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Self-assembly of colloidal lignin particles in a continuous flow tubular reactor

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Abstract

A scalable tubular flow reactor was designed and developed for the continuous formation of colloidal lignin particles (CLPs). The reactor consists of a series of tubes, inside which many static mixing elements are equipped to aid in the formation of a homogeneous dispersion of CLPs. The colloids were formed instantaneously through self-assembly upon the addition of the lignin solution into water. The effects of flowrate, length of the tubes and static mixing elements on the particle size, stability and CLP yield after drying were determined. It was found that a higher flowrate of lignin solution within the testing range of 32-240 mL/min resulted in smaller sized CLPs. Optimizations of the mixing length and the static mixing elements to 3 m and at least 1m, respectively, could ensure an efficient mixing, thus resulting in CLP dispersions with smaller size of lignin particles (200 nm – 400 nm) and high lignin concentrations (up to 2.8 wt. %) along with yields up to 95 %. The TEM images indicated that the formed colloids are composed of lignin particles of regular shape and with good stability. The tubular reactor offers better control of particle size which ensures the

formation of colloidal dispersions with narrower particle size distribution in comparison to a stirred mixer reactor. Furthermore, using a tubular reactor enables the continuous production of CLPs, making it suitable for scale up and industrial applications.

Keywords: Colloidal lignin particles; self-assembly; continuous flow tubular reactor; static mixing elements; particle size; lignin nanoparticles

1. Introduction

Within the forest industry, it is of high interest to convert lignin into high value-added products. So far, the inherent inhomogeneity and lack of reactivity of lignin have created barriers for its large-scale use. Of the several million tons of lignin produced as a byproduct in bio-refineries, less than 5 % is used in applications other than energy generation. The deficit of commercial lignin products clearly indicates the need for the development of new upgrading technologies for utilization of the lignin streams from pulp mills and bio-refineries for large-scale commercial applications.

For the last few decades, researchers have actively studied for means of upgrading lignin into high value products for use in several value added applications like antibacterials[1], adhesives[2–6], functional surface coatings[7] and nanocomposites[8–12]. Colloidal lignin particles have been shown to increase ductility of cellulose based composites and introduce anti-oxidative and UV-protective properties, giving benefits in many coating and composite applications[11, 13–14]. Our published techno-economic analysis has indicated a production cost of 0.99 €/kg for unfunctionalized CLPs, making them competitive against many petrochemical polymers[15]. PF resins, which are typically used as adhesives, are materials that CLPs can potentially replace.

A market comparison done by Visuri[16] indicated that lignin products could replace 25–35 % of the applications PF resins are currently used for.

Several methods have been reported in literature for the formation of colloidal lignin particles (CLPs) or lignin nanoparticles. The production of aqueous lignin nanoparticle dispersions was first reported by Frangville et al.[17], wherein lignin nanoparticles (LNPs) were prepared from commercial grade lignin by dialysis using ethylene glycol as a solvent. The dialysis method of producing LNPs was also adopted by Lievonen et al.[18], wherein tetrahydrofuran (THF) was used as the solvent. Qian et al.[19] in their study reported the formation of LNPs by dropwise addition of water to acetylated solution of lignin in THF. Gilca et al.[20], modified lignin through ultrasonication to produce LNPs. Chen et al.[21] prepared LNPs based on hydrotropic chemistry by making use of an aqueous solution of sodium p-toluene sulfonate. One of the most widely used CLP formation method is nanoprecipitation[22], where spherical lignin particles with uniform particle size and good stability are obtained by the addition of water into lignin solution in organic solvent[23–29].

Converting lignin into CLPs enables improved properties in terms of colloidal behavior and surface chemistry, thus making lignin into a more widely usable raw material[11,22, 30–32]. The most important properties of CLPs are their particle size and zeta potential, which helps to determine the stability of the colloidal dispersion. These properties vary based on the formation process. The parameters affecting the CLP formation include the solvent system, concentration and characteristic of the lignin used as a raw material, mixing speed, pH and salt concentration[33]. Leivonen et al.[18] studied the stability of the nanoparticle dispersion as a function of time, salt

concentration and pH. It was reported that the lignin nanoparticle dispersion remained stable for over two months in pure water at room temperature and aggregation was induced at very low pH or in the presence of high salt concentration. The effect of solvent environment on CLPs was studied by Lintinen et al.[34], wherein smallest particle diameters were obtained in a solvent mixture of THF and ethanol and in a mixture of THF, ethanol and water.

