

---

This is an electronic reprint of the original article.  
This reprint may differ from the original in pagination and typographic detail.

Lintinen, Kalle; Xiao, Yao; Bangalore Ashok, Rahul; Leskinen, Timo; Sakarinen, Ekaterina; Sipponen, Mika; Muhammad, Farooq; Oinas, Pekka; Österberg, Monika; Kostiainen, Mauri  
**Closed cycle production of concentrated and dry redispersible colloidal lignin particles with a three solvent polarity exchange method**

*Published in:*  
Green Chemistry

*DOI:*  
[10.1039/c7gc03465b](https://doi.org/10.1039/c7gc03465b)

Published: 01/01/2018

*Document Version*  
Peer-reviewed accepted author manuscript, also known as Final accepted manuscript or Post-print

*Published under the following license:*  
Unspecified

*Please cite the original version:*  
Lintinen, K., Xiao, Y., Bangalore Ashok, R., Leskinen, T., Sakarinen, E., Sipponen, M., Muhammad, F., Oinas, P., Österberg, M., & Kostiainen, M. (2018). Closed cycle production of concentrated and dry redispersible colloidal lignin particles with a three solvent polarity exchange method. *Green Chemistry*, 20(4), 843-850. <https://doi.org/10.1039/c7gc03465b>

---

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.



## Closed Cycle Production of Concentrated and Dry Redispersible Colloidal Lignin Particles with a Three Solvent Polarity Exchange Method

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

[www.rsc.org/](http://www.rsc.org/)

Kalle Lintinen, Yao Xiao, Rahul Bangalore Ashok, Timo Leskinen, Ekaterina Sakarinen, Mika Sipponen, Farooq Muhammad, Pekka Oinas, Monika Österberg, Mauri Kostiainen\*

Lignin, an aromatic biopolymer, is the main by-product of pulp manufacture, and has been under intense study, as it offers great promise as an alternative for petrochemical polymers. However due to its heterogeneity, the applications where lignin can be used have been limited, leading to the vast majority of it being burned for fuel. Colloidal lignin particles (CLPs) offer a means to disperse lignin homogeneously into both water and other media, such as polymers. However, no means thus far have been presented that would allow for a large-scale production of CLPs. Herein we show an industrially scalable closed cycle process of CLP production. In the process, a concentrated solution of lignin in tetrahydrofuran (THF) and ethanol (EtOH) is added into the non-solvent water, instantaneously forming CLPs through self-assembly. The organic solvents are recovered and reused in the process. The aqueous CLPs are concentrated by ultrafiltration and the concentrated particles are spray dried, leading to redispersible microclusters. CLPs can be used in multiple applications, such as Pickering emulsions and composite materials. A significant portion of the 50 million tons of lignin produced by the pulp industry could be made into CLPs with this low cost process, which would open a whole new class of materials for industrial applications.

### Introduction

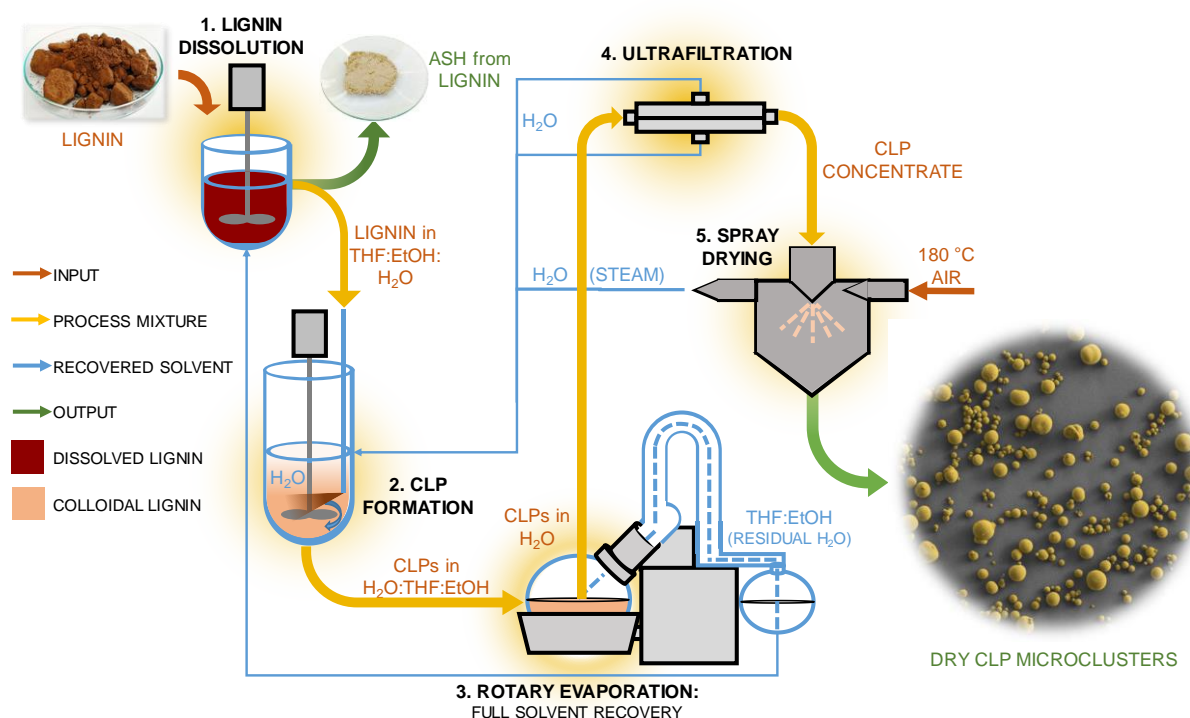
Several high volume applications of lignin are already studied or already in use, such as binders and adhesives<sup>[1–5]</sup> carbon materials<sup>[6,7]</sup> and sources of chemicals.<sup>[8–13]</sup> When lignin is transformed into colloidal lignin particles (CLPs), its inherent heterogeneity and poor dispersibility can be overcome and several high end applications,<sup>[14]</sup> such as antibacterials and biocides,<sup>[15,16]</sup> controlled drug delivery,<sup>[17–21]</sup> functional surface coatings<sup>[22]</sup> and nanoglues<sup>[23]</sup> are enabled. Multiple methods for the production of CLPs have been presented,<sup>[24–28]</sup> but most of them consume a significant amount of reagents and energy and/or the products are so dilute that their large scale production demands applications associated with high-value end products. For the wide adoption of colloidal lignin into bulk applications such as materials and foodstuff, the production cost of the colloids must drop significantly and redispersible powdery products must be developed. Ideally, the process should not involve any functionalization, not consume any

