Di Tang

The Preparation of Colloidal Particles in a Continuous Process

Designing a tubular reactor for the formation of colloidal lignin particles

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The thesis states a research offered by Aalto University that involves the production of colloidal lignin particles, which have various applications in material industry. The existed process of preparing colloidal lignin particles uses a batch process that does not fit in the purpose of sustainability. Thus, this research project it is intended to develop a continuous process by designing a tubular reactor to improve the preparation of colloidal lignin particles. The experimental results indicate that the tubular reactor has positive effect on formation of colloidal lignin particles in sustainable and energy efficient way. Further study can be carried out by upscaling the current research.

Keywords	Colloidal particle formation, Tubular reactor

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Contents

1 Introduction

1.1 Background of the study

Lignin, as a natural wood-based biopolymer that has been harvested and researched widely for decades, has been identified to be sustainable and eco-friendly in many uses, but more potential applications are still in study. Recent researches indicate that colloidal lignin particles have enormous sustainable and economical potential in material industry like adhesive and coating technology.

Lignin can be dissolved under certain circumstances by mixing with some chemical solvents to form colloidal nano-particles. Batch mixing has been applied in the current process to produce colloidal lignin particles. As regards the energy saving and economic efficiency, developing a continuous process from batch process is the solution to improve chemical process (1). Based on preliminary study, the preparation of lignin particles has been developed in small scale with batch processing. As shown in Figure 1 that lignin is dissolved in several solvents and water is pre-added in a mixing tank where the prepared lignin solution is added later. By using mechanical mixer, water and lignin solution are mixed to form colloidal particles.

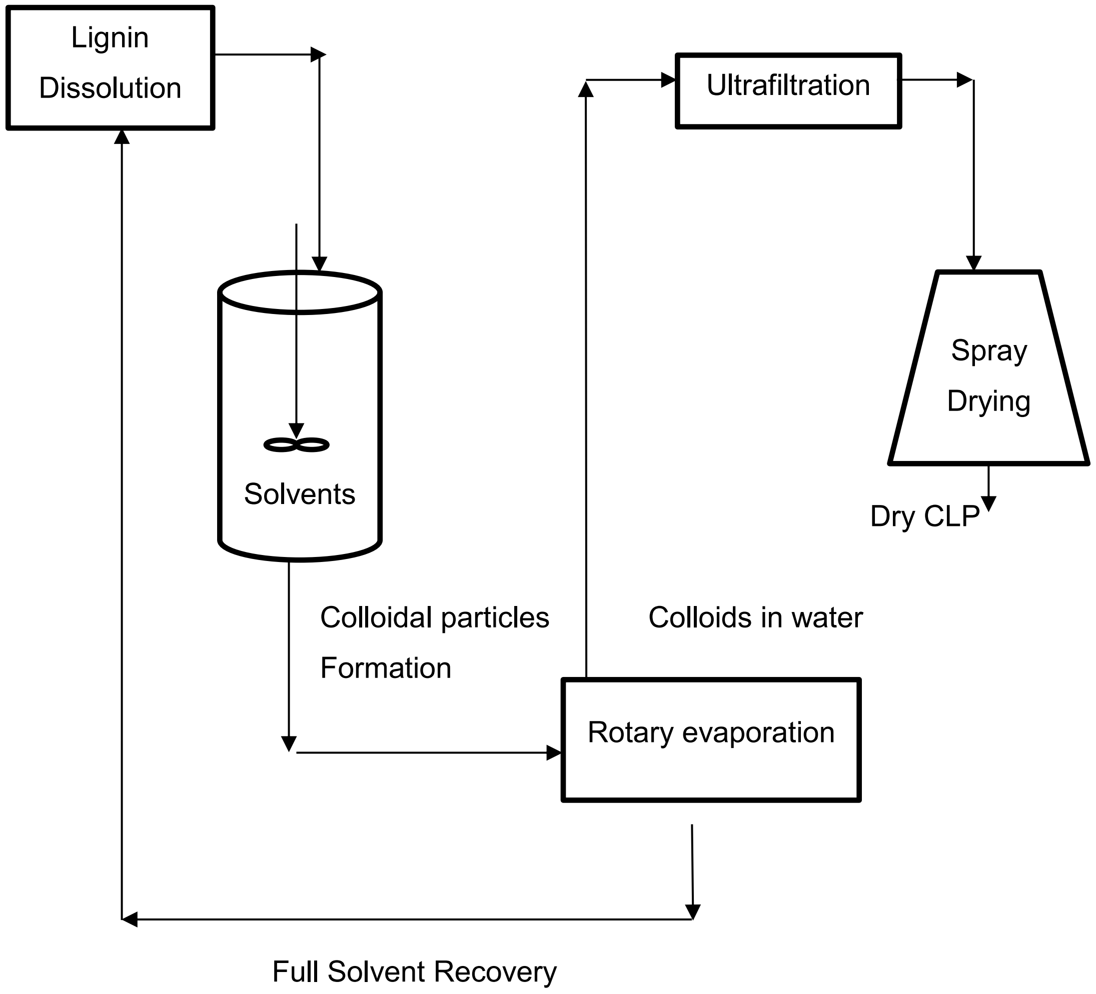


Figure 1. Batch process for colloidal particle production (2)

In order to improve the energy and economic efficiency, an innovative solution has come up that this batch process can be modified into continuous process. Based on the design of the continuous process, lignin is dissolved with solvents in a mixing tank, followed by flowing through a tubular reactor to form colloidal lignin nano-particles. Tubular reactor is vessel through which flow is continuous at steady rate (3). However, it remains the question if and how the lignin particle preparation can be done effectively using continuous process by developing a tubular reactor.

