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Research Article

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Waste free Technologies for Production of Nanocrystalline Cellulose and its Composites

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Abstract
In this paper, waste-free technologies are proposed for the production of nanocrystalline cellulose (NCC), its semi-finished products and composites. The following optimal conditions for the cellulose hydrolysis stage were found: concentration of sulfuric acid 40 wt.%, temperature 80oC, duration 1 h, acid to cellulose ratio 7. After hydrolysis stage, the depolymerized cellulose was separated from the acid, washed, diluted with water and disintegrated to release individual nanocrystalline particles. Finally, the diluted dispersion of NCC was evaporated to obtain a commercial product such as concentrated NCC paste. For the production of composites, the acid in unwashed hydrolyzed cellulose was neutralized and precipitated with calcium base (e.g. calcium hydroxide) in order to obtain a white pigment, calcium sulfate (CS). Moreover, the spent sulfuric acid and acidic wastewater were collected and treated with a special auxiliary reagent to reuse and convert the acid into a valuable by-product, selling of which significantly reduces the cost of NCC. The wastewater collected after washing, neutralization and evaporation was purified and returned back to the technological cycle. To reduce the production cost, expensive stages - disintegration and evaporation of diluted dispersion, should be eliminated; as a result, cheap semi-finished products containing aggregates of NCC or its composite with inorganic particles of CS were manufactured along with by-product.

Keywords: Nanocrystalline cellulose, Composites, Semi-finished products, Process optimization, Utilization of Chemicals, Recycling of wastewater, Waste-free technology

Introduction

Currently nanocrystalline cellulose (NCC) is a subject of extensive research due to its unique features such as nano-sizes, rod-like shape, increased crystallinity, high mechanical properties, developed specific surface, biodegradability, insolubility in common organic solvents, reduced hydrophility, as well as resistance to diluted acids and alkalis, increased temperatures and proteolytic enzymes, etc. [1]. In general, NCC can be used in a variety of applications, such as composite materials, packaging, papermaking, biotechnology, medicine, etc. [2-6]. However, the widespread use of NCC is limited by its high cost estimated at $30 per kg.

Nanocrystalline cellulose, like microcrystalline cellulose (MCC), is obtained by acid hydrolysis of non-crystalline cellulose domains to achieve the level-off degree of polymerization (LODP). However, unlike MCC, a higher acid concentration is required to obtain NCC. For example, 55-65 wt.% sulfuric acid (SA) is used in the technology of NCC instead of 10-15 wt.% acid in the production of MCC [7-16]. This is due to the fact that aside from hydrolysis to LODP, sulfuric acid at increased concentrations and moderate temperatures causes erosion of local contacts between aggregates of nanocrystallites, as well as partial esterification of hydroxyl groups on their surface with the formation of negatively charged anions of sulfonic groups, ASGs: (-OSO2-) [17-19].

The mutual electrostatic repulsion of ASGs located on surface of nanocrystallites facilitates the disruption of nanocrystalline aggregates into individual nanocrystallites (INC) at the subsequent intensive ultrasonic or mechanical treatment of diluted dispersions of hydrolyzed cellulose in an aqueous medium. In addition, ASGs prevent re-sticking of INC and thereby provide the phase stability of NCC in colloidal dispersions.

The history of NCC began more than 70 years ago, when Rànby reported that colloidal suspension of cellulose particles can be obtained by controlled cleavage of cellulose fibers catalyzed by sulfuric acid [20]. Currently, NCC is prepared from cellulose of various origins: wood pulp, cotton fibers, bast cellulose fibers, MCC, tunicin and some others. Typical hydrolysis conditions of initial cellulose are: concentration of sulfuric acid 55-65 wt.%, temperature 40-50^{o}C, time 1-2 h [7-15]. Nanocrystalline particles obtained from various celluloses have lateral dimensions from 4 to 40 nm and lengths from 50 to 500 nm.