In the present work, the continuous formation of colloidal lignin particles by three solvent polarity exchange method[34] under flow conditions in a tubular flow reactor equipped with static mixing elements (SME) is investigated for the first time. The produced colloids are compared with colloids produced in batch processes at comparable conditions. Tubular reactor is chosen since it offers several advantages in comparison to conventional stirred mixing reactors, including fast mixing, product homogeneity, narrow particle distribution, efficient heat and mass transfer due to high surface-to-volume ratio, easy scale-up and higher safety. Stirred tank reactors have generally good mixing depending upon several factors such as stirring speed, impeller type, impeller number and viscosity. However, in case of large tanks the power requirement is huge and the heat transfer is not so efficient, thereby making the process development and scale-up rather difficult for large-scale industrial applications. The use of static mixing elements for continuous operations is a promising alternative for systems based on conventional mechanical stirrers for mixing since suitable mixing performance can be achieved at a reduced cost. In addition, the energy and maintenance requirements are quite low in comparison to systems that employ the use of conventional mechanical stirrers for mixing.

2. Experimental

2.1 Materials

LignoBoost Lignin obtained from UPM (Bio Piva 100), tetrahydrofuran (99%, Sigma Aldrich), ethanol (Altia A7) and tap water (19 ppm Ca, 5.8 ppm Na, 39 ppm Fe) were used in the experiments of this study. All the chemicals were of analytical grade and used without any further purification. The static mixing elements were purchased from Sulzer Ltd.

2.2 Preparation of lignin solution

The lignin solution was prepared in a similar way to the method outlined by Lintinen et al[28]. 267.2 g of lignoboost kraft lignin (182 g solids with 1.5 wt. % inorganic ash) was dispersed in 447.2 g of water under continuous stirring to produce a homogeneous slurry. 670.8 g of ethanol and 755 g of tetrahydrofuran (THF) was added into the slurry, resulting in immediate lignin dissolution. The inorganic ash present in lignin precipitated and the lignin solution was separated by decanting. 159.8 g of water was added to the stirred solution to round up the ratio. The lignin concentration in the stock lignin solution is 7.9 wt. % with solvent composition of 30.1 wt. % water, 32.8 wt. % of THF and 29.2 wt. % of ethanol. CLP dispersions with lignin concentration up to 3 wt. % were produced by diluting the stock solution with a solvent mixture having an identical solvent ratio to the lignin solution and thereafter contacting with water in the tubular flow reactor.

2.3 Colloid formation in continuous flow tubular reactor

The formation of CLPs is near-instantaneous when the water content of the dispersion is more than 75 wt. %, whereas lignin in a solvent mixture with less than 75 wt. % of

water results in the formation of aggregates. Thus, the mass transfer from the organic solution to water needs to be quite efficient to prevent the prolonged exposure of lignin to a solvent environment in which it is neither soluble nor can the CLPs assemble into large particles. The principle of immediate dilution of the lignin solution could be facilitated by injection of lignin solution into a large stirred tank, but a shortcoming of such reactor design is the potential mixing of the already formed concentrated aqueous CLPs with the concentrated lignin solution that is being injected, leading to aggregation. Therefore, a tubular reactor setup wherein lignin solution and water are introduced continuously could potentially help solve such a situation.

Fig. 1 shows the continuous flow tubular reactor set-up operating at room temperature and atmospheric pressure. The reactor consists of 4 tubes with a total tube length of 4 m. Water (W) and lignin solution (LS) enters the tubular reactor from inlet 1 and 2, respectively. The lignin solution self-assembles into colloids after encountering water, and the forming lignin particles pass over a mixing length of 3m in tubes equipped with static mixing elements, which aid in the formation of a homogeneous dispersion at the outlet. Two sampling points are provided to check the consistency of the dispersion. Table 1 shows the tubular reactor specifications.