1.2 Objectives

The research includes analyzing the factors that affect the formation of colloidal particles and design the tubular reactor for tests. Parameters like pressure, flow rate and mixing duration time in the tube are the key factors. Finding out how are they related to each other gives theoretical support for developing the continuous process. Therefore, the following objectives will be implemented during the study:

1) Identifying the factors that affect the experiment
2) Designing and simulating the tubular reactor
3) Testing the tubular reactor and analysis of the results
4) Optimizing the process for further research

2 Methodology

Understanding the properties of lignin and colloidal particles is fundamental to begin the research. Throughout the study of existed document literature, it helps to comprehend the concept and working mechanism of colloidal lignin particles. By going through the current chemical process in the project, it targets to identify key factors that have impact on experiments and make hypotheses to ongoing design. Experiment is the main method to execute this research. Designing tubular reactor based on hypotheses, experimental test will analyze the feasibility and efficiency of reactor and optimization can be carried out according to the results.

Therefore, to reach the goals I intend to start the research by following stages:

1) Review of the existed research documents
2) Study of the ongoing process in the project
3) Proposing hypotheses
4) Implementation of my own design based on hypotheses
5) Experimental test for analysis
6) Optimization of the design according to results

3 Literature review

3.1 Lignin

As one of the main polymers of lignocellulosic materials, it is also the only aromatic polymer present in wood. It is concentrated located mainly in the region of the middle lamella (4). Figure 2 illustrates the precise position of lignin in lignocellulose.

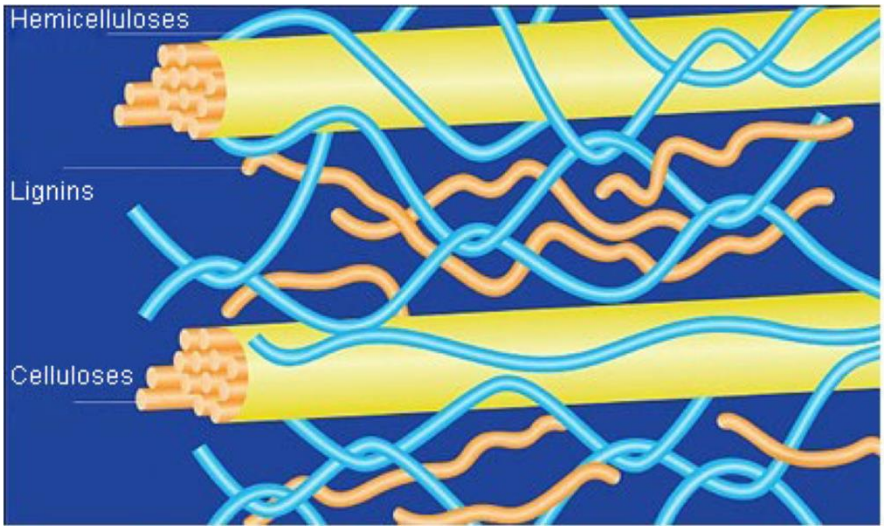


Figure 2. The position of lignin in lignocellulose (5)

Most of the lignin can be generally classified into three main categories: softwood, hardwood and grass lignin. But except from native lignin, some by-products from chemical pulp industry are defined as industrial based technical lignin, like Kraft lignin that derived from Kraft.

Lignin can be defined as a polyphenolic material arising primarily from enzymic dehydrogenative polymerization of three phenylpropanoid units, which are coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol, respectively (6). Lignin classification is traditionally done according to the precursors of the polymer. Guaiacyl lignin (G) is typical of softwood species and it is formed mostly of trans-coniferyl alcohol precursors, with the remainder consisting mainly of trans-p-coumaryl alcohol which contains p-hydroxyphenyl (H) units. (4)

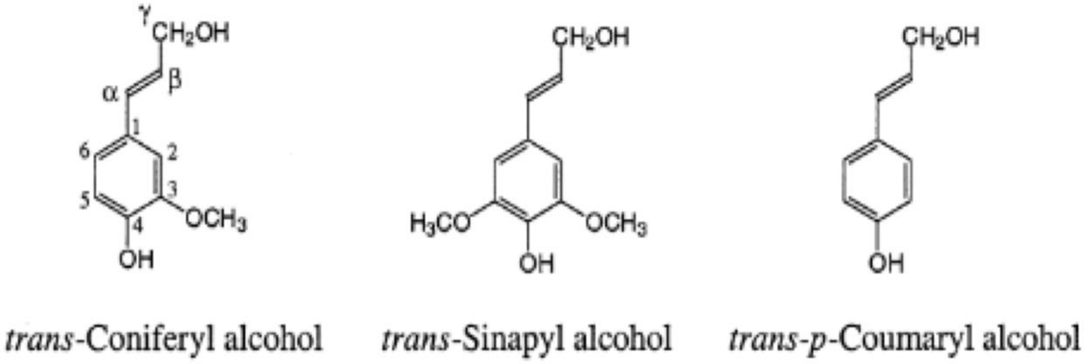


Figure 3. The structural unites of lignin (6)

LignoBoost softwood kraft lignin (68.1 wt%) is the type of lignin we use as raw material in preparing lignin solution, it is provided by VTT Technical Research Center of Finland.

3.2 Colloidal nano-particle

Colloids represents an intermediate stage between solutions and suspensions, not only in particle size but also properties. Hence they own some of the properties that both microscopic and macroscopic have and make them more adaptable to some special applications or functions.

