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PAPER

Techno-economic assessment for the large-scale production of colloidal lignin particles

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The purpose of this study is to investigate the techno-economic feasibility of an environmentally sustainable and green process for the cost-effective large-scale manufacturing of colloidal lignin particles. The process involves the instantaneous formation of colloidal lignin particles (CLPs) through self-assembly when a concentrated solution of lignin in tetrahydrofuran (THF) and ethanol is introduced into water. The capacity of the plant is assumed to be 50 kt/yr. of dry colloidal lignin and Aspen plus simulation program is used for the mass and energy balance calculations. The process equipment design and pricing are carried out based on relevant literature and vendor data. Results show that the total investment cost for a plant integrated with an existing pulp mill or bio-refinery is 36 M€ and the annual operating cost is 46 M€. The project lifetime is assumed as 20 years and the cost of production of colloidal lignin is found to be 0.99 €/kg (in case of integration) and 1.59 €/kg (without integration). The revenue for the process comes mainly from selling the colloidal lignin particles and additional revenue is generated from high pressure and low-pressure steam condensate sold as district heat. The payback period with a CLP selling price of 1.10 €/kg is found to be roughly 5 years. A minimum profitability requirement of 10 % is considered for the techno-economic analysis and the internal rate of return (IRR) is calculated as 17 % making the process viable and profitable. In addition, a sensitivity analysis is carried out to evaluate the effect of raw material price and ethanol revovery on the operating cost. Colloidal lignin has the potential to compete favorably as a renewable replacement for petroleum based feedstock like polyethylene, polypropylene, polythethylene terephthalate (PET) and phenol and can be used in attractive applications like phenol formaldehyde (PF) resins, foams, carbon fillers, bactericides and composites.

Introduction

Lignin is the most underutilized component of lignocellulosic biomass. Each year around 40-50 million tons of lignin is produced as black liquor and close to 95 % of this is burnt to produce energy because of the good heating value of lignin. Currently, just 5 % of the industrial grade lignin is utilized in the manufacturing of value added products such as binders, dispersants, additives and surfactants.[1] If the existing pulp mills want to capitalize on the rather low value of lignin, its quality needs to be improved. The use of lignin in many high-volume applications such as adhesives[1–5], carbon materials[6,7] and as source of chemicals[8–13] have already been studied or are currently in application. The inherent heterogeneity and poor dispersibility associated with lignin can be overcome by transforming it into colloidal particles., They are easily dispersible and do not cause sedimentation thereby enabling the use of lignin in applications related to adhesives, controlled

drug delivery[14–18], functional surface coatings[19] and nanocomposites.[20]

Several methods have been reported to produce colloidal lignin particles (CLPs),[21-23] but most of them are energy intensive and consume considerable number of reagents. Moreover, the products are very diluted, thereby making their use appropriate only in high-end applications that might not require large-scale production. The CLP preparation methods described by Yiasawas et al. and Qian et al. involves the use of hazardous chemicals such as toluene diisocyanate and pyridine.[22,23] Furthermore, for obtaining highly concentrated dispersions, significant quantity of water needs to be evaporated thereby making the process energy intensive. So far, no large-scale methods for producing CLPs have been reported that can overcome these challenges.

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†Electronic Supplementary Information (ESI) available: [details regarding equipment sizing, equipment cost estimation and profitability assessment]. See DOI: 10.1039/x0xx00000x

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Therefore, if it is desired to produce CLPs on a large scale to facilitate their use in bulk applications such as materials and foodstuff, it is necessary to develop an economical and energy efficient process that can produce a concentrated product with a low cost of production and minimum usage of reagents. Lintinen et al. developed an industrially scalable and feasible process[24] to produce CLPs that is used in this work as a basis for the design and techno-economic assessment of a large-scale continuous flow process for producing commercially significant amounts of dry colloidal lignin. In the process, a concentrated solution of lignin immediately forms colloidal lignin through self-assembly after encountering water. The solvents are recovered for reuse in the process and the colloids are efficiently concentrated using ultrafiltration and spray dried.