A typical method for obtaining of NCC was proposed by Bondenson et al. [15]. According to this method, the initial cellulose was treated with 63 wt.% sulfuric acid at 45°C for 2 h. Then the acid was removed, and the hydrolyzed cellulose was washed, diluted with water and subjected to ultrasonic treatment for 30 min, resulting in a stable dispersion of NCC in water is obtained. Since the entire amount of the reagent was lost and the yield of NCC did not exceed 30%, the conditions for isolation of NCC were far from optimal. Besides, the loss of all sulfuric acid and 70% of initial cellulose significantly increases the production cost of NCC.

The main purpose of this work was development of optimal waste-free technology for production of NCC, its semi-finished products and composites by improving the hydrolysis conditions, as well as by complete collecting of the spent reagent (SA) and its use for the production of valuable by-products.

Experimental

Materials and chemicals

Bleached Kraft pulp from Weyerhaeuser, USA (92% α-cellulose, DP = 1100) was used as a starting cellulose raw material. Concentrated sulfuric acid and other required commercial chemicals were purchased from the “Alibaba” company.

Production process

Sheets of Kraft pulp were cut into pieces of 5-10 mm and placed in a laboratory reactor. The cut cellulose was moistened with water, and then a calculated amount of 75-80 wt.% sulfuric acid (SA) was slowly added with cooling and stirring until the required final concentration of the acid and the liquid module from 7 to 10 were obtained. This method ensures uniform distribution of the acid in the cellulose and uniformity of the hydrolysis process. After that, the reactor was heated to the required temperature and acid hydrolysis of cellulose was carried out with a constant stirring. The process was stopped by diluting the acid 10 times with cold water. The hydrolyzed cellulose was separated from the diluted acid by centrifugation. The obtained depolymerized cellulose was washed, adjusted to pH 5-6 with carbonate buffer and finally washed with distilled water using a centrifuge.

To produce a composite, the hydrolyzed cellulose was not washed, while the residual SA was treated with a calcium base, e.g. calcium hydroxide, to precipitate particles of a white pigment - calcium sulfate ($CaSO_4$) into a NCC-containing slurry, as follows:

$$H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H2O$$

To isolate nanoparticles, the washed depolymerized cellulose or its composite with inorganic pigment were diluted with water to a 2% concentration and disintegrated 15 times in high-pressure homogenizer APV-2000 at a pressure of 100 MPa. Since the diluted dispersion is inconvenient for transportation and use, the aqueous dispersion of nanoparticles was evaporated in a vacuum evaporator at 50°C to obtain a marketable product such as concentrated paste of NCC.

In the waste-free technology, the spent acid and acidic washing waters are collected together and neutralized with a special auxiliary reagent, for example with hydroxylapatite, Ca5(PO4)3OH. As a result, the sulfuric acid is almost completely utilized and turns into a valuable by-product, superphosphate fertilizer, as follows:

$$7H_2SO_4 + 2Ca_5(PO_4)_3OH \rightarrow 3Ca(H_2PO_4)_2 \text{ x } 7CaSO_4 + 2H_2O$$

The wastewater collected after washing, neutralization and evaporation was purified and returned back to the technological cycle for dilution and washing.

In order to obtain the cheap semi-finished products containing aggregates of nanoparticles, the stages of disintegration and evaporation were eliminated.

Methods of investigation

The degree of crystallinity of the cellulose samples was determined by method of wide angle X-ray scattering, WAXS [21]. Size and shape of the nanoparticles were studied by method of field emission gun scanning electron microscopy [22]. The average degree of polymerization, DP, was measured by the viscosity method using diluted solutions of cellulose and nanocellulose in Cadoxen [23]. Content of sulfonic groups in nanoparticles was calculated from a sulfur assay [24]. Other characteristics of the NCC were found by methods [21].

Economic calculations

To implement the economic calculations the following parameters were taken into account (Table 1).