The colloidal state of particles has three important characteristic features: particle size, particle shape and surface chemical properties. In general, a colloid can be any particle whose size includes a linear dimension in the range from 1~10 nm to 500~1000 nm. (7) The ASTM E2456-06 standard (8) has given a definition on nanoparticle that is sub-classified as ultrafine particle with lengths in two or three dimensions between 1 nanometer to 100 nanometer. The shape cannot be described precisely and it could be very complicated, but colloidal size particles can be classified as: corpuscular (spherical and ellipsoid), laminar (disc- or plate-like) or linear (rod- or needle-like). As for the surface charge, all particles in dispersion require a surface electrical charge when in the contact with a polar medium like water. (9)

The ways of producing nanoparticles can divide into three classes: (1) the monomer is polymerized during the preparation process to eventually form nanostructures; (2) an insoluble polymer is subjected to a physical process resulting in nanoparticles; (3) a soluble polymer is cross-linked in a suitable way. (10) Precipitation is a way to produce lignin nano-particles. Chemical precipitation is a process that can separate solid substance from a solution, by changing the composition of solvent to decrease the solubility of the substance in it or changing the structure of the substance to become insoluble.

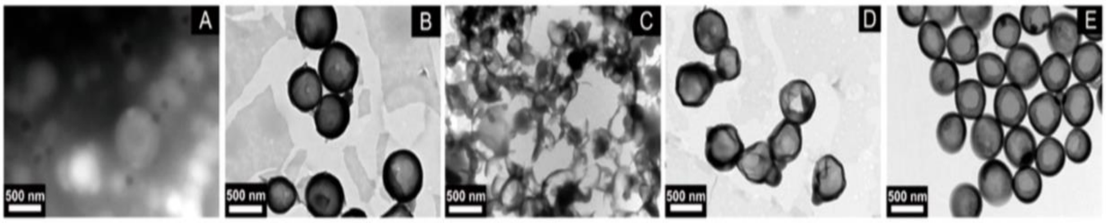


Figure 4. Transmission electron microscopy (TEM) images of the samples obtained from dispersions at different water contents at an initial lignin concentration of 0.5 g/l. (A) 0 vol%, (B) 20 vol%, (C) 40 vol%, (D) 50 vol%, (E) >80 vol% (11)

As it is shown in Figure 4 that the precipitation process of lignin dissolved in certain solvents with the addition of water is observed by TEM. The series of images gives clear view that how lignin nano-particles being organized and formed.

Generally, the surfaces of particles possess both chemical and physical properties. The nano-particles that in the range of 1 – 100 nm has very special properties due to the increase of surface area, which decides their physical and chemical interaction (12). The reason why colloidal nano-particles being special is their surface area increases as their sizes decrease (13). And this makes one of the possible application to be reinforcement of polymers, which shows the potential advantage of producing colloidal lignin nano-particles (14).

3.3 Reactors for chemical process

As the core of a chemical process, a reactor takes responsibilities of promoting chemical reaction at proper condition and producing desired products. Thus, designing reactors is affected by many factors that should be considered beforehand. There are plenty of different types of reactor for various purposes. Three main basic types of reactor will be discussed here as the batch reactor, the continuous stirred-tank reactor and the tubular.

3.3.1 Comparison of Batch reactor with Tubular reactor

A batch reactor is usually used in a discontinuous process that a stirred tank is pre-filled with reactants and emptied after the reaction. This type of reactor has limited quantities for each process so that large production has to be accomplished in multiple times. By emptying and refilling the reactor every time, a series of preparation steps should be done as well. This results in time-consuming and unproductivity. But it also has advantages that if multiple similar processes are needed, the reactor can be utilised individually for different purposes.

The current reactor used for preparation of colloidal lignin particles is this type of batch reactor. It has been functioning efficiently but not economical and energy efficient for up-scaling the research.

The continuous stirred-tank reactor (CSTR) is similar to the batch reactor with the addition of inlet and outlet that reactants can flow into and out of the reactor simultaneously.

The volume, pressure, temperature and flow rate usually can be assumed to be stable once the reaction reaches stead-state. The advantage of CSTR comparing to batch reactor is when handling large quantities of reactions, as it is unnecessary to carry out in multiple times. It is designed for a continuous process that no changes in reactants or reaction condition required. Nevertheless, if multiple steps in a process should be done separately and immediate product need to be stored, the CSTR does not possess superiority.

Another type of continuous reactor is tubular reactor, or as called plug flow reactor (PFR). It is a reactor that consist of cylindrical pipe in which fluids can flow constantly. Tubular reactor has a wide range of selection in chemical industry the highest conversion per reactor volume of other types of reactor (15).

Typically, the pressure, temperature, flow rate and composition are assumed that no variability occurs in the pipe. The necessary volume needed to reach a particular conversion of tubular reactor is lower than that of stirred-tank reactor, in the meanwhile of keeping the merits of continuous process (16). In my research, tubular reactor has more advantages in controlling the filling of reactants and empting immediate products, as the amount of water and lignin solution require to follow certain ratio to perform precipitation in the reactor. No extra mechanical mixer need for pushing the reaction and the pipes are available for implementing static mixing elements. Therefore, the tubular reactor has the most suitable technical requirements, energy efficiency and easy upscaling of the further research.

4 Hypothesis

With the basic understanding of the formation of colloidal particles and the mixing principle of lignin solution with water, it is hypothesized that the formation of colloidal particles varies from the mixing amount at unit time, which will be affected by the different ways of mixing at different conditions. It can be assumed that the longer time they mix at the larger contact area, the better quality of colloidal particles will form.

In other words, a fixed amount of lignin solution meeting with correspondently amount of water to form colloidal particles has direct connection with the following three factors: contact area of different Solutions, duration of mixing and the velocity of flow in the process of mixing. Both the design of tubular reactor and test methods will reflect on results. Therefore, the hypotheses are proposed separately for the design of tubular and experimental methods.