reagents, consume very little energy, and the product should be concentrated and process fast enough to minimize investments in equipment. Thus far, no large-scale production method for lignin colloids has been presented that overcomes these obstacles.

Recently, we showed that just by direct introduction of a THF solution of lignin into water 200 nm particles could be obtained at close to 1 wt. % concentration.<sup>[29]</sup> In this work, an energy efficient, high volume process of producing both concentrated and dried colloidal lignin particles is introduced. Spherical lignin particles are obtained by dissolving a high concentration of soft wood kraft lignin in a mixture of tetrahydrofuran (THF), ethanol (EtOH) and water. When this solution is added to a small volume of water, the lignin self-assembles into colloidal spheres at a concentration up to 2.8 wt. %. Due to the increase in CLP concentration, the energy consumption of water removal can be minimized. We present a proof-of-concept process where the organic solvents are recovered and reused and the colloids are efficiently concentrated by ultrafiltration and further dried by spray drying. The colloids have an average diameter of ca. 200 nm and a zeta potential of ca. -40 mV, depending on the exact conditions of the CLP formation. After drying, the particles can be efficiently redispersed. There is no loss of solvent in this process and the energy consumption is low (55 MJ/kg of dry CLPs). In the process, minor impurities such as ash and low molecular weight sulfur compounds are separated based on solubility differences, hence increasing the quality and homogeneity of CLPs.

Department of Bioproducts and Biosystems  
School of Chemical Engineering  
P.O. Box 11100, Aalto FI-00076, Finland  
E-mail: [mauri.kostiainen@aalto.fi](mailto:mauri.kostiainen@aalto.fi)

Electronic Supplementary Information (ESI) available: A more detailed description of the five-step CLP process. Supplementary videos of the CLP formation in a batch reactor and a supplementary video on the solvent recovery by rotary evaporation. See DOI: 10.1039/x0xx00000x



**Figure 1.** The process scheme for colloidal lignin particle (CLP) production. **1.** Lignin is dissolved in a mixture of THF and EtOH, with residual water from the solvent recovery. Ash from lignin is removed in this step. **2.** CLPs are formed upon the addition of lignin solution into water. **3.** Organic solvents are recovered with rotary evaporation (solvent reused in step 1.) **4.** The aqueous dispersion of CLPs is concentrated by ultrafiltration (filtered water is recycled into step 2.) **5.** CLP concentrate is spray dried (heat of steam used in step 3. and water reused in step 2.)

## Results and discussion

We developed a five-stage CLP production process, presented in **Figure 1**. While our simulations were conducted with distillation equipment, we show the process with a 20 L rotary evaporator as was realized in the experiments. **1.** Lignin is dissolved in a mixture of THF, EtOH and water. The small amount of ash present in lignin is removed by decanting the lignin solution. **2.** The lignin solution is introduced into water, forming a colloidal dispersion of lignin in water:THF:EtOH. **3.** Organic solvents are evaporated in a 20 L rotary evaporator. The recovered THF:EtOH with residual water is used to dissolve lignin in step 1. **4.** The aqueous dispersion of CLPs is concentrated by ultrafiltration. The filtered water is recycled into step 2. **5.** The concentrated CLP dispersion is introduced into a spray drier where finely sprayed colloidal particles are passed through a stream of 180 °C air, producing redispersible microclusters of dry CLPs and steam. The heat of steam can be used in step 3 and the water in step 2.

With the proof-of-concept sized reactor, we were able to produce several 10 kg batches of 1.7 wt. % CLPs (see details in the supporting information). The organic solvents were recovered by rotary evaporation from the combined batches and an aqueous CLP dispersion was used for ultrafiltration tests. A regenerated cellulose (RC) membrane (150 000 g mol<sup>-1</sup> molecular weight cut-off) was found to produce the highest

permeate flux of 100 mL m<sup>-2</sup> min<sup>-1</sup>. The permeation speed could be maintained until the dispersion volume matched the internal volume of the equipment. At this point the concentration of the dispersion was 14.3 wt. %. With this setting the permeate held a minute portion of the smallest CLPs (<100 nm in size). However as the permeate is fully reused in CLP formation there is no loss of lignin in the process. Thus, it can even be considered that a membrane with larger pore sizes, but which allows for a faster permeation speed, could be used.