2. Methods

2.1 Process Overview

The simplified process flow diagram is shown in Fig. 1 and illustrates the five main processing steps:

- *Lignin solution preparation:* Lignin is dissolved in a solution consisting of tetrahydrofuran, ethanol and water
- *Formation of CLP dispersion:* The colloidal dispersion is formed in the tubular reactor where the lignin solution self-assembles into colloids after encountering water.
- *Ultrafiltration:* The aqueous CLP dispersion is concentrated up to 25 wt. % using ultrafiltration
- *Solvent recovery:* The solvents are recovered by distillation in two stages and recycled back for reuse in the dissolution of lignin. The loss of solvents in the process is less than 1 %.
- *Product recovery:* The concentrated dispersion is spray dried to obtain CLP in dry powder form.

2.2 Techno-Economic Assessment (TEA) Approach

The feasibility of the process is evaluated based on a techno-economic assessment that includes conceptual process design to develop a detailed process flow diagram, energy and material balance calculations using commercial process simulation tools such as Aspen Plus, fixed capital and investment cost estimations using detailed factorial method via spreadsheets, profitability assessment and sensitivity analysis of key parameters affecting the process.

The annual operating cost is calculated as the sum of variable and fixed costs based on the mass and energy balance calculations using Aspen plus process simulations. The fixed costs include labour, employee benefits, supervision, laboratory, insurance and taxes, maintenance and plant overhead as summarized in table 1. The production is carried out in continuous shift work with 25 employees including shift workers, supervision, quality control, safety, R&D, marketing

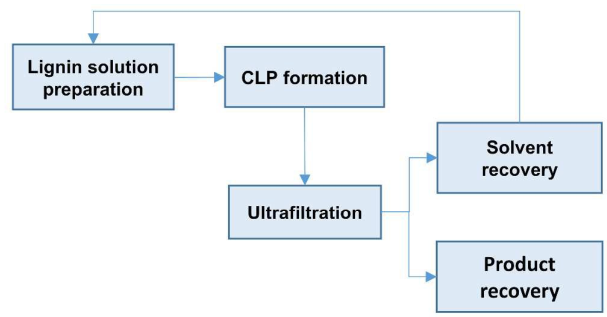

Figure 1. Simplified block flow diagram for the large-scale production of CLPs.

and management. The number of shifts is five and the plant is operated throughout the year.

The variable costs include raw materials, utilities and operating supplies. The main raw materials for the process include THF, ethanol, water and lignin. The utilities include electricity for pumps, cooling water for condensers, low-pressure (LP) and high-pressure (HP) steam for re-boilers and air heater, respectively. The raw material and utility costs estimated based on literature and current market prices are summarized in table 2.

The fixed capital investment (FCI) is estimated by multiplying the total equipment purchase cost with two factors

as shown in eqn (1). The first factor accounts for the physical plant cost and includes costs related to equipment installation, piping, instrumentation and buildings. The second factor takes into consideration costs related to design and engineering, contractor fee and contingency. All costs are converted to 2017 prices in Euros by considering the chemical engineering plant cost indexes (CEPCI) and currency conversion.

$$FCI = Purchase\ cost\ of\ equipment * 3.15 * 1.40 \quad (1)$$

$$Total\ Investment = FCI + \ OSBL + working\ capital + start - up\ capital \quad (2)$$

The profitability of the process is evaluated based on the payback period, return on investment (ROI) and internal rate of return (IRR). The project lifetime is 20 years and the equipment lifetime is 10 years with a straight-line depreciation model. The investment is done in year 0 and the plant operation begins in year 1. At the end of the equipment lifetime, the investment is deducted in year 10 to renew the equipment and a construction period of 3 months is applied, thereby lowering the cash flow

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Table 1. Assumptions for techno-economic assessment

Component	Assumed basis
Basis year for evaluation	2017
Project lifetime	20 years
Equipment lifetime	10 years
Profitability requirement	10 %
Taxation rate	20 %
Working capital	10 % of FCI
Start-up capital	10 % of FCI
Outside battery limit (OSBL)	40 % of FCI
Operating supplies	1 % of FCI
Employee Benefits	40 % of labour costs
Supervision	30 % of labour costs
Laboratory	20 % of labour costs
Insurance and taxes	3 % of FCI
Maintenance	6 % of FCI
Plant overhead	1 % of FCI
Administration	20 % of labour costs

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Table 2. Raw material and utility prices