When in the consideration of designing the tubular reactor, it is hypothesized that:

1. Creating more injection points of lignin solution to mix with the water will perform better mixing;
2. Having turbulence inside of the tubes to offer a better chance for Solutions to flow and mix well together;
3. Different shapes of mixing elements inside of the tubes are not necessary, but might be helping in mixing in the same way;
4. The longer the tubes are, the better mixing will be;
5. The bigger size of the tubes is, the smoother mixing and easier flows will pass through the tubes.

When in the consideration of designing the experiments, it is hypothesized that:

1. Keeping the constant pressure, temperature and flow rate offers stable mixing environments;
2. The slower the flow rate of Solutions is; the better mixing is;
3. The longer duration of fluids running in the tubular reactor, the better formation of colloidal particles.

All the assumptions are raised before the actual design and experiments that are carried out, but in the logical way that they can be tested step by step. In the following topics, the detailed execution of all the hypotheses and thoughts will be stated and proved.

5 Design of tubular reactor

5.1 Designs and limitations

How the colloidal particle preparation can be done effectively using continuous process by developing a tubular reactor is one of the key issue of this study. As it is stated in the theoretical background that the tubular reactor is vessel through which flow is continuous at steady rate. With the continuous injection of lignin solution, the water is supposed to mix up and form colloidal particles in short time, as it is hypothesized. Thus, the original design of the tubular reactor is by running through with water from the very beginning of the reactor, the lignin solution is equally divided to be injected into the reactor at different points. As it is shown in the Figure 5.

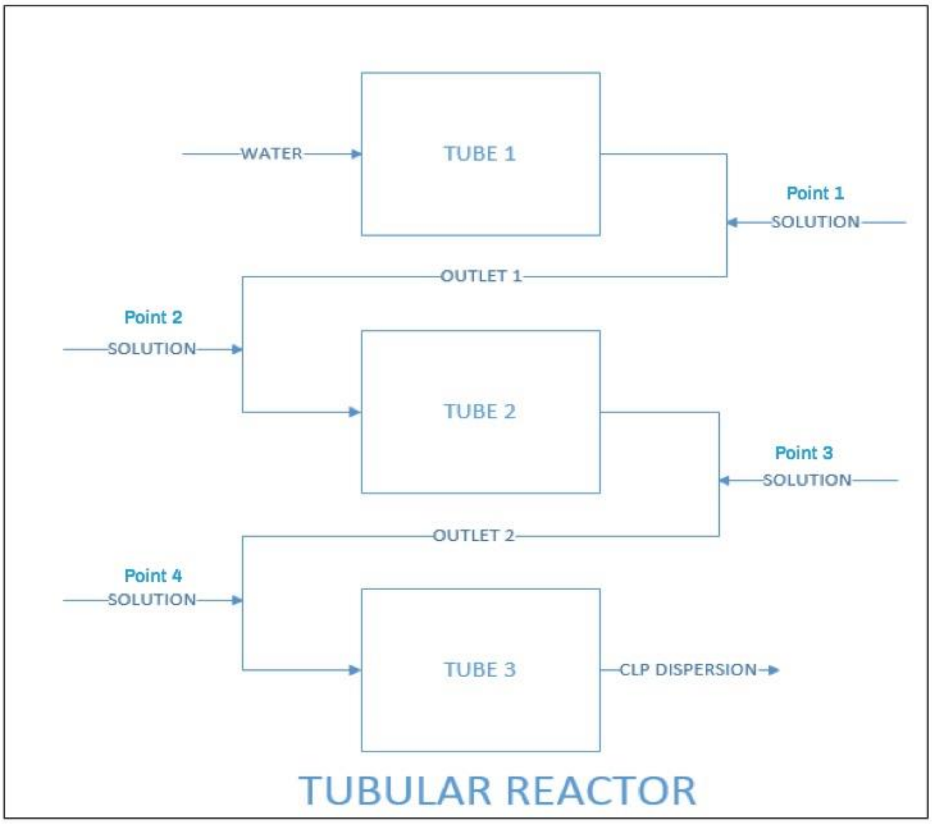


Figure 5. Design of tubular reactor

The water flows in from the beginning of the tube (Input) with a constant flow rate, on the right side of the turning point (Point 1) comes in the first injection of lignin solution and two fluids mix up in the second tube. When they reach the turning point on the left side

(Point 2), here comes the second injection of lignin solution, which will continue to join the mixture and form colloidal particles. Then at the second turning point on right side (point 3), the last injection of lignin solution will be added into the reactor and when the final solution comes out at the output of the tubular reactor, the colloidal particles should be formed well.

But there are some limitations and impracticability to execute this design:

- The three injection points of lignin solution are located separately on different sides of the reactor that it is difficult to build the connections and tubing, since the lignin solution has to come from one source and can be provided continuously.
- Inadequate pumps that can offer the same pressure and flow rate to all these injection points.
- With the fluids flowing in the tubular reactor, the lignin solution injected from the Point 3 has less water to mixing with, so it might have negative effect on the formation of colloidal particles.

After considering the limitations listed above, the design has been updated and improved. The injection Point 2 of the tubular reactor has been discarded, this turning point of the tube can be used for a sample taking point. So the second version of the tubular reactor turns to be having two injection points on the right side, with the same water input in the beginning.

But in practical construction of the tubular reactor, there are still problems remaining:

- The pressure inside of the tube at injection Point 1 and Point 2 is different, which results the difference in the injection flow rate.
- The lignin solution injected from point 2 has way less duration of mixing in the tubular reactor than its from Point 1, which could result in inadequate mixing and form bad quality of colloidal particles.
- If longer tubes are added to the reactor for the purpose of better mixing that comes from Point 2, it will be inefficient and uneconomical.

With all the attempts and hypotheses that have tried before, the design of the tubular reactor has been finalized. The water will be pumped from the Input to flow continuously in the tubular reactor, while the lignin solution is set to be injected from only one point after the first tube. Mixing process of these solutions will carry out in the following three tubes and the final solution containing colloidal particles will come out of the reactor from the Output. In addition, there two sample points located on each side of the reactor so that it can be used to analyze the mixing in process.