Spray drying of the CLP concentrate produced a fine dry powder of spherical CLP microclusters, which can be redispersed in water (see supporting information). The cluster size seems to be related to the droplet size produced by the spray drier. Thus the increase of CLP concentration can have a minor influence on the size of the aggregates. As the laboratory scale spray-dryers are not optimized for energy efficiency we used known data for industrial spray dryers for the estimation of energy consumption of drying. With an energy consumption of 3 MJ/kg for the evaporation of water,<sup>[30]</sup> the heat of distillation of a 14.3 wt. % CLP dispersion is 18 MJ/kg (**Table 1**). This is already less than half of the 36 MJ/kg required to recover 94 % of EtOH and 100 % of THF from a 2.8 wt. % CLP dispersion. The dissolution of lignin into the solvent mixture and CLP formation are slightly exothermic processes, which require only mixing and pumping. The only other significant consumer

**Table 1.** Major lignin consumers of power in the CLP process and the lignin concentration at each stage.

Process	Major power consumption	Energy consumed MJ/kg CLP produced	Lignin concentration wt. %
Lignin dissolution	Minimal energy of mixing	~0 <sup>a</sup>	7.6
Formation of colloidal lignin spheres	Minimal energy of mixing	~0 <sup>a</sup>	2.8
Recovery of solvents.	Heat of distillation	36	4.2
Ultrafiltration of CLPs.	Blade rotation/ pressure generation	1	14.3
Spray drying of CLPs.	Heat of distillation	18 <sup>b</sup>	100
<b>Total process</b>		<b>55</b>	

<sup>a</sup> Both lignin dissolution and colloid formation are exothermic events.

<sup>b</sup> The heat of spray drying can be used in the recovery of solvents.

of power in the process is the ultrafiltration step, which consumes below 1 MJ/kg to concentrate a CLP dispersion from 4.2 wt.% (concentration after solvent recovery, see calculation in supporting information) to 14.3 wt. %. Thus the overall power consumption of the process is 55 MJ/kg CLP, which can already be considered feasible for an industrial process. With the current electricity price of 28 €/MWh (Nordpool, July 12<sup>th</sup> 2017) the cost of energy for CLP production would be 0.47 €/kg (actual

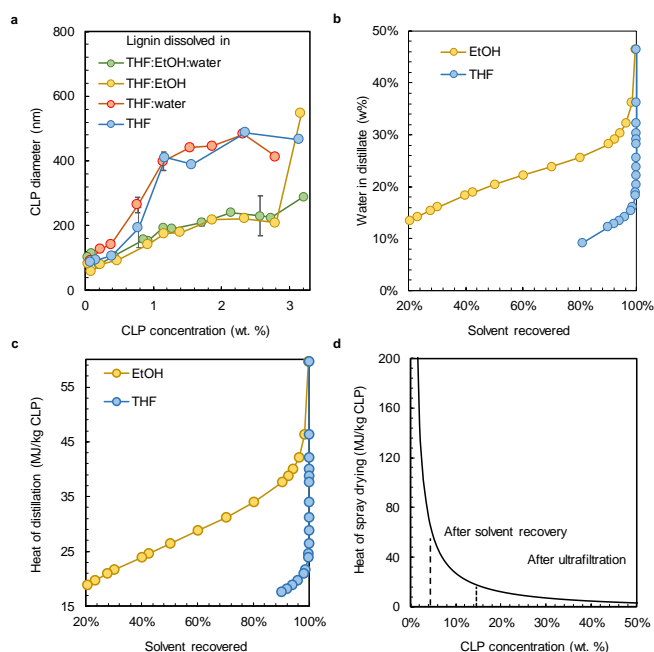
cost would be significantly lower with the use of excess heat of pulp mills). With the production cost of purified lignin (Valmet estimate for LignoBoost™ softwood kraft lignin) being below 0.5 €/kg, the production cost of CLPs from black liquor to dry particles would be below 1 €/kg.

To the best of our knowledge, there are no other spherical nanoparticulate products that can be produced at this cost.

This proof-of-concept process acts as a guideline for the production of a truly continuous flow closed cycle CLP production plant. Of the five-stage process the first three, i.e. lignin dissolution, CLP formation and solvent evaporation are batch processes in the current iteration, but the last two, i.e. ultrafiltration and spray drying are continuous flow processes, which we are currently developing.

At the moment the five stages are separate, but with the output of each stage being the input of the following one. While the recovered THF:EtOH mixture in the distillation experiment with a rotary evaporator contained more water than was suitable for the optimized process, it was shown (see discussion in supporting information) that the separation efficiency obtained with a distillation column would allow for the full recycling of the solvents in the process. The calculated energy consumption of the final spray drying step for a 14.3 wt. % CLP concentrate is already significantly lower than that of the distillation of organic solvents. The concentration obtainable by ultrafiltration could possibly be much higher than the current one. However, based on the distillation simulations, a higher impact on the power consumption of the process is the organic solvent recovery.

The effect of lignin concentration and the solvent environment on the size of the formed lignin colloids is shown in **Figure 2a**. When lignin is dissolved in a mixture of THF and ethanol (**Figure 2a**, yellow dots), the particle diameter forming from a dilute solution is ca. 70 nm (PDI for all fully colloidal samples ranging from 0.1 to 0.2). When the lignin concentration is increased, the particle diameter increases gradually to ca. 200 nm at 2.8 wt. % CLP concentration in the solvent mixture. After this point, the particle diameter increases rapidly and is already 550 nm at 3.1 wt. % CLP. With 2.8 wt. % lignin in the solvent mixture, the fraction of non-colloidal aggregate is less than 1 % of the lignin (measured from the dried aggregate). Beyond this point, the concentration of colloidal lignin decreases and the majority of



**Figure 2.** Experimental, simulated and calculated data on the CLP process. a) CLP diameter as a function of the final CLP concentration in the aqueous dispersion before solvent removal. Lignin dissolved in various solvent mixtures. Data points with an error bar show an average of two experiments with error bars presenting the data range. Other data point represents a single experiment. b) The fraction of water in the simulated distillate fraction as a function of the solvent composition. Each simulation produces a data point both for THF and for EtOH. c) The heat of distillation for each simulated distillation (the amount of water collected is omitted for clarity). Simulation details in supporting information. d) Calculated heat of spray drying of an aqueous CLP dispersion as a function of the CLP concentration. Details of the calculations in supporting information.

lignin precipitates. We assume that the influence of EtOH is primarily to prevent the aggregation of the forming colloidal lignin particles, which enables the increase of lignin concentration.

