Industrial Crops and Products 93 (2016) 76–87

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Analysis of the sulfuric acid hydrolysis of wood pulp for cellulose nanocrystal production: A central composite design study

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ARTICLE INFO

Article history:
Received 20 November 2015
Received in revised form 25 January 2016
Accepted 28 January 2016
Available online 20 February 2016

Keywords:
Cellulose nanocrystals
Acid hydrolysis
Central composite design
Yield
Sulfate group density

ABSTRACT

Cellulose nanocrystals (CNCs) are most commonly prepared by sulfuric acid hydrolysis of a purified cellulose starting material but the effects of hydrolysis conditions on CNC yield and properties are incompletely understood. In this study, we use a rotatable central composite experimental design to elucidate parameter interactions between three design factors, acid concentration (x_1), hydrolysis temperature (x_2), and hydrolysis time (x_3), over a broad range of process conditions and determine their effect on yield and sulfate group density. Parameter ranges are 55–65 wt.% for x_1, 45–65 °C for x_2, and 30–180 min for x_3. Regression models of the experimental yield data reveal significant two-factor interactions of x_1 with each x_2 and x_3, whereas x_2 has no significant two-factor interaction with x_3. The models predict maximum yields of 66–69% at optimum process conditions of 57–58 wt.% (x_1), 64–67 °C (x_2), and 134–156 min (x_3). At these conditions, the sulfate group density is predicted to be between 241 and 265 mmol/kg. The sulfate group density is linearly dependent on acid concentration and hydrolysis temperature and not dependent on hydrolysis time. Maximum sulfate group density can only be achieved at the expense of yield. The results presented here provide a foundation for subsequent, sequential optimization using narrower parameter ranges, allowing further optimization of the hydrolysis conditions and potentially enabling higher yield.

1. Introduction

Cellulose is a natural, non-toxic, biodegradable, high-molecular-weight polymer and one of the most abundant renewable materials, produced in massive quantities by nature each year. With the growing need for natural renewable materials, cellulose and cellulose derivatives are regaining much attention for high-end applications in recent years. Furthermore, the increased level of understanding and advances in the development of nanotechnologies have created a need for nanoscale cellulose materials. Derived from long cellulose fibers, nanoscale cellulose particles are drawing growing interest from both industry and academia. Different terms have been used to refer to cellulose nanoparticles, including cellulose nanocrystals (CNCs), cellulose whiskers, cellulose nanowhiskers, and nanocrystalline cellulose. Here, the term CNCs is used to refer to crystalline cellulose particles with dimensions smaller than 1 μm.

Nanocellulosic materials are of great interest for a breadth of applications, ranging from reinforcing composite fillers to next generation biomedical and electronics applications (Shatkin et al., 2014). However, their widespread implementation is limited by their production cost, which is currently higher than the target of $2–5 per pound for CNCs from virgin wood pulp (Cowie et al., 2014). While current costs may be suitable for niche applications, larger commercial markets cannot bear such high cost. To achieve broad market integration, the production cost must be substantially reduced to costs competitive with comparable nanoparticle additives. Successful realization of high volume CNC use for commercial markets therefore requires a reduction of production costs, which may be partially achieved through a substantial increase of CNC yield during the synthesis and production process.

For the production of CNCs, the classic and most widely used method is acid hydrolysis of a purified cellulose starting material. Different inorganic acids, most commonly sulfuric and hydrochloric acid, have been used for this purpose (Nickerson and Habrle, 1947; Rånby, 1951; Mukherjee and Woods, 1953; Battista et al., 1956; Revol et al., 1992; Araki et al., 1998). When the colloidal stability of CNC suspensions is important, sulfuric acid is preferable because,

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http://dx.doi.org/10.1016/j.indcrop.2016.01.048
0926-6690/

in addition to cleaving the cellulose microfibrils, it esterifies some of their surface hydroxyl groups (Marchessault et al., 1961). The obtained CNCs will then bear negative charges from the dissociated surface sulfate groups ($pK_a = 2.46$, Wang et al., 2011). The resulting repulsive electrostatic forces between the negatively charged CNCs will prevent CNC aggregation. Thus, the surface charge density of CNCs plays a key role in the colloidal stability of their suspensions.