Component	Price	
Lignin	400	€/ton[25] (Integrated),
	1000	€/ton[26] (Non-integrated)
Tetrahydrofuran (THF)	3070	€/ton[27]
Ethanol	389	€/ton[28]
Cooling water	5	€/m^3
Electricity	80	€/MWh[29]
Low-pressure steam (LP)	20	€/ton
High-pressure steam (HP)	40	€/ton
District heating	79	€/MWh[29]

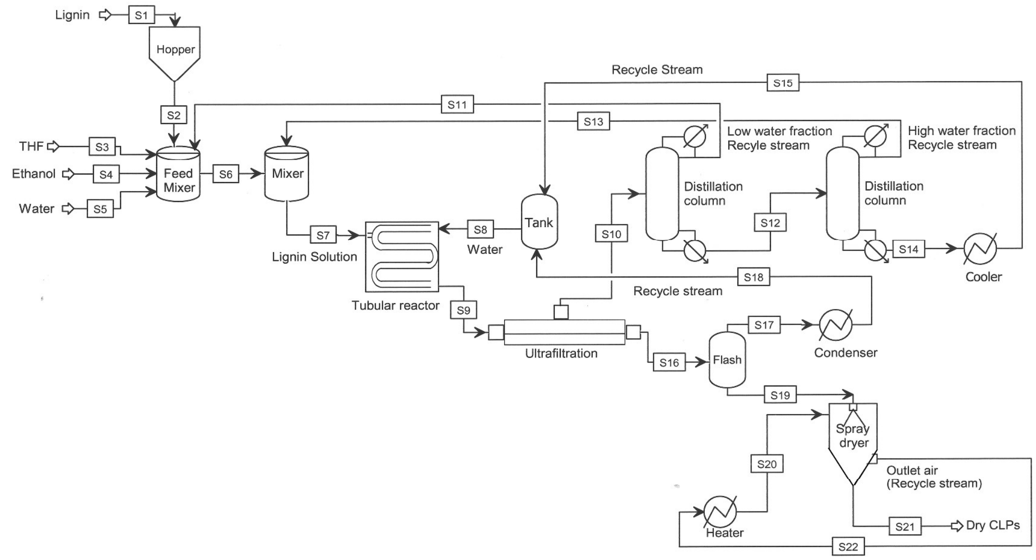

Figure 2. Process simulation flow diagram for large-scale production of colloidal lignin particles.

for this year. The profitability requirement for the investment is chosen as 10 % and this is varied by adjusting the net present value (NPV) in year 20 to zero to determine the internal rate of return. The equations used in the calculations of NPV, ROI and payback period can be found in the supplementary information.

3 Results and Discussions

3.1 Process simulation

The large-scale production of colloidal lignin particles was simulated using Aspen Plus simulation program. The thermodynamic package used is non-random two-liquid model (NRTL) and lignin is modelled as a non-conventional component. The simulation process flow diagram is shown in Fig. 2. The process begins with the dissolution of lignin in a solvent mixture comprising of THF, ethanol and water. The dissolution occurs in the feed mixer and the lignin solution at 20 °C enters the continuous flow tubular reactor, which contains static mixing elements to enable the formation of a uniform and homogeneous CLP dispersion. Water and lignin solution are flowing counter currently resulting in rapid formation of self-assembling colloidal lignin particles. The process is slightly exothermic and since there is only mixing that occurs within the tubular reactor, it was modelled as a mixer in Aspen Plus. Before proceeding with the recovery of solvents, it is necessary to ensure that no colloidal lignin enters the distillation column. This is achieved by introducing the CLP dispersion at 23 °C into an ultrafiltration unit where it is concentrated up to 25 wt. %. In the ultrafiltration module, a pressure drop of 1 bar is present. The module used in tests was Valmet's Opticycle C. The ultrafiltration unit was modelled as a separator block in Aspen Plus. The permeate stream containing the solvents is introduced into the distillation column, which was modelled in Aspen Plus by making use of the rigorous modeling approach. The solvents are recovered using two distillation columns which are operated 0.25 bar and 0.15 bar respectively. In the first distillation, a high THF and low water containing fraction (82 wt.% THF, 9 wt.% H_20 and 8 wt.% EtOH) is recovered at 29 °C and in the second distillation, a low THF and high water containing fraction (38 wt.% THF, 15 wt.% H_2O and 47 wt.% EtOH) is recovered at 31 °C.