If energy intensive refluxing is to be avoided in solvent recovery, the recovered solvent mixture will contain a certain amount of water evaporating as an azeotrope with the solvents. In our simulations (see supporting information) we show that all of THF and the majority of EtOH can be collected as a mixture containing 30 wt. % water. Thus, the effect of water on the particle formation was also tested. With lignin in a solvent mixture with 30 wt. % water (**Figure 2a**, green dots), the particle formation was almost identical to the CLP formation from a solution with just THF and EtOH.

When CLPs are formed from a solution of lignin in just THF (**Figure 2a**, blue dots), the formed particles are very similar in size to those from THF:EtOH at low lignin concentrations (up to 0.4 wt.%, with a particle diameter of 110 nm). However at higher lignin concentrations the particle diameter starts to increase rapidly, crossing a threshold concentration between 0.8 wt. % lignin and 1.2 wt. % lignin, where the average particle size increases to 410 nm and a significant fraction of the lignin starts to precipitate. At 2.8 wt. % lignin the fraction of the precipitate is already nearly 100 % of the lignin mass.

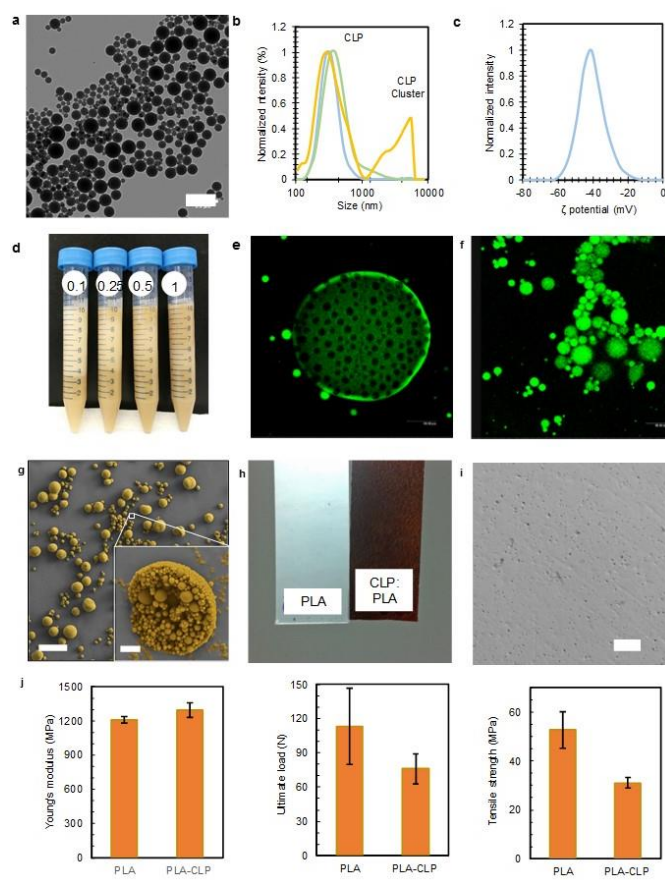
When CLPs are formed from a solution of lignin in THF with 30 wt. % water, the CLP formation is nearly identical compared to that of lignin in just THF (**Figure 2a**, red dots). Thus the influence of residual water at least up to 30 wt. % is minimal regardless of whether EtOH is used or not. However when the water content is increased much above 30 wt. % the solution no longer remains stable enough to be used for CLP formation (data not shown).

The recovery of solvents without reflux leads to a higher fraction of water in the distillate the larger the recovered solvent fraction. Based on process simulations (**Figure 2b**, see supporting information for more details), it is possible to recover all of THF and 94 % of EtOH with 30 wt. % water. This recovered solvent mixture can be further used to dissolve lignin, which enables a closed cycle production of CLPs.

A small fraction of the EtOH (6 % of EtOH) remains in the aqueous CLP dispersion in this case. However, over 70 % of the aqueous phase will be recovered in the ultrafiltration step and reused in CLP formation, leading to no loss of THF and less than 2 % loss of EtOH in the final process. For full recovery of EtOH, without reflux, the distilled solvents would contain 45 wt. % of water. However as most of the aqueous phase will be reused after ultrafiltration, there is no need for 100 % solvent recovery in the distillation stage.

Even without refluxing of the solvent, the heat of evaporation of water in the azeotrope is the largest fraction of energy consumption in the distillation. With a CLP concentration of 2.8 wt. %, full organic solvent recovery consumes 53 MJ energy for 1 kg of CLP dry mass (**Figure 2c**, see more thorough description in supporting information). With 94 % EtOH recovery the energy consumption is 36 MJ/kg CLP. As most of the EtOH remaining in the aqueous phase can be recovered upon recycling of the

permeate from ultrafiltration, even a lower degree of EtOH recovery would be economically feasible.