Besides the type of acid, many other experimental parameters affect the properties of CNCs, including the starting material (*e.g.* wood pulp, cotton fibers, microcrystalline cellulose (MCC), bacterial cellulose), the acid concentration, the acid-to-cellulose ratio, the hydrolysis temperature, the hydrolysis time, the mode and speed of agitation, and the work-up procedure. The production of CNCs of a desired size or surface charge requires a detailed understanding of these effects. The choice of process conditions, however, will also inevitably affect CNC yield. Historically, hydrolysis conditions were optimized to produce CNCs that readily form colloidal liquid crystalline phases (Revol et al., 1992; Revol et al., 1994; Dong et al., 1998). Unfortunately, the high sulfuric acid concentration of 64–65 wt.%, required to achieve good colloidal properties, results in low CNC yields on the order of 21–44% (Dong et al., 1998; Hamad and Hu, 2010; Wang et al., 2012). Low yields contribute substantially to CNC production costs and maximizing CNC yield may generate significant cost reduction, assuming similar production processes.

The most efficient way to optimize a production process and maximize yield is the design of experiments (DOE) method. DOE is a systematic approach for determining the relationship between different process parameters ($x_1, x_2, x_3, \ldots$) and process outputs (y_1, y_2, $y_3, \ldots$). DOE approaches generally take less time and require fewer runs than traditional optimization approaches and enable the identification of parameter interactions and prediction of optimum process conditions for a desired output. Bondeson et al. (2006) were the first to use a DOE approach to study the production of CNCs from MCC by sulfuric acid hydrolysis. They applied response surface methodology (RSM) in combination with a Fractional Factorial Resolution V experimental design to optimize the concentration of MCC, sulfuric acid concentration, duration and temperature of hydrolysis, and duration of sonication. The obtained model predicted a maximum yield of 40% for an MCC concentration of 10.2 g/100 mL, an acid concentration of 63.5 wt.%, a hydrolysis temperature of 44 °C, a hydrolysis time of 130 min, and a sonication time of 30 min. Experimentally, however, the optimized conditions resulted in a CNC yield of only 30%. More recently, Zou et al. (2012) used a three-factor, three-level orthogonal design to study the same process and reported experimental yields in excess of 82% and optimum reaction conditions of 33 wt.% for the acid concentration, 43 °C for the hydrolysis temperature, and 108 min for the hydrolysis time. Fan and Li (2012) used the same approach to determine the optimum reaction conditions for the preparation of CNCs from cotton pulp fibers by sulfuric acid hydrolysis. They reported a maximum experimental yield of 64% at an acid concentration of 64 wt.%, a hydrolysis temperature of 50 °C, and a hydrolysis time of 5 h. Tang et al. (2011) used a Box–Behnken experimental design to optimize the preparation of CNCs from MCC with cation exchange resin in an ultrasonic reactor. The predicted optimum reaction conditions, i.e., a resin-to-MCC ratio of 10 (w/w), a hydrolysis temperature of 48 °C, and a hydrolysis time of 189 min, resulted in an experimental yield of 50%. Lu et al. (2013) used the same approach to optimize the preparation of CNCs from filter paper by ultrasonic wave and microwave-assisted sulfuric acid hydrolysis. They reported an experimental yield of 86% at optimum reaction conditions, i.e., a hydrolysis temperature of 70 °C, a sulfuric acid concentration of 53%, and a hydrolysis time of 1.5 h. Wang et al. (2012) used a Box–Wilson central composite design (CCD) to optimize the hydrolysis of bleached kraft eucalyptus pulp for minimal cellulose loss. The obtained model predicted a maximum CNC yield of 64% at a sulfuric acid concentration of 60 wt.% and a hydrolysis temperature of 58 °C. The influence of hydrolysis time on CNC yield was not discussed in detail and the highest experimental yield reported was 60%. More recently, the team reported experimental yields in excess of 70% at acid concentrations of 58 and 62 wt.% and hydrolysis temperatures of 56 and 50 °C, respectively (Wang et al., 2014; Chen et al., 2015). The experimental CNC yields were in good agreement with yields predicted by a kinetic model, which revealed a complex dependency of CNC yield on acid concentration, hydrolysis temperature, and hydrolysis time.

In this study, we use a three-factor, rotatable CCD to analyze the production of CNCs from softwood sulfite pulp by sulfuric acid hydrolysis and, specifically, to elucidate the relationships between the sulfuric acid concentration, hydrolysis temperature, hydrolysis time