The solvents recovered from the first distillation column are recycled back to the feed mixer for reuse in the dissolution of lignin and the recovered solvents from the second distillation column are recycled back to the mixer for further dilution of lignin. The bottom product consisting of mostly water is recycled back for reuse in the tubular reactor. The concentrated CLP dispersion from the ultrafilter is transferred into a flash recovery unit where the remaining solvents are recovered. The liquid phase from flash unit consisting of 65 wt.% water and 35 wt.% CLPs is introduced into a spray drier operated adiabatically. Hot air enters the drier at 180 °C and the colloidal lignin particles are spray dried and obtained in dry

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powder form. The mass balance for the large-scale production of colloidal lignin particles is shown in Fig. 3.

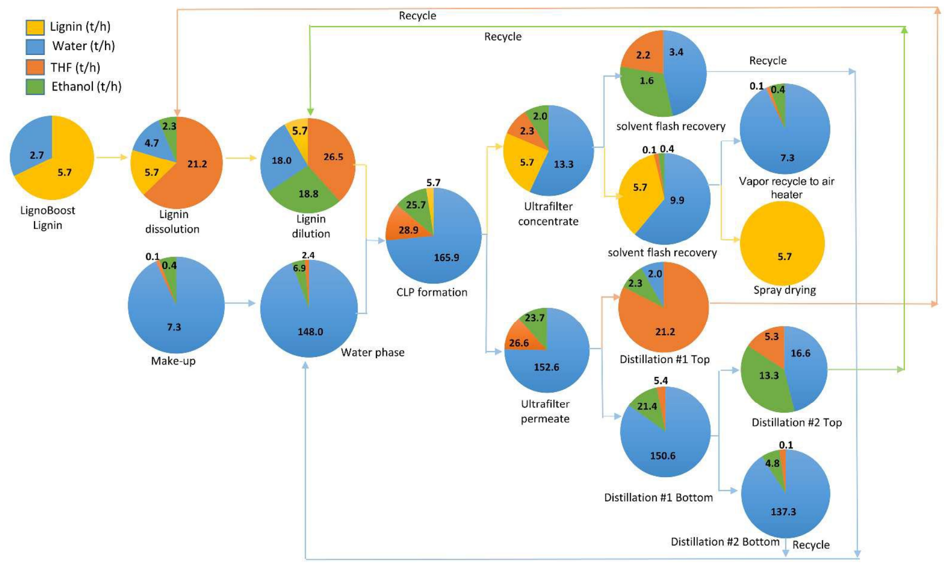

Figure 3. Mass balance for large-scale production of colloidal lignin particles (50 kt/yr.) All the reagents used are marked with a unique colour and the proportion of reagents is displayed as a pie chart. The lignin containing process streams are indicated with the colour of lignin and the solvent containing streams are indicated with the colour of the majority solvent.

3.2 Process economics

The equipment is sized[30–32] and the fixed capital investment is estimated based on the purchased equipment cost calculated from literature[33,34] and vendor quotes. Fig. 4 shows percentage contribution of individual equipment to the total fixed capital investment. The ultrafilter unit is the most expensive and contributes to 35 % of the fixed capital costs followed by the spray dryer, which contributes 18 %. The high equipment cost in case of the ultrafilter is offset by its relatively low energy duty (~1 MW) and the spray dryer operated adiabatically consumes only a low amount of energy. The contribution of each process equipment to the overall energy consumption (67 MW) is presented in Fig. 5. The solvent recovery step consumes the most energy (64 %) and can be reduced based on the desired recovery of ethanol during the distillation step. The total investment (sum of FCI, OSBL, start-up capital and working capital) is calculated as 36 M€ for both the integrated and non-integrated scenarios.

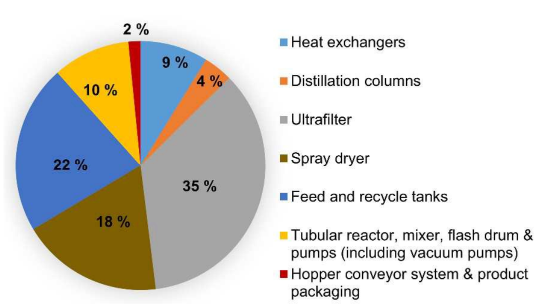

Figure 4. Percentage contribution of equipment to the fixed capital investment.