Table 1: Cost of initial pulp, chemicals, and electricity

Item	Average cost
Kraft pulp	$600 per ton
Sulfuric acid, 98 wt.%	$200 per ton
Hydroxylapatite	$120 per ton
Calcium hydroxide	$100 per ton
Sodium carbonate	$150 per ton
Electricity	$0.15 per kwh

When calculating the production cost the following expenses were taken into account: the cost of initial cellulose, acid and other chemicals; the cost of energy consumption for heating, mixing, dispersion disintegration and evaporation; as well as salary, equipment depreciation, overhead costs, projected production growth and percentage of profit.

Results and discussion

Comparison of conventional and optimal technology for production of NCC

Studies have shown that to produce NCC the acid concentration can be significantly reduced if the temperature of cellulose hydrolysis is increased [25]. At the same time, an increase in the NCC yield was also observed. If instead of 63 wt.% acid, the 40 wt.% sulfuric acid is used at the hydrolysis stage, then to produce the

NCC, the hydrolysis temperature should be increased from 45 to 80°C. If the acid concentration decreases from 63 to 40 wt.%, the cost of hydrolysis can be reduced by $716 per ton of initial pulp. On the other hand, raising the hydrolysis temperature from 45 to 80°C requires a small additional electricity consumption, of $33 per ton of initial pulp. Thus lowering the acid concentration is more beneficial than raising the hydrolysis temperature. As a result, the total cost of hydrolysis process can be reduced by $683 per ton of initial pulp, while the yield of hydrolyzed cellulose (HC) doubled (Table 2).

Table 2: Hydrolysis conditions of conventional [15] and optimal technologies

Parameters	Conventional technology	Optimal technology
Acid concentration, wt.%	63	40
Temperature, oC	45	80
Time, h	2	1
Acid to cellulose ratio	10	7
Yield of HC, %	30	61
Hydrolysis cost, $/t cellulose	1336	653

The conventional technology of NCC production includes the following main stages:

1. Acid hydrolysis
2. Removal of acid
3. Washing of acidic depolymerized cellulose
4. Dilution of washed depolymerized cellulose and intensive disintegration in the aqueous medium
5. Optional stage: Evaporation of NCC dispersion to obtain the concentrated paste of NCC

According to calculations, the total cost of conventional technology is estimated at $12,036 per ton of 40% paste of NCC or $30,090 per ton of solid NCC. This technology is unprofitable, since during NCC production the entire amount of sulfuric acid and about 70% of initial cellulose pulp are lost.

Unlike conventional technology, the proposed optimal technology for production of NCC is waste-free, since it provides collecting and complete utilization of the acid for the production of a valuable by-product, as well as recycling of wastewater. Such technology includes the following main stages:

1. Acid hydrolysis
2. Separation of hydrolyzed cellulose from acid, washing and neutralization
3. Dilution of washed depolymerized cellulose and intensive disintegration in the aqueous medium
4. Evaporation of NCC dispersion to obtain the final product such as concentrated paste of NCC
5. Treatment of the spent acid and acidic washing waters with hydroxylapatite (HAP) to obtain a by-product: superphosphate (SUP)
6. Purification and return the water to the technological cycle

As follows from the calculations (Table 3), the use of spent acid to obtain the by-product, SUP-fertilizer, and its sale at a price of $200 per ton of fertilizer can reduce the cost of main product, such as 40% paste of NCC, to $8,152 per ton of the paste or $20,380 per ton of solid NCC. It is about 1.5 times less than the cost of NCC produced by the conventional technology.

Table 3: Estimated production cost of NCC paste using the optimal technology

Parameters	Value
Preliminary cost of NCC	$21,152 per ton of NCC
Cost of the used HAP	$443
Selling cost of the obtained by-product	-$1215
Final cost of 40% paste of NCC	$8,152 per ton of the NCC paste

Electron microscopic studies showed that NCC contains rod-like nanocrystalline particles with average sizes of 150 x 15 nm (Figure 1).