**Figure 3.** a) TEM image of a CLP dispersion (scale bar 500 nm); b) DLS graph of a 1.7 wt. % CLP dispersion prepared from lignin dissolved in THF:EtOH:water (blue), CLP microclusters formed upon spray drying suspended in water (yellow) and redispersed CLPs (green); c) zeta potential graph of the 2.8 wt. % dispersion; d) Pickering emulsion of 1:1 v:v water: rapeseed oil 1 h after preparation: concentrations from 0.1 wt. % to 1 wt. % CLP; Confocal microscope images of Pickering emulsions with CLPs: e) 0.1 wt. % CLP (o/w emulsion); f) 1 wt. % CLP; g) False colored SEM image of spray dried CLPs. Each ball is a redispersible microcluster of CLPs (as seen in a broken cluster in the inset). Scale bar 50  $\mu\text{m}$  (inset 1  $\mu\text{m}$ ); h) 1:2 w:w ratio CLP:PLA composite film; i) SEM image of the same film. Scale bar 50  $\mu\text{m}$ .; j) Tensile test results of the PLA:CLP composite. The data is an average of triplicate measurements, with the error bar marking standard deviation

When the CLP dispersion is concentrated by ultrafiltration, the need of energy intensive spray drying is minimized. Calculations show (**Figure 2d**, see description in supporting information) that at above 8 wt. % CLPs in water, the energy consumption of distillation exceeds that of spray drying. It is important to note that most of the energy input into spray drying can be reused in the solvent recovery stage. Thus, in this case the only significant energy consumption is for the solvent recovery. Also it can be seen that while the effect of EtOH on CLP formation at high concentration is crucial, the minimization of the energy consumption requires the minimization of the use of EtOH.

TEM image shows the colloids to be spherical (**Figure 3a**). DLS shows an average particle diameter of 230 nm (**Figure 3b**) and a zeta potential of -38 mV (**Figure 3c**) for a 2.8 wt. % CLP

dispersion. The pH and salt stability of CLPs was shown to be good in our previous publication<sup>[26]</sup> and we found no significant difference in CLPs prepared either via dialysis or via rapid solvent exchange. Lignin is stable in the temperature range of the solvent exchange process and even the brief introduction of CLPs into a stream of 180 °C air does not alter the CLPs in any perceptible way. However, in our recent publication we showed that a sustained exposure of the aqueous CLPs to temperatures above 144 °C under pressure induced sufficient cross-linking to make them stable against THF. The dry CLP microaggregates are very soft, as there is very little interaction with the clusters with relatively smooth surfaces. Conversely, we expect the individual CLP particles to be harder, much like polymer microbeads. To show that CLPs can be used in large-scale applications, we present Pickering emulsions as an example application with the colloids<sup>[31]</sup> and polylactide (PLA)-CLP composites as an example application with dry particles. Both application have been presented before, but not with colloidal lignin particles that could be produced at industrial scale.<sup>[32–35][36]</sup> Aqueous CLP dispersions were used to produce Pickering emulsions with 1:1 volume ratio of rapeseed oil and water, with emulsion stability increasing as the initial aqueous concentration of CLPs increases from 0.1 to 1 wt. % CLPs (**Figure 3d**). The lowest CLP concentration produced a heterogeneous emulsion system with distinct double emulsion droplets (**Figure 3e**), whereas at 1% CLP concentration, free and clustered oil droplets were observed (**Figure 3f**). Pickering emulsions produced in the presence of CLPs could prove useful in interfacial catalytic reactions<sup>[37,38]</sup> or as templates for fabrication of structured biomaterials.<sup>[39,40]</sup> We observed that the CLP concentrate forms micrometer scale clusters (**Figure 3g**) upon spray drying. The cluster size is determined by the size of a single droplet produced by the atomizer in the spray dryer. These microcluster can be mechanically broken and the CLPs can be redispersed either in water (size and zeta potential remains nearly unchanged, as seen in Figures 3b and 3c) or into molten Polylactide (PLA, Photograph in **Figure 3h** and SEM image in **Figure 3i**). Initial tensile tests (**Figure 3j**) show that the mechanical properties of a PLA film can be at least to some extent retained even with a high loading of CLPs. While we anticipate improvements in mechanical properties with more studies, the initial studies show that CLPs can be used at least as a biodegradable filler with the more expensive PLA.

## Experimental

### Lignin dissolution with pure solvents

139 g of LignoBoost softwood kraft lignin (68.1 wt. % or 94.9 g of solids, of which 1.5 wt. % is inorganic ash) was dispersed in 435 g of water under stirring to produce a homogenous slurry. 625 g of technical ethanol (Altia A7) and 704 g of technical THF (CABB chemicals) was added into the stirred slurry, resulting in the immediate dissolution of lignin. The inorganic ash precipitated and the lignin solution was separated by decanting. The stirred solution was diluted to a water content of 610 g (including the water in the lignin and the water used to produce

the lignin slurry). The concentration of lignin in the solution was 4.67 wt. % and the solvent composition 34.6:30.7:30.0 w:w THF:EtOH:water. (Lignin can be dissolved into this solvent composition at least up to 8.5 wt. %). Several batches with this composition were prepared to produce a 1.7 wt. % CLP dispersion for solvent recovery and ultrafiltration tests.

### Lignin dissolution with recovered solvents

294 g of lignin (200 g lignin solids) was added into 982 g of THF:EtOH:water mixture (83:8:9 w:w THF:EtOH:water, emulating the 1<sup>st</sup> distilled fraction of the solvent recovery simulation), resulting in the dissolution of lignin within a few minutes. The solution was diluted with 1610 g of THF:EtOH:water mixture (12:45:43 w:w THF:EtOH:water, emulating the 2<sup>nd</sup> distilled fraction of the solvent recovery simulation). The concentration of lignin in the solution was 6.93 wt. % and the solvent composition 34.9:27.9:30.4 w:w THF:EtOH:water. CLPs could be made at least up to a concentration of 2.8 wt. % from this solution.