The annual operating cost is affected by the price of raw material lignin. Depending on the energy content of lignin and the current price of biomass for energy, the lignin would cost about 300 €/ton.[25] Therefore, the assumed lignin price of 400 €/ton in case of the integrated scenario is found to be reasonable. On the other hand, in case of the non-integrated scenario, the price of raw material lignin is assumed to be 1000 €/ton based on the current selling price of lignin which is around 800 €/ton.[26] The annual operating cost consists of fixed and variable costs as shown in Fig. 6 and is calculated as 46 and 76 M€ for the integrated and non-integrated scenarios respectively. Therefore, it makes sense that the process should be integrated with an existing pulp mill or bio-refinery as this would significantly reduce the operating cost.

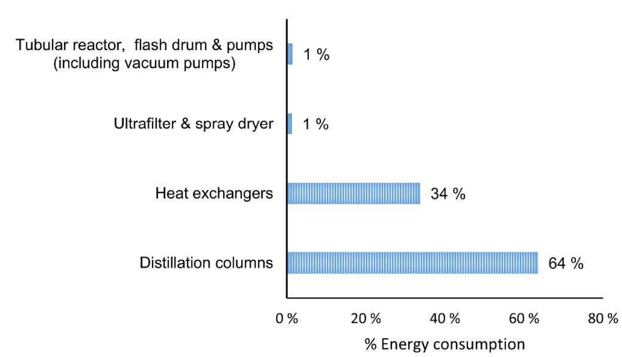

Figure 5. Percentage contribution of process units to total energy consumption.

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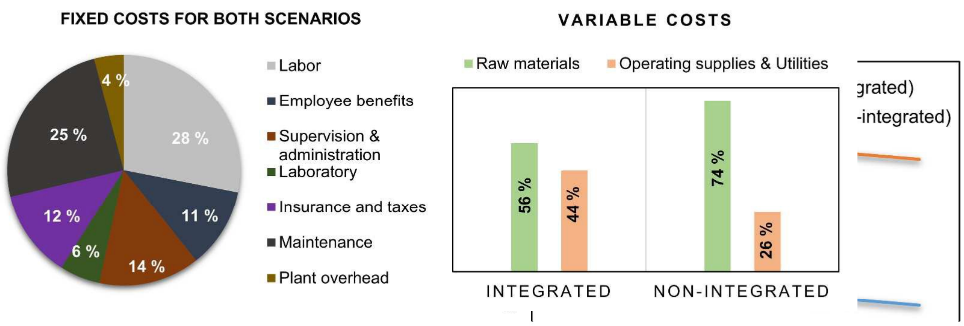

Figure 6. Annual operating cost distribution for integrated and non-integrated scenarios.

3.3 Profitability Assessment

The profitability of the process is evaluated based on the payback period, return on investment and internal rate of return.

The cost of the production of colloidal lignin is determined by adjusting the NPV at year 20 to zero and is found to be 0.99 €/kg and 1.59 €/kg for the integrated and non-integrated scenarios respectively. The selling price of colloidal lignin is fixed based on the desired payback period and in this case is calculated such that we obtain a payback period of roughly 5 years. From Fig. 7, it is seen that when the CLP selling price is 1.10 €/kg for the integrated case and 1.70 €/kg for the non-integration scenario, the calculated payback period is 5 years. In Fig. 8, the NPV is plotted as a function of time over the entire lifetime of the project. The NPV is calculated for the integrated scenario with a base CLP selling price of 1.10 €/kg. For the investment we assume a minimum profitability requirement of 10 % and the internal rate of return is calculated by iterating the profitability requirement till the NPV reaches a value of zero in year 20. The IRR and ROI for the integrated scenario is found to be 17 % and 20 % respectively. Since the internal rate of return is more than the minimum profitability requirement, the project could be considered as viable and profitable.

Figure 7. Sel ses
calculated fo

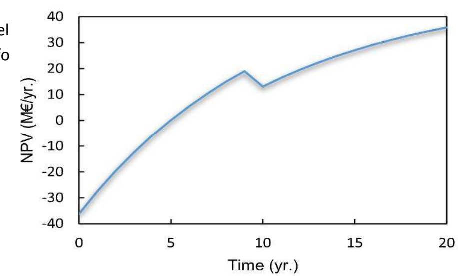

Figure 8. NPV plotted as a function of the payback period.