Equipment

- Peristatic pump for water: Watson Marlow 323 series, rotor speed 0 - 400 rpm, flow rate 0.9 - 2000 ml/min, operation temperature range 4ºC - 40 ºC
- Peristatic pump for lignin solution: Watson Marlow 101U/R, rotor speed 2 - 32 rpm, flow rate 3.25 – 53 ml/min.
- Reactor tubes: three metallic tube, one transparent Teflon tube.
- Tubing for water and lignin solution: Tygon.

Materials

It has been a great challenge to look for the suitable materials for different parts of the tubular reactor, since one of the chemical composition in lignin solution is a highly corrosive product that very few materials can be resistant.

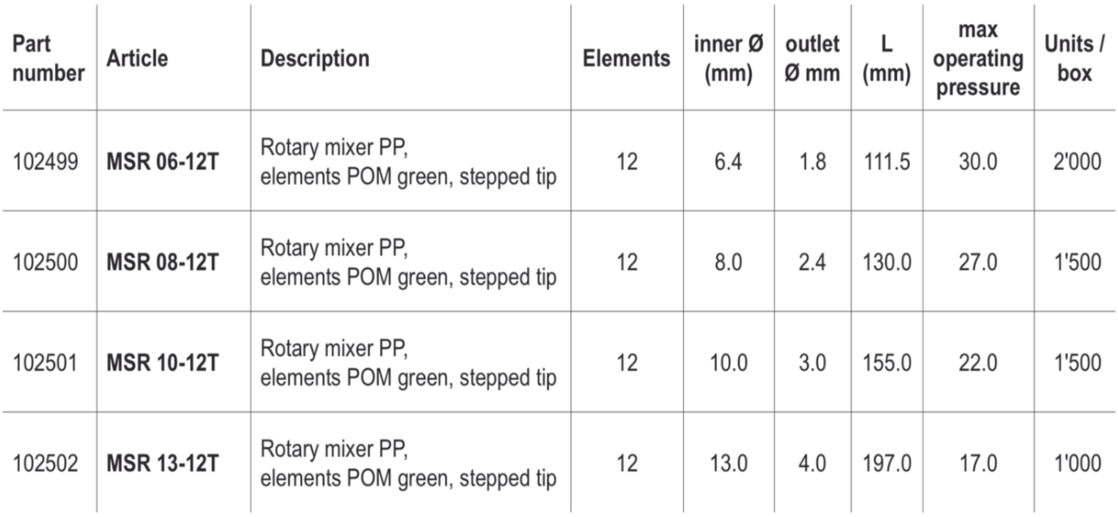
The four reactor tubes have to be not only resistant to corrosion, but also have strong hardness to connect with metallic parts. And it better to be transparent so that the observation to mixing process inside will be easy.

Tubing for water and lignin solution is the most difficult material to look for. Teflon cannot be used due to the hardness. Normal rubber tubes are not corrosion resistance. Another material is Tygon which after being tested for running lignin solution continuously for over 10 hours, it still stays in good condition. So the Tygon tubing was chosen for running water and lignin solution.

Mixing elements, also called as internal mixer or static mixer, is used for creating turbulence inside of the reactor tube. There are two different kinds of shape in our selection: box-shaped mixer and rotary-shaped or helical-shaped mixer.

Figure 6. Box-shaped static mixer (17)

Lignin solution is an adhesive solution that will easily stick on the wall of tube or the internal mixing elements under the condition of insufficient mixing with water, so too much turbulence will result in unsmooth flow and insufficient mixing. Therefore, the rotary-shaped mixer is chosen to be the mixing elements that inserted into the reactor tubes. The supplier of these mixing elements is Sulzer and there are several models available for use, as shown in Figure 8. The material of mixing elements is polypropylene, which has been tested that it is lignin solution resistance.



Part number	Article	Description	Elements	inner Ø (mm)	outlet Ø mm	L (mm)	max operating pressure	Units / box
102499	**MSR 06-12T**	Rotary mixer PP, elements POM green, stepped tip	12	6.4	1.8	111.5	30.0	2'000
102500	**MSR 08-12T**	Rotary mixer PP, elements POM green, stepped tip	12	8.0	2.4	130.0	27.0	1'500
102501	**MSR 10-12T**	Rotary mixer PP, elements POM green, stepped tip	12	10.0	3.0	155.0	22.0	1'500
102502	**MSR 13-12T**	Rotary mixer PP, elements POM green, stepped tip	12	13.0	4.0	197.0	17.0	1'000

Figure 7. Sulzer Static Mixer MIXPAX^{TM} MS (17)

Safety

Safety valves are used at water input, lignin solution injection point and sample points, which can release the pressure that is over 7 bar if any clogging happens in the reactor.

6 Experiments

The main test of using designed tubular reactor to prepare colloidal particles will be carried out in full mixing length with full mixing elements, but control groups will also be tested under two main circumstances: having limited, no mixing elements. It targets to prove what are the main elements in tubular reactor and what affects the formation of colloidal particles.

6.1 Experimental procedure

The main experiment is designed to follow the steps below: Calibrate the pumps to ensure the settings of rotor speed that match the flow rates. Calculate the flow rates for running water and lignin solution. Test the solutions with the reactor at a small volume to see if the calculation works. Water starts entering the reactor first, followed by lignin solution entering the reactor and keep the lignin solution and water finishing at the same time. Analyze the product from previous small test and make improvements. If the previous step works well, level up the test volume gradually to bigger size. Analyze the final product.