### CLP formation in a 100 mL flask

Lignin dissolved in either THF, THF:EtOH (13:11 w:w), THF:water (70:30 w:w) or THF:EtOH:water (13:11:10 w:w) was poured in one go (in less than 1 s) into water stirred in a 100 ml round bottom flask with a magnetic stirrer. The CLPs formed within seconds of the solution mixing with water. The final water content for each experiment was 76 wt. % of the solvents and the mass of each dispersion was 23.1 g. After the formation of the CLPs, the organic solvents were removed by rotary evaporation at 40 °C.

### Determination of non-colloidal aggregate in CLP dispersions

After the removal of the organic solvents, the amount of lignin aggregate was determined from select samples. The colloids were filtered through cotton and the non-colloidal aggregate was washed with water to remove residual colloids. The aggregate was separated from cotton by dissolving with THF and the collected solution was dried first at room temperature and then in a 110 °C oven overnight.

### CLP formation in a batch reactor

A steady stream of 4.07 kg of lignin solution (4.67 wt. % lignin, 34.6 wt. % THF, 30.7 wt. % EtOH, 30.0 wt. % water) was added into 7.00 kg of water in a batch reactor under stirring over a few minutes. (See supplementary video), producing a CLPs dispersion (1.71 wt. %) immediately upon contact. Several similar batches were prepared for the ultrafiltration tests.

### Rotary evaporation

10 L of the CLP dispersion was sucked into a 20 L rotary evaporator under vacuum. At a water bath temperature of 80 °C and a pressure of 120 mbar and a 50 °C vapor temperature 2.7 L of azeotropic mixture of solvents was collected (39 wt. % THF, 23 wt. % ethanol, 38 wt. % water) in 61 minutes. At this point, the distillate was visually observed to switch from mostly organics to mostly water. In further 22 minutes 0.9 L of aqueous

mixture (1 wt. % THF, 7 wt. % ethanol, 92 wt. % water) was collected.

#### Particle dispersion characterization

The mean particle size and electrophoretic mobility of the lignin samples were measured using a Malvern Zetasizer Nano-ZS90 Instrument (UK). Zeta potential data were obtained from electrophoretic mobility data by applying the Smoluchowski model. Measurements were repeated three times for each sample to check the reproducibility.

#### TEM

Transmission electron microscopy was performed on a FEI Tecnai 12 (USA) operating at 120 kV. Water dispersions were applied on a carbon film support grid, incubated for 2 minutes and excess water was removed by blotting the side of the grid onto filter paper. Imaging was done in the bright-field mode with slight underfocus.

#### FE-SEM

Field-emission scanning electron microscopy (Zeiss Sigma VP) was used to investigate the microstructure and morphological features of spray dried colloidal lignin particles (CLPs) and CLP:PLA (poly lactic acid) composites. CLPs were loosely scattered on double sided carbon tape fixed on the FESEM metal stubs. Excess CLPs were shaken off by applying compressed air. In order to observe the CLP: PLA composites under FESEM, composite films were cut with a sharp blade and mounted on a metal stub using same procedure. To avoid the occurrence of charging, a gold sputter was applied prior to observation on Zeiss Sigma FE-SEM. SEM micrographs were acquired at an accelerating voltage of 1.5 kV at various magnifications in secondary electron detector (SE) mode. CLPs were highlighted by false coloring using Photoshop. Original images are presented in the Supplementary Information.

#### Determination of solvent composition in distillate

The distillates were analyzed by HP Agilent 6890 gas chromatograph equipped with a Zebron WAXplus column (60m x 0.25 mm x 0.25  $\mu$ m). GC standards were prepared of solvent mixtures with the signals of EtOH and THF visible as retention peaks. As water is not visible in common GC columns, the water content was calculated against a reference with no water.

#### CLP ultrafiltration

Ca. 28 L of 2.8 wt. % of aqueous CLPs were pumped into an OptiFilter CR250 (Valmet Technologies Inc.) ultrafiltration device with two membranes with a combined area of 0.09 m<sup>2</sup> under a pressure difference of 1.0 bar. Initially polyethersulfone membranes (PES, MWCO of 150 000 g/mol) were used for 68 minutes. Samples of the permeate were collected and the concentrate was fed back into the feeding tank. After PES, the membranes were switched to polysulfone (PS, MWCO of 100 000 g/mol) and regenerated cellulose (RC, MWCO 500 000 g/mol). The filtration was run for 219 minutes; with samples collected of each permeate. During the last hour of the test, the

temperature was increased to 42 °C to find out the dependence between the capacity and the temperature. Ca. 3.5 L of concentrate with a solid content of 14.3 wt. % was collected in the experiment.

#### Spray drying of CLPs

The 14.3 wt. % CLP concentrate was injected into a GEA Mobile Minor™ spray drier at a rate of 10 ml/min. A stream of 180 °C air was passed through the chamber. Microaggregates of dry CLPs were collected.

#### Redispersion of CLPs

Reversibility of spray dried aggregates was tested as follows. 3 g of CLPs and 100 g of water were mixed and sample for light scattering analysis was taken after light swirling. Then the mixture was placed in ultrasonication with Sonorex digitec ultrasonic bath (Bendelin, Germany) for 10 minutes to obtain colloidal dispersion, which was again analysed. To test redispersion for application purposes, 27 g of dried CLP were mixed with 27 g of water, and after short vortex mixing, another 36 g portion of water was added with mixing. Colloidal dispersion could be formed by 4 minute agitation with Ultra-Turrax T18 basic homogenizer (IKA, Germany) or ultrasonication bath.