The effect of plant capacity on the cost of production and the selling price of CLP, total investment and annual operating cost is shown in Fig. 9 and 10 respectively. Upon decreasing the plant capacity to one-tenth of its existing capacity, it is observed that there is a reduction in the total investment and operating cost and on the other hand, the cost of production of CLP increases to 1.71 €/kg in comparison to 0.99 €/kg for the integrated case (50 kt/yr.). Therefore, having a larger plant capacity can make the process more viable and profitable by bringing down the cost of production of colloidal lignin thereby bringing the price closer to the level of petrochemical polymers, such as such as PET, polyethylene and polypropylene.

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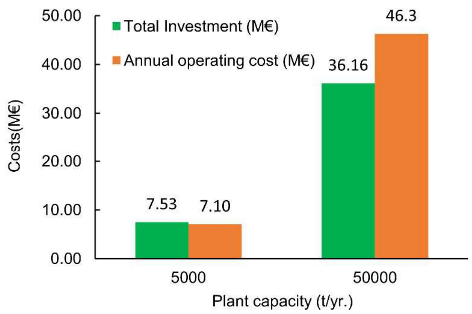

Figure 9. Effect of plant capacity on the total investment and annual operating cost.

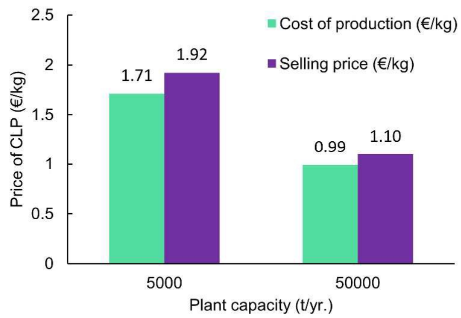

Figure 10. Effect of plant capacity on the cost of production and selling price of CLP.

3.4 Sensitivity Analysis

The effect of lignin price on the process is quite significant as observed from Fig. 11. For the base case in which the process will be integrated with an existing pulp mill or bio-refinery the cost of raw material lignin is 0.4 €/kg based on the energy costs involved in the production of lignin from black liquor. In figure 11, the price of lignin is varied within a range of ± 20 % to evaluate its effect on the cumulative cash flow over the entire lifetime of the project. On comparing with the base case in which we obtain a cumulative cash flow of 153 M€ at the end of the project lifetime, it is observed that a 20 % increase in the price of lignin brings down the cumulative cash flow to 90 M€ while a 20 % decrease in the lignin price makes the cumulative cash flow jump to 216 M€.

The recovery of ethanol makes the process energy intensive and hence it is decided to recover 80 % of ethanol in the distillation top product. There is no need to recover ethanol up to 90 or even 100 % since the ethanol in the bottom product is recycled to the tubular reactor along with the water phase for reuse in the formation of CLP dispersion up to 2.80 wt.%. Fig. 12 shows the percentage change in the operating costs with respect to the percentage of ethanol recovered. It can be observed that when the ethanol recovery is 60 %, there is 3 % reduction in the annual operating costs in contrast to the scenario with 100 % ethanol recovery in which case, the annual operating cost increases by 8 %.

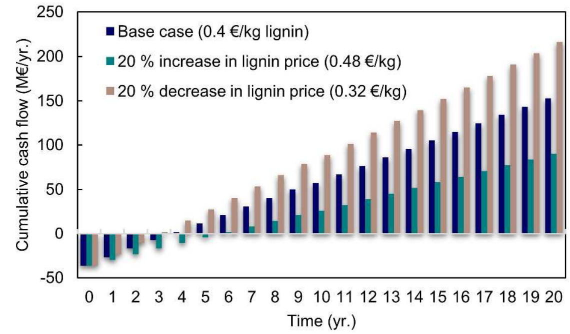

Figure 11. Effect of variation in lignin price on the cumulative cash flow over the entire lifetime of the project.