6.1.1 Calibration of pumps

Peristatic pump for water uses the rotor speed for setting, I have tested the relationship between rotor speed and flow rate, the results are shown in the Table 1 below:

Table 1 Water Pump Watson Marlow 323 series flow rate test

Rotor Speed rpm	Flow Rate ml/min
5	15.8
10	33.1
20	66.7
30	99.5
50	165.8

Peristatic pump for lignin solution uses its own setting and the connection with the flow rate has been tested and shown in Table 2 below. Due to the oldness of pumps, the flow rate is not proportional to the setting of pump, they do not follow the linear growth.

Table 2 Lignin solution pump Watson Marlow 101U/R flow rate test

Pump Settings	Flow Rate ml/min
5	2.2
10	4.5
30	13.5
50	22.5
80	35.8
90	41.9
99 (Max)	49.5

6.1.2 Calculation of flow rate

Colloidal particles are formed when lignin solution is being added into water with the ratio of 1:1.71 respectfully (2). Lignin solution has the density of 0.92 g/ml and the water density is 1g/ml.

For instance, 250 ml of Lignin solution:

$$m(\text{Lignin solution}) = V(Solution\ X) \times \rho(\text{Solution})$$

Therefore, mass of Solution is

$$250\ \text{ml} \times 0.92\ \text{g} / \text{ml} = 230\ \text{g}$$

$$m(\text{water}) = m(Solution\ X) \times 1.71$$

So mass of water is

$$230\ \text{g} \times 1.7 = 393.3\ \text{g}$$

Volume of water is 393.3 ml

Based on the design of experiment, water and lignin solution are supposed to finish the entry to the reactor at the same time, which the duration of each pumping into the reactor should be almost the same. Since the water will start entering the reactor first, so the duration of water input can be slightly longer than that of lignin solution.

Thus,

$$250\ \mathrm{ml}\ \div 393.3\ \mathrm{ml} = 0.63\ \approx\ R(\mathrm{Lignin\ solution}) \div R(water)$$

So suppose the flow rate of water is 10 rpm, which is 33.1 ml/min using Pump Watson Marlow 323.

Then duration of water:

$$t(\mathrm{water}) =\ 393.3\ \mathrm{ml}\ \div 33.1\ \mathrm{ml/min} =\ 11.9\ min$$

Therefore, the duration of lignin solution has to be less than 11.9 mins, if it finishes in 11 minutes.

Then flow rate of lignin solution:

$$250\ \mathrm{ml}\ \div 11\ \mathrm{min} = 22.7\ \mathrm{ml}\ /\ \mathrm{min}$$

Therefore, when carry out the experiment of mixing 250 ml of Solution, the water needed is 393.3 ml. The flow rate of water should be 33.1 ml/min and pump setting is 10 rpm. The flow rate of lignin solution should be 22.7 ml/min and pump setting is 50.

This is an example of calculating the flow rate and pump settings for testing 250 ml of lignin solution, when upscaling the test volume to 1 l, 2 l and etc., the calculation method stays the same.

6.1.3 Trial-test results

The experiment started with testing 250 ml lignin solution, using Pump Watson Marlow 323 for water and Pump Watson Marlow 101U/R for lignin solution. The pump settings have been adjusted by following the calculation above.

The water pump was turned on 15 seconds before the lignin solution pump was on to make sure the water is already inside of reactor before the lignin solution enters. Water flow rate was set to be 33.1 ml/min and lignin solution flow rate was set to be 22.7 ml/min. Both of them should finish pumping in 11 minutes but unfortunately, Lignin solution finished way slower than water, which resulted in the failure of this test run.

For the second test run, I decreased the flow rate of water to balance with the duration of lignin solution. Water flow rate was 15.8 ml/min and lignin solution flow rate was still 22.7. The time taken of water was more than doubled of that of Lignin solution, which was again failed.

For the third trial, the flow rate of water was increased slightly than in second test and the flow rate of lignin solution stayed same, which is 25.3 ml/min and 22.7 ml/min respectively. The lignin solution finished 3 minutes earlier than water, that can be considered test done acceptably. However, when analyzing the final product, the colloidal particles were not formed well as there were many visible big particles existed in the solution. Figure 8 illustrates clearly the product quality.

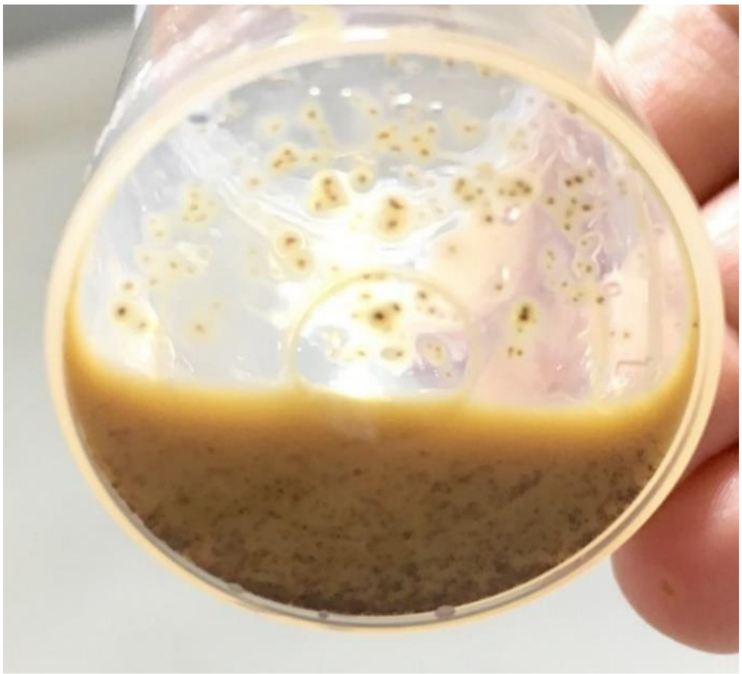


Figure 8. Product of test 3

In the fourth and fifth test run, I tried to up-scale the amount of lignin solution from 250 ml to 500 ml using the same flow rates and the results were not satisfying. The detailed data and results of all five tests are presented in the following Table 3.