#### CLP-rapeseed oil Pickering emulsion

Rapeseed oil (5 mL) was emulsified with 5 mL of CLPs at 0.1, 0.25, 0.5 and 1 wt. % concentrations by vortex mixing and shaking the immiscible phases in a screw cork tubes during 30 s. Formed emulsions were imaged within 3 min from their preparation and again after 1 h equilibration at room temperature. The Pickering emulsions were stained with Nile red and imaged by confocal laser scanning microscope (Leica DMRXE, Germany) using a 20  $\times$  objective in air mode. Compression of the emulsion was avoided by using a spacer between the microscope glass and the cover slide.

#### CLP:PLA composite

7.5 g of spray dried CLPs and 17.5 g of PLA pellets (Easy fill™, FormFutura, Netherlands) were mixed in a plastic container, and then dried in a vacuum oven at 40 °C overnight. Mixture was loaded into mixer (Plasti-corder, Brabender, USA) at 200 °C and blended at 50 rpm for 5 minutes. Both reference PLA and the PLA-CLP blend were processed similarly. From the cooled blend, 2 g portions were placed in a hydraulic press (Vakomet KRO-260, Lakeuden Hydro Oy, Finland) and allowed to melt at 195 °C between mylar sheets for 5 minutes, and pressed with 100kN force for 3 minutes. For tensile testing the film was cut into 1 cm strips and thickness of each strip was determined by micrometer (Lorentzen & Wettre, ABB, Switzerland) using 10 measurements. Tensile testing for films was carried out with universal testing machine (33R-4467, Instron, UK), using 1kN load cell and 5 mm/min pulling rate. Triplicate measurements with cut strips from at least two different films were used to calculate the average strength for material.

## Conclusions

In summary a proof of concept process for colloidal lignin particle (CLP) production with a possibility of full reuse of solvents and a minimization of consumed energy per kg of CLP has been realized. Process simulations based on the experimental data of the batch reactor allow for the design of a continuous flow process. The energy consumed in the process is ca. 55 MJ/kg dry CLP that can already enable a production cost that allows their use in a wide range of applications. This work will form the basis of a continuous flow process, the design of which is currently in progress. The potential applications of CLPs range from medical, <sup>[15]</sup>[17–20] material<sup>[22]</sup>[23,32,33] to food technology.<sup>[36]</sup> It was shown that the produced CLPs can be used in applications requiring dry particles and aqueous dispersions. Currently we are adapting the process into the production of functional colloidal lignin products, such as adhesives, coatings, antibacterials and biomedical applications.<sup>[41]</sup>

## Conflicts of interest

K.L, Y.X, R.B.A., T.L., P.O., M.Ö., and M.K. 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).

## Acknowledgements

We thank the Finnish Funding Agency for Innovation (TEKES) for a consortium project (COLIAD, #905/31/2016). T. Leskinen acknowledges the Academy of Finland for the academy project (TabioMat, #276696). M. Sipponen thanks Academy of Finland for funding (SLIGN, 296547). M. Österberg acknowledges the Academy of Finland for the academy project (#278279). The following persons are greatly appreciated for their work contribution: Seppo Jääskeläinen and Timo Ylönen (Aalto University, Espoo, Finland) for their contribution to construction of the CLP reactor, Heidi Meriö-Talvio (Aalto University) is acknowledged for her laboratory assistance and Steven Spoljaric for assistance in PLA:CLP extrusion experiments.

## Notes and references

### On the nomenclature

While the recent literature describes lignin particles ranging from 10 nm to 1000 nm as nanoparticles, we consider the term lignin nanoparticle (LNP) as misleading, as most published particles have a particle size of above 100 nm, which is not within the IUPAC definition of a nanoparticle. Thus, we use the term colloidal lignin particle (CLP), which encompasses a particle size range of 1 nm to 1000 nm. We advise the term CLP to be used for any lignin particles above 100 nm in size.

- [1] H. Lei, A. Pizzi, G. Du, *J. Appl. Polym. Sci.* **2008**, *107*, 203.
- [2] S. H. Ghaffar, M. Fan, *Int. J. Adhes. Adhes.* **2014**, *48*, 92.
- [3] N.-E. El Mansouri, A. Pizzi, J. Salvado, *J. Appl. Polym. Sci.* **2007**, *103*, 1690.