Figure 1. Continuous flow tubular reactor set-up for the formation of colloidal lignin particles (A: Water; B: Lignin solution; C: Colloidal dispersion; P 1, P 2: Peristaltic pumps; SP 1, SP 2: Sampling points; FCV 1-5: Flow control valves; SME: Static mixing elements)

Table 1. Continuous flow tubular reactor specifications

Tubular reactor parameters	
Total tubular reactor length [m]	4
Mixing length [m]	1 - 3
Mixing element length [m]	1 - 3
Tube diameter [m]	0.01
Mixing element diameter (m)	0.01
Flowrate of lignin solution [mL/min]	32 - 240
Flowrate of water [mL/min]	47 - 349

2.4 Colloid formation in stirred mixing reactor (SMR)

Lignin solution obtained by dissolving lignin in a mixture of solvents (THF, ethanol and water) was poured in one go (in less than 1 s) into water stirred in a 100 ml beaker

with a mechanical stirrer. The CLPs formed by self-assembly within seconds of the solution mixing with water.

2.5 Particle size and zeta potential analysis

A Malvern Zetasizer Nano-ZS90 (UK) was used to analyze the mean average particle sizes and zeta potentials of the CLP dispersions. The zeta potential data were obtained from the electrophoretic mobility measurements by applying the Smoluchowski model. Five scans were recorded for zeta potential and triplicate scans for the average particle size measurement using dynamic light scattering (DLS) in order to check the reproducibility.

2.6 Transmission electron microscopy

Transmission electron microscopy (TEM) images from the CLP dispersions were obtained using FEI Tecnai 12 (Hope, CA, USA) operating at 120 kV. Water dispersions were applied onto a carbon film supported grid and incubated for a duration of 2 minutes. The side of the grid was blotted onto a filter paper to remove excess water. The imaging was performed in bright field mode with slight under focus.

2.7 CLP drying

Samples of 5g were collected from the CLP dispersions obtained using the continuous tubular flow reactor and air dried at room temperature for 7 days followed by oven drying for 3 hours at 110 °C to ensure that the CLPs are completely dry.

3. Results and Discussion

The sequence of formation of CLPs within the tubular reactor is shown in Fig. 2. The CLPs are formed by nanoprecipitation of dissolved lignin polymers from the organic solvents. Lignin dissolved in a solvent mixture consisting of water, ethanol, and tetrahydrofuran enables high solubility of lignin and suppresses aggregation during colloid formation. Upon mixing of the lignin solution with a non-solvent, the dissolved lignin takes a solid particle form, i.e., the lignin solution upon encountering water self assembles into colloids as seen from the color change of black lignin solution to opaque beige. Since lignin solution and water are introduced continuously into the reactor, this enables the production of colloidal dispersions with much higher lignin concentrations in comparison to batch mixing processes. The formation of colloids is instantaneous, and the presence of sufficient mixing length along with static mixing elements ensures efficient mixing, resulting in homogeneous CLP dispersion with uniform particle size at the outlet.

Figure 2. Sequence of formation of a 2.8 wt. % CLP dispersion using lignin solution and water flowrates of 32 mL/min and 47 mL/min respectively (Video available in supplementary information).

3.1 Effect of flowrate, mixing elements and mixing length on the particle size

The tubular flow reactor is intended for use in industrial applications such as adhesives that often require CLP dispersions with high lignin concentrations (>2 wt. %). CLP dispersions up to 3 wt. % were prepared using the continuous flow tubular reactor for two different flowrates of lignin solution (LS) and water (W), to determine the effect of flowrate on the average particle diameter of the CLPs. Experiments were done without

static mixing elements and by using a mixing length (ML) of 3 m. As expected, a higher flowrate resulted in the formation of smaller sized CLPs, as shown in Fig. 3. The experiments were replicated twice, and the average particle sizes were determined. Furthermore, the CLPs produced using the stirred mixing reactor had relatively larger particle size even with a higher stirring speed of 750 RPM.

Figure 3. Effect of variation in flowrate on average particle size of CLPs.

Experiments were also carried out using different configurations of mixing length (ML) and static mixing elements to produce CLP dispersions within the concentration range of 2 – 3 wt. % and to determine the influence of mixing length and static mixing elements on the average particle diameter of the CLPs. When no static mixing elements were used, the average particle diameter decreased with an increase in the mixing length up to 2 m. Further increase in the mixing length resulted in no change in the particle size. On the other hand, the use of at least 1 m of static mixing elements along with a mixing length of 3 m resulted in the formation of comparatively smaller

sized CLPs. The use of additional mixing elements had very little influence on the particle size as seen in Fig. 4. Moreover, it was particularly challenging to obtain CLP dispersions with lignin concentration above 2.8 wt. % due to significant sedimentation of unstable colloids within the tubular reactor and the sedimented colloids could also be seen visually on the bottom of the collection vessel after a few minutes.