Table 3 Initial test results

Trial No.	Water (ml)	Lignin solution (ml)	Flow rate (water) (ml/min)	Flow rate (Lignin solution) (ml/min)	Time (water)	Time (Lignin solution)	Result
1	393.3	250	33.1	22.7	11 min	> 11 min	Failed
2	393.3	250	15.8	22.7	24 min	11 min	Failed
3	393,3	250	25.3	22.7	15.5 min	12.5 min	Done
4	786.6	500	25.3	22.7	32 min	24 min	Failed
5	786.6	500	33.1	27	24 min	21.5 min	Done

6.1.4 Results

The failed test results did not match the theoretical assumption and calculation was out of surprise. Based on the calculation of flow rates, the duration of water and lignin solution are supposed to be the same. But instead, water finished way faster than lignin solution. It is figured that the key reason of this situation is the pressure difference at different points of reactor caused by different pumps.

Pump Watson Marlow 323 is a powerful pump that can be up to 2000 ml/min at 400 rpm, it creates more pressure into the reactor in individual peristatic push even at a low rotor speed, compared with Pump Watson Marlow 101U/R that has maximum flow rate of only 49.5 ml/min. So water with more pressure was pumped into reactor while the lignin solution was facing counter-flow pressure, the Pump Watson Marlow 101U/R was not powerful enough to push against it and resulted in lower flow rate of lignin solution injected into the reactor. Thus, the practical results were different from calculation.

Therefore, in order to keep the pressure equilibrium at each point in the reactor, I decided to change the Pump Watson Marlow 323 to Pump Watson Marlow 101U/R so that both water and lignin solution have the same pump.

6.1.5 Improved test

After being changed the pumps, the first test started from 250 ml lignin solution using the same flow rate as calculated. And in order to keep water input and lignin solution injection at the same pace, both pumps were turned on at the same time as well. The test ended up with water and lignin solution finishing almost the same and the formation of colloidal particles was good, as the final solution is milk-coffee-looked with no big particles existed in the solution, like shown in Figure 9.

Figure 9. Sample from test 1

In the following tests, volume of lignin solution and water has been up-scaled gradually and flow rates have been adjusted accordingly. All of the following tests have reached targets successfully and detailed results can be found in following Table 4.

Table 4 Improved test results

Trial No.	Water (ml)	Lignin solution (ml)	Flow rate (water) (ml/min)	Flow rate (Lignin solution) (ml/min)	Time (water) (min)	Time (Lignin solution) (min)	Result*
1	787	500	37.8	24.4	21	21	Good
2	1575	1000	37.8	24.4	42	41	Very good
3	2360	1500	37.8	24.4	63	62	Very good
4	3147	2000	37.8	24.4	83	82	Very good
5	3933	2500	38.2	24.4	103	103	Very good
6	4720	3000	42.8	27.1	111	111	Very good

- “Done” represents the test is finished smoothly but product is unsatisfying with some visible big particles remaining
- “Good” represents the test is finished smoothly and product is a clear milk-coffee-looked solution with very few amount of visible small particles remaining
- “Very good” represents the test is finished smoothly and product is a clear milk-coffee-looked solution with no visible particles

6.1.6 Control group

It has been tested that tubular reactor with full mixing elements can lead to a very good formation of colloidal particles. Now the control group tests with limited length and mixing elements will be carried out. The experiment operation runs the same as previous, except part of mixing elements will be removed from reactor or mixing length will be shortened.

6.1.6.1 Limited mixing elements

- Mixing with only 2/3 of mixing elements
- 250 ml of lignin solution with 395 ml of water
- Flow rate of water is 37.8 ml/min and lignin solution is 24.4 ml/min
- Result is shown in Figure 10 that final solution is clear and milk-coffee-looked, but small amount of big particles remaining in the solution

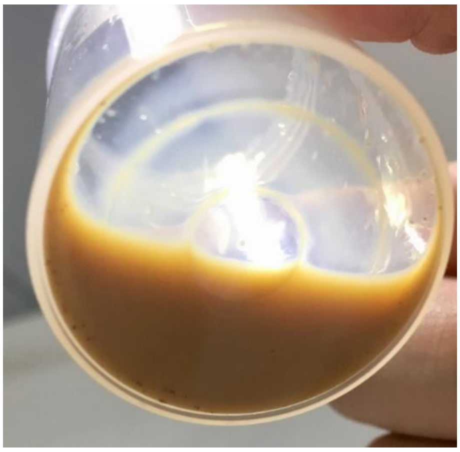


Figure 10. Result from using only 2/3 of mixing elements

- Mixing with only 1/3 of mixing elements
- 250 ml of lignin solution with 395 ml of water
- Flow rate of water is 37.8 ml/min and lignin solution is 24.4 ml/min
- Final solution has large amount of big particles remaining in the solution as shown in Figure 11

Figure 11. Result from using only 1/3 of mixing elements

- Mixing with completely no mixing elements
- 250 ml of lignin solution with 395 ml of water
- Flow rate of water is 37.8 ml/min and lignin solution is 24.4 ml/min
- The final solution is darker with huge amount of big particles precipitated at the bottom, as shown in Figure 12

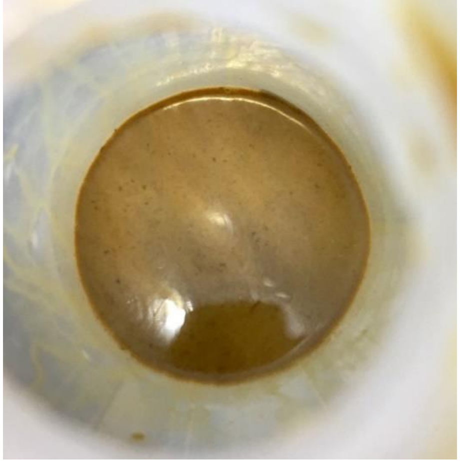


Figure 12. No mixing elements

6.2 Discussion

Comparing the results from main experiments and control groups, it has proved that mixing length and mixing elements are the key factors affecting the formation of colloidal particles in the tubular reactor. The full mixing is the ideal length and longer mixing would be unnecessary and uneconomical. Mixing elements are crucial in the reactor to create turbulence and enhance mixing between water and lignin solution to formation colloidal particles.

