academic merit?
Yes

Are sufficient details of methods and analysis provided to allow replication by others?
No

If applicable, is the statistical analysis and its interpretation appropriate?
Yes

Are all the source data underlying the results available to ensure full reproducibility?
Partly

Are the conclusions drawn adequately supported by the results?
Partly

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: electrocatalysis

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.

Author Response 11 Dec 2024

Álvaro Cabeza Sánchez

First of all, we would like to thank the review and the provided comments. Below, we explain how we have addressed them:

- *There is no experimental proof that vanillin can be obtained in such high yield as required for the process after scale-up. The authors should take the low yield into account or provide experimental proof for the reactor concept. I do not ask for building the reactor, but the difficulties for scale-up regarding yield should be discussed.*

Answer: The aim of the research paper is not focused on the experimental work but on the evaluation of the technology developed inside the LIBERATE-project at a relevant scale. Thus, the idea is to provide insights into the expected economic and environmental performance of the LIBERATE approach and investigate whether it could be translated into an industrial environment by evaluating the main burdens. In this way, other researchers can get an idea of the “current” performance of this lignin valorisation approach. On the other hand, it is true that the scale implemented in the model cannot be substantiated with

experimental data from a plant of the same capacity. However, in the course of the LIBERATE-project, a scale-up from lab to pilot scale (TRL6) was done by SINTEF obtaining similar yields in both scales. Thus, it was demonstrated that the technology could be used at different scales without significant losses in the yields. Furthermore, in the evaluation, scale-up approaches (like numbering for the electrochemical reactor) were included to have a more realistic evaluation. The reference to the related paper was included in the document.

- The references omit the major developments in the field of electrochemical lignin depolymerization. For instance, using carbonate electrolytes have been recently reported to be efficient solvent systems ref[1]. There are several more recent advancements in the field. The introduction is short and could be extended.

Answer: As previously mentioned, the work focused on the evaluation of the technology and not on the experimental part. Thus, the literature review was focused on those works where economic/environmental data were provided. However, we references on the field of electrochemical lignin depolymerization accordingly.

- *What about the stability of the electrodes during long-term electrolysis? Nearly all published articles just focus on relatively short time frames. However, for many catalyst systems the leaching of the electrode provides many problems.*

Answer: The electrochemical cell for PODIC production was opened at the end of the project and the state of the electrodes was evaluated. However, the authors of this paper are not the owners of this information and the results were not made public by the manufacturer. Thus, if someone is interested in further work on these electrodes, we recommend directly contacting the electrochemical cell manufacturer (CONDIAS, https://www.condias.de/en-gb)

Competing Interests: No competing interests were disclosed.