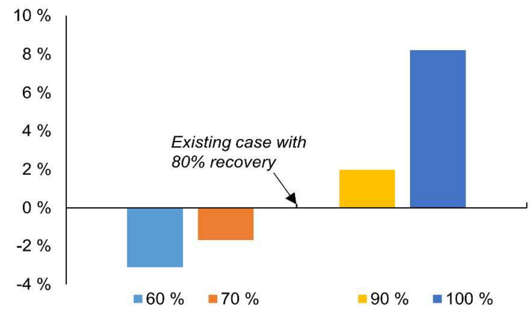

Figure 12. Effect of changes in ethanol recovery on the annual operating cost.

4 Environmental concerns

The large-scale CLP production method described is a closed loop process that requires the use of limited amount of organic solvents (THF and ethanol). More than 99 % of the organic solvents are recovered and recycled within the process for reuse in the dissolution and dilution of LignoBoost lignin. The solvents are recovered in the form of mixtures, thereby reducing the need for energy intensive distillation and making the process very energy efficient. The outlet air stream exiting the spray dryer contains the remaining traces of organic solvent vapors and it is recycled back to the air heater for reuse in the spray drying process. This means that there are no greenhouse gas (GHG) emissions to the atmosphere making the process environmentally sustainable and green. The process does not produce any waste streams apart from ash which is present as a minor impurity in LignoBoost lignin and is removed in the beginning of the process by decantation and can find use in land applications.[37,38] It is to be noted that ash is present even when burning lignin for power, which is the most traditional use of lignin in pulp mills.

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The biodegradability of lignin is especially attractive considering its minimal impact on the environment. Based on many life cycle assessment (LCA) studies, the "zero-burden" approach has been adopted to evaluate the environmental burdens associated with the use of lignin as a raw material. Such an approach assumes that lignin is produced as a waste stream in pulp mills and biorefineries and as a result there is zero impact occurring by its use in the process (i.e., the upstream environmental burdens are not considered).[39] Typically, in pulp mills and bio-refineries lignin is recovered as a side product and owing to its good heating value is extracted from black liquor and combusted in a boiler to generate energy in the form of steam and electricity. The average lifecycle GHG emissions when lignin is used as an energy source onsite at the biorefinery is 0.038 kg CO_2 eq/MJ[40] and in case of energy generation using renewable wind energy is 0.0072 kg CO_2 eq/MJ.[41]

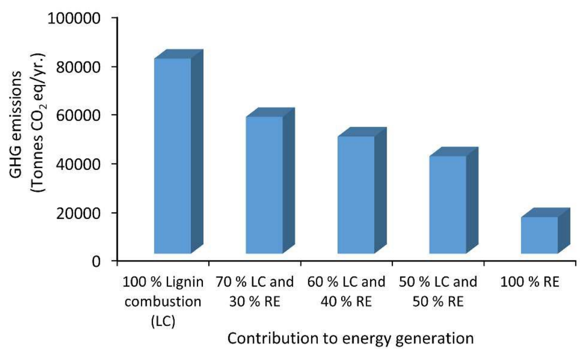

Figure 13. GHG emissions for different energy generation scenarios.

For the CLP process, purchased utilities such as electricity, low-pressure and high-pressure steam are assumed to be produced using renewable sources and any additional process heat that is generated in the process from the LP and HP steam condensate is sold as district heat, generating additional revenue from the process. There is no steam and electricity generation within the process, which could contribute to a carbon footprint. Nevertheless, five different scenarios have been presented for energy generation and the greenhouse gas emissions are expressed in tons of CO_2 eq./yr. as shown in Fig. 13. It is seen that when renewable wind energy (RE) is used to meet the energy demand of the process, there is significantly lower GHG emissions in comparison to the other scenarios where lignin is either combusted entirely or is used partly with renewable energy.

5 Economic potential of colloidal lignin particles

In the current scenario, CLPs can compete with petrochemical based feedstock like polyethylene, polypropylene and polyethylene terephthalate which are priced similarly as seen from Fig. 14. The price of phenol varies between 800-1000 €/ton and the market price determined for CLPs is 1100 €/ton based on using LignoBoost lignin as a raw material for the CLP process. LignoBoost lignin is more expensive since it is a purified form of lignin and therefore, the CLPs produced are more uniform, standardized and refined. Depending on the source of lignin, cost of production of CLPs can be reduced even more and brought down to the level of phenol.