Figure 4. Effect of mixing length (ML) and static mixing elements (SME) on particle diameter of CLPs (LS flowrate: 240 mL/min; W flowrate: 349 mL/min).

3.1 CLP yield

Beisl et al.[20] reported the yields of lignin nanoparticles prepared using different processing methods. Myint et al.[35] used CO₂ precipitation and reported yields in the range of 51 to 88 %. Ago et al.[36] used aerosol processing and reported yields higher than 60 %. In our case, the CLP yields were determined using equation 1, with the reference being the mass of the dry CLPs obtained using the stirred mixing reactor, resulting in a CLP yield of 96 %, which is quite close to the highest yield obtained with

the tubular flow reactor. The collected samples showed no visual signs of aggregation and any difference in the weight of the dried CLPs was attributed to the deposition of CLPs inside the tubes of the reactor and some loss arising during drying. After optimization of the mixing length and static mixing elements to 3 m and 1 m, respectively, yields up to 95 % could be achieved for CLP dispersions with high lignin concentrations, as seen in Fig. 5.

$$CLP \text{ yield (\%)} = \frac{\text{Mass of CLPs recovered after drying (g)}}{\text{Mass of CLPs in sample (g)}} * 100 \quad (1)$$

Figure 5. CLP yields after drying for 2.6 and 2.8 wt. % dispersions obtained using different configurations of mixing length and static mixing elements (LS flowrate: 240 mL/min; W flowrate: 349 mL/min).

3.2 Particle size distribution, shape and stability

The particle size controls the appearance and stability of the colloidal dispersion. The following deductions can be made regarding their properties: 1) The CLP dispersions appear more transparent when the average particle size is below 100 nm, and 2) A rough size limit for proper colloidal stability is 500 nm. The TEM analysis revealed the particles to possess regular sphere shape with good stability (-40 mV), as seen from the TEM images and zeta potential curve shown in Fig. 7. Moreover, the use of static mixing elements in the tubular flow reactor resulted in the formation of CLPs with narrower particle size distribution when compared to CLPs obtained without mixing elements or by using the stirred mixing reactor, which is evident both from the particle size distribution, as shown in Fig. 6(a) and from the TEM images shown in Fig. 7.

Figure 6. (a) Particle size distribution and (b) correlogram obtained with different configurations of mixing length and static mixing elements in the tubular reactor and when using a stirred mixing reactor.

265

266 Figure 7. (a), (b) TEM image of 2.8 wt. % CLP dispersion obtained with 3 m of mixing length and 1 m
 267 static mixing elements. (c) TEM image of 2.8 wt.% CLP dispersion obtained without static mixing
 268 elements and with 3 m of mixing length. (d) zeta potential graph of a 2.8 wt.% CLP dispersion.

269

270 The CLP dispersions prepared with the tubular flow reactor were found to remain
 271 stable for at least one week without any specific signs of aggregation and changes in
 272 the particle size, as seen in Fig. 8, which indicates that the solvents present in the CLP
 273 dispersion should be separated as soon as possible or preferably within a week.
 274 Furthermore, there were no chemical changes between the CLPs obtained the first

minute and hours later. The lack of change in the chemical structure of lignin in CLPs has been reported previously using ^1H -NMR and ^{31}P -NMR spectroscopy[18].

Figure 8. Stability of a 2.8 wt. % CLP dispersion prepared using 3 m of mixing length and 1 m of static mixing elements: (a) zeta potential and (b) particle diameter of CLPs as a function of time.

Conclusion

The self-assembly of CLPs using three solvent polarity exchange method in a continuous flow tubular reactor was investigated. The results indicated that a higher flow rate, use of static mixing elements and sufficient mixing length resulted in the formation of homogeneous CLP dispersions with small particle size and lignin concentrations up to 2.8 wt. % without significant sedimentation. In comparison to a conventional stirred mixing reactor, the tubular flow reactor offered efficient mixing and a narrower particle size distribution. The obtained CLPs were found to be stable for at least one week, and the TEM analysis indicated that the formed colloidal particles have regular sphere shape. Furthermore, after drying CLP yields up to 95 % could be

achieved at high lignin concentrations. The tubular flow reactor forms an integral part of the CLP process by facilitating the continuous production of CLPs, thereby enabling scale-up and use in industrial applications. The properties of the produced CLPs enable applications such as adhesives, composites, and coatings.

Conflict of interest

R.B.A, Y.X., K.L., 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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