A new discovery in colloidal particles formation process was found in the experiments that there is an intermediate stage before the target colloidal particles are formed. As it is known that our target colloidal particles are in nano size, which was assumed to be formed immediately when lignin solution is mixed with water. Later in the observation of mixing process in tubular reactor, micro-sized particles are actually formed firstly before the colloidal nano-particles are formed. This can be defined as an intermediate stage in the formation of colloidal nano-particles.

Experiments have been done separately to prove the intermediate stage:

1. Prepare a sample of 10 ml lignin solution
2. Add 5.2 g of water into the sample
3. Shake it to well mixed and the solution looks dark with lots of big particles
4. Then continue to add 5.2 g of water and mix it well, the solution looks lighter and some big particles disappeared with just very small particles remaining
5. Add the last 5.2 g of water into the solution and mix it, then almost all the visible particles disappeared

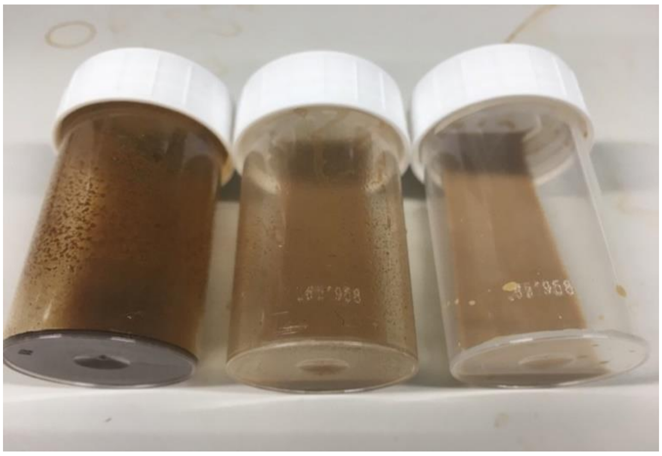


Figure 13. Different particle size formation stage

So it is recognized that when water is continuously added into lignin solution, big particles are formed first, followed by micro-sized particles and nano-particles are formed at final. But it should be noticed that the intermediate stage does not stay long, otherwise the particles at this stage would form permanently and fail to form nano-particles, no matter how much water added for mixing. Figure 13 presents the solution at different stages of forming colloidal nano-particles.

7 Analysis

Weighing the colloidal particles that formed from the process and compare with the amount of raw material added is one way to analyze the efficiency of tubular reactor. Sample 1-3 were taken from successful tests with 500 ml, 1000 ml and 1500 ml lignin solution respectively. Sample 4 was taken from the test with only 1/3 of mixing element.

The final solution contains the colloidal particles and several solvents that can be easily evaporated. So the four samples were dried in lab for five days to evaporate solvents and only colloidal particles will be left.

Figure 14. Dry samples of colloidal particles

It can be seen from Figure 15 and Table 5 that the quality of formed colloidal particles is excellent and the efficiency of tubular reactor is quite high. Sample 4, which has only 67%, has proved again that insufficient mixing would result losses in forming colloidal particles.

Table 5 Percentage of CLP recovery

Sample	Weight of Lignin solution	Conc. of CLP (Wt. %)	Weight of CLP before drying	Weight of CLP after drying	$\frac{Weight\ of\ CLP\ after\ drying}{Weight\ of\ CLP\ before\ drying}$
1	23.60 g	1.71	0.59 g	0.54 g	92%
2	26.37 g	1.71	0.66 g	0.61 g	92%
3	16.51 g	1.71	0.41 g	0.39 g	93%
4	28.70 g	1.71	0.72 g	0.48 g	67%

8 Conclusion

According to the experiment results, the designed tubular reactor has been proved to have positive effect on the formation of colloidal particles. As stated in hypotheses that flow rate, turbulence and mixing duration are the key factors to the colloidal particle formation. Flow rate of water and lignin solution has to be calculated based on the fact that both water and lignin solution start and finish at the same time. It offers a static environment for water and lignin solution to mix evenly and smoothly. The ideal mixing length is with full mixing elements, longer duration does not improve the colloidal particle formation and less duration will definitely result in insufficient mixing. In terms of mixing elements, they take crucial responsibility to create turbulence inside of reactor for better formation of colloidal nano-particles.

However, there are still some improvements can be made in the future research. Based on the current tubular reactor design, the first meter of tube does not function for mixing, as the injection of lignin solution is located between first and second tube. So the first tube can be designed shorter for the purpose of more economical and energy saving. When considering to up-scale the process in further research, pumps for water and lignin solution should be replaced with larger power so that flow rates can be increased and mixing process has better perform. Also all the tubes in reactor can be replaced with transparent Teflon, mixing will be observed easily and problems can be identified quickly.

In summary, the conversion from batch process to continuous process by designing the tubular reactor shows significant improvements in the preparation of wood-based material colloidal particles. The tubular reactor may also be used for the formation and crystallization of other types of colloidal particles.

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