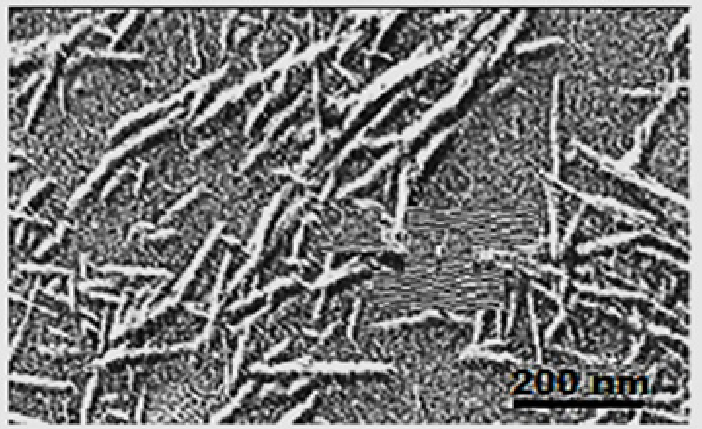

Figure 1: SEM image of rod-like NCC

Main features of NCC isolated by optimal method are shown in Table 4.

Table 4: Features of NCC

Feature	Value
Type of crystalline polymorph	CIβ
Crystallinity degree, %	75-77
Average particle length, nm	130-180
Average particle width, nm	10-20
Degree of polymerization	100-120
Specific gravity, g/cm^3	1.58-1.59
Specific surface area, m^2/g	100-300
Content of -OSO$_2$-groups, meq/kg	35-40

Waste-free technologies for production of semi-finished products containing aggregates of NCC and its composites with inorganic pigment

Calculations have shown that the stages of disintegration of hydrolyzed cellulose and evaporation of dilute aqueous dispersions of NCC are very expensive and significantly increase the total production cost of nanocrystalline cellulose. Therefore, it is most advantageous to eliminate these stages. The proposed waste-free technology allows producing a cheap semi-finished product containing aggregates of NCC along with production of valuable by-product.

Main stages of this technology are the following:

1. Acid hydrolysis
2. Separation of hydrolyzed cellulose from the acid, washing and neutralization
3. Concentration of 20% slurry into 40% paste
4. Treatment of the spent acid and acidic washing waters with hydroxylapatite (HAP) to obtain the by-product, SUP-fertilizer
5. Purification and return the water to the technological cycle
6. The scheme of production of such semi-finished product is shown in Figure 2.

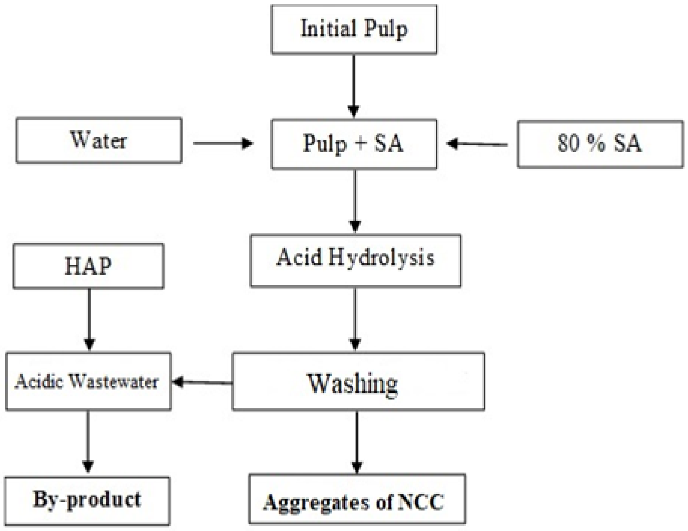

Figure 2: General scheme for production of NCC aggregates together with by-product

Taking into account both the production cost and the selling value of the by-product (SUP), it can be calculated that the final cost of the semi-finished product (aggregated NCC) will be low, estimated at $1,500 per ton of 40% paste or $3,750 per ton of solid NCC semi-finished product.