- [4] A. Tejado, C. Peña, J. Labidi, J. M. Echeverria, I. Mondragon, *Bioresour. Technol.* **2007**, *98*, 1655.
- [5] M. Wang, M. Leitch, C. (Charles) Xu, *Eur. Polym. J.* **2009**, *45*, 3380.
- [6] D. A. Baker, T. G. Rials, *J. Appl. Polym. Sci.* **2013**, *130*, 713.
- [7] J. M. Rosas, R. Berenguer, M. J. Valero-Romero, J. Rodriguez-Mirasol, T. Cordero, *Front. Mater.* **2014**, *1*, 1.
- [8] J. Zakzeski, P. C. a Bruijninx, A. L. Jongerius, B. M. Weckhuysen, *Chem. Rev.* **2010**, *110*, 3552.
- [9] D. Stewart, *Ind. Crops Prod.* **2008**, *27*, 202.
- [10] M. Kleinert, T. Barth, *Chem. Eng. Technol.* **2008**, *31*, 736.
- [11] A. J. Ragauskas, G. T. Beckham, M. J. Biddy, R. Chandra, F. Chen, M. F. Davis, B. H. Davison, R. A. Dixon, P. Gilna, M. Keller, P. Langan, A. K. Naskar, J. N. Saddler, T. J. Tschaplinski, G. A. Tuskan, C. E. Wyman, *Science* **2014**, *344*, 1246843.
- [12] A. Rahimi, A. Ulbrich, J. J. Coon, S. S. Stahl, *Nature* **2014**, *515*, 249.
- [13] Q. Bu, H. Lei, A. H. Zacher, L. Wang, S. Ren, J. Liang, Y. Wei, Y. Liu, J. Tang, Q. Zhang, R. Ruan, *Bioresour. Technol.* **2012**, *124*, 470.
- [14] P. Figueiredo, K. Lintinen, J. T. Hirvonen, M. A. Kostianen, H. A. Santos, *Prog. Mater. Sci.* **2018**, *93*, 233.
- [15] A. P. Richter, J. S. Brown, B. Bharti, A. Wang, S. Gangwal, K. Houck, E. A. Cohen Hubal, V. N. Paunov, S. D. Stoyanov, O. D. Velev, *Nat. Nanotechnol.* **2015**, *10*, 817.
- [16] A. P. Richter, B. Bharti, H. B. Armstrong, J. S. Brown, D. Plemmons, V. N. Paunov, S. D. Stoyanov, O. D. Velev, *Langmuir* **2016**, *32*, 6468.
- [17] K. Lintinen, M. Latikka, M. H. Sipponen, R. H. A. Ras, M. Österberg, M. A. Kostianen, *RSC Adv.* **2016**, *6*, 31790.
- [18] P. Figueiredo, K. Lintinen, A. Kiriazis, V. Hynninen, Z. Liu, T. Bauleth-Ramos, A. Rahikkala, A. Correia, T. Kohout, B. Sarmiento, J. Yli-Kauhaluoma, J. Hirvonen, O. Ikkala, M. A. Kostianen, H. A. Santos, *Biomaterials* **2017**, *121*, 97.
- [19] M. P. Vinardell, *Int. J. Mol. Sci.* **2017**, *18*, 1219.
- [20] L. Dai, R. Liu, L. Hu, Z. Zou, C. Si, *ACS Sustain. Chem. Eng.* **2017**, *5*, 8241.
- [21] P. Figueiredo, C. Ferro, M. Kemell, Z. Liu, A. Kiriazis, K. Lintinen, H. F. Florindo, J. Yli-Kauhaluoma, J. Hirvonen, M. A. Kostianen, H. A. Santos, *Nanomedicine* **2017**, *12*, 2581.
- [22] S. Jiang, A. Van Dyk, A. Maurice, J. Bohling, D. Fasano, S. Brownell, *Chem. Soc. Rev.* **2017**, *46*, 3792.
- [23] S. Rose, A. PrevotEAU, P. Elzière, D. Hourdet, A. Marcellan, L. Leibler, *Nature* **2014**, *505*, 382.
- [24] L. Chen, J. Dou, Q. Ma, N. Li, R. Wu, H. Bian, D. J. Yelle, T. Vuorinen, S. Fu, X. Pan, J. Zhu, *Sci. Adv.* **2017**, *3*, e1701735.
- [25] Y. Qian, Y. Deng, X. Qiu, H. Li, D. Yang, *Green Chem.* **2014**, *16*, 2156.
- [26] M. Lievonen, J. J. Valle-Delgado, M.-L. Mattinen, E.-L. Hult, K. Lintinen, M. a. Kostianen, A. Paananen, G. R. Szilvay, H. Setälä, M. Österberg, *Green Chem.* **2015**, 1416.
- [27] C. Frangville, M. Rutkevicius, *ChemPhysChem* **2012**, *27695*, 4235.
- [28] D. Tian, J. Hu, R. P. Chandra, J. N. Saddler, C. Lu, *ACS Sustain. Chem. Eng.* **2017**, *5*, 2702.
- [29] T. Leskinen, M. Smyth, Y. Xiao, K. Lintinen, M. Mattinen, M.



- A. Kostianen, P. Oinas, M. Österberg, *Nord. Pulp Pap. Res. J.* **2017**, *32*, 586.
- [30] C. G. J. Baker, K. A. McKenzie, *Dry. Technol.* **2005**, *23*, 365.
- [31] M. H. Sipponen, M. Smyth, T. Leskinen, L.-S. Johansson, M. Österberg, *Green Chem.* **2017**, 5831.
- [32] I. Spiridon, K. Leluk, A. M. Resmerita, R. N. Darie, *Compos. Part B Eng.* **2015**, *69*, 342.
- [33] O. Gordobil, I. Egüés, R. Llano-Ponte, J. Labidi, *Polym. Degrad. Stab.* **2014**, *108*, 330.
- [34] E. Fortunati, W. Yang, F. Luzi, J. Kenny, L. Torre, D. Puglia, *Eur. Polym. J.* **2016**, *80*, 295.
- [35] D. Tian, J. Hu, J. Bao, R. P. Chandra, J. N. Saddler, C. Lu, *Biotechnol. Biofuels* **2017**, *10*, 192.
- [36] M. Ago, S. Huan, M. Borghei, J. Raula, E. I. Kauppinen, O. J. Rojas, *ACS Appl. Mater. Interfaces* **2016**, *8*, 23302.
- [37] Z. Wei, Y. Yang, R. Yang, C. Wang, *Green Chem.* **2012**, *14*, 3230.
- [38] M. Pera-Titus, L. Leclercq, J. M. Clacens, F. De Campo, V. Nardello-Rataj, *Angew. Chemie - Int. Ed.* **2015**, *54*, 2006.
- [39] T. E. Nypelo, C. A. Carrillo, O. J. Rojas, *Soft Matter* **2015**, *11*, 2046.
- [40] M. Tortora, F. Cavalieri, P. Mosesso, F. Ciaffardini, F. Melone, C. Crestini, *Biomacromolecules* **2014**, *15*, 1634.
- [41] T. Leskinen, J. Witos, J. J. Valle-Delgado, K. Lintinen, M. Kostianen, S. K. Wiedmer, M. Österberg, M.-L. Mattinen, *Biomacromolecules* **2017**, *18*, 2767.