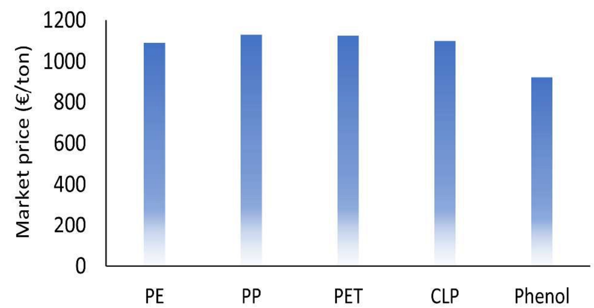

Figure 14. Market price comparison of CLPs with petrochemical-based feedstock.

Although CLPs are today slightly expensive but being environmentally friendly they can still compete favorably with phenol for applications in PF resins. Assis et al. used the aerosol method to produce lignin macro- and nanoparticles and have reported the manufacturing costs to be in the range of 800 to 1000 €/ton based on the type of raw material used.[42] This price is quite close to the cost of producing CLPs reported in this paper at 990€/ton.

A preliminary assessment for the economic potential of colloidal lignin nanoparticles is carried out by identifying the most attractive applications of CLPs from economic perspective and global market size as summarized in the Table 3. Based on the assessment, it can be seen that while it might be particularly attractive to use CLPs in emulsion stabilizers and UV protection materials given the high price of some of the currently used materials in these applications, however these might not be the best applications from an economic perspective as most of these products represent a smaller market size in comparison to the use of CLPs in phenol formaldehyde resins as a replacement for phenol, foams, composite reinforcement materials, bactericides and fillers which have a far bigger market size making it highly attractive

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for large scale manufacturing and commercialization of CLP based products.

Table 3. Economic potential of colloidal lignin particles

Application of CLPs	Products used currently	Market price (€/ton)	Global market size (kt/yr.)
Emulsion stabilizers	Gum arabic	1500-3000[43]	60[44]
Foams (as a raw material)	Polyurethane	2000-3000[45]	10000[46]
UV protection products	Phenolic benzotriazoles	15000-20000[47]	12[48]
Anti-bacterial products	Titanium dioxide	2000-2500[49]	7000[50]
Carbon fillers	Carbon black	1000[51]	12000[52]
Phenol-formaldehyde resins	Phenol (in production)	800-1000[53]	5000[54]
Composite reinforcement	Glass fibers	1100-2200[55]	8000[56]

6 Conclusion

The techno-economic assessment was carried out for a new environmentally sustainable and green process for the efficient and cost-effective manufacturing of large quantities of colloidal lignin particles. For a process facility with an annual production of 50 kt of dry colloidal lignin, the selling price with a payback period of five years is found to be 1.10 €/kg when the process is integrated with an existing pulp mill and 1.70 €/kg for the non-integrated scenario. The price of lignin as raw material and the percentage of ethanol recovered during distillation are identified as the most crucial variables for reducing the process operating cost. With a profitability requirement of 10 %, the internal rate of return and return on investment is calculated as 17 and 20 % respectively, thereby making it a viable and profitable process.

Based on a preliminary assessment carried out to evaluate the economic potential of colloidal lignin particles, it was found that with a selling price of 1.10 €/kg, CLPs offer a great potential to be used in large-scale applications. These include PF resins[36] where CLPs can be used as a replacement for petroleum-based phenol. In addition, CLPs have potential applications in foams, anti-bacterial products such as bactericides, carbon fillers and nanocomposite manufacture. With cost-effective CLP production methods, commercially viable products come increasingly into view.

Conflicts of interest

K.L, R.B.A, P.O., M.A.K and M.Ö., declare potential financial interests in the future development and commercialization of the CLP process. Aalto University has filed a Finnish provisional patent application (FI 20175947).

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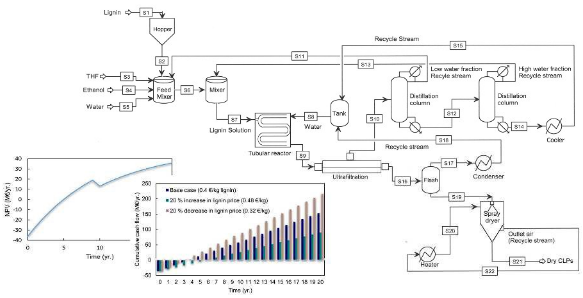
Graphic:



Text:

Economical large-scale production of colloidal lignin particles