Optimal waste-free technology can also be used to obtain a semi-finished composite containing NCC aggregates and particles of white inorganic pigment - calcium sulfate. To obtain such semi-finished product, the reaction system after the hydrolysis step was diluted with water, for example, by a factor of 10 and centrifuged. As a result, cca 20% paste of depolymerized cellulose containing the diluted acid was obtained. Thereafter, diluted acid in the paste was neutralized with calcium hydroxide to convert it into calcium sulfate. The obtained composite paste was concentrated by high-pressure filtration to 40% solids content. The spent acid, separated by centrifugation, was treated with HAP to obtain SUP, the sale of which makes it possible to reduce the cost of the composite to $1,440 per ton of 40% paste or $3,600 per ton of solid composite. Analysis showed that solid composite contains 81% aggregates of NCC and 19% CaSO4.

The obtained semi-finished products containing aggregated NCC or its composite with the white pigment (CaSO4) are intended for the sale to consumers, who can mix them with other components and then grind if there is a need to destroy aggregates and isolate free nanoparticles of cellulose and pigment. Such nano-materials can be used, for example, as fillers, pigments and thickeners in ink, paint and coating formulations. Other potential applications of semi-finished products can be their use as carriers of therapeutically active substances, fillers or thickeners for biotechnology, medicine, pharmaceuticals, cosmetics, hygiene and some other areas, where the used components are even more expensive than NCC products. An example of such applications is the use of the proposed semi-finished nano-products in compositions of dentifrice. The comparative cost of the nano-products obtained by different technologies is shown in Figure 3.

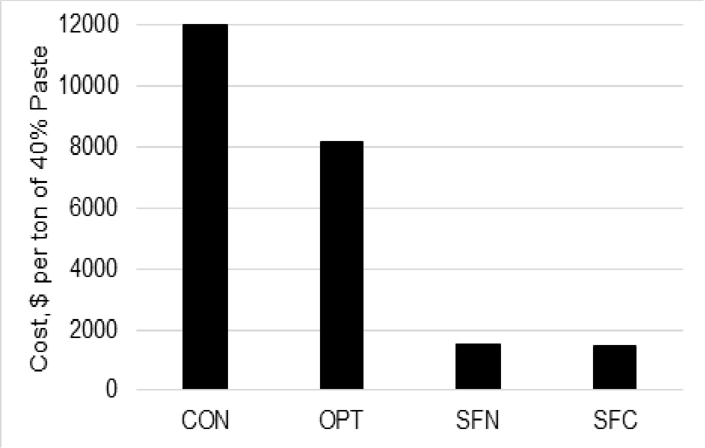

Figure 3: Production cost of nano-products obtained by conventional technology of NCC (CON), optimal technology of NCC (OPT), waste-free technology of semi-finished NCC (SFN) and waste-free technology of semi-finished composite (SFC)

As follows from the results, the implement of waste-free technologies for the manufacturing of semi-finished nano-products can reduce the production cost by 8 times compared to the cost of conventional technology, and thereby makes these new waste-free technologies cost-effective and competitive.

Conclusions

The following optimal conditions of the hydrolysis stage were found: concentration of sulfuric acid 40 wt.%, temperature 80oC, duration 1 h, acid to cellulose ratio 7. To release individual nanocrystalline particles, the diluted dispersion of depolymerized cellulose was intensive disintegrated in an aqueous medium. To obtain a trade product, such as concentrated paste of NCC, the diluted dispersion of NCC was evaporated. To produce composites, the sulfuric acid in unwashed hydrolyzed cellulose was treated with calcium hydroxide in order to obtain white pigment, calcium sulfate. Moreover, the spent acid was collected and treated with hydroxylapatite to produce the valuable by-product, superphosphate, selling of which significantly declines the cost of NCC. To reduce the production cost, the expensive stages - disintegration and evaporation of diluted dispersion, were eliminated. The proposed waste-free technology allows producing cheap semi-finished products containing aggregates of NCC or its composites with inorganic pigment, along with valuable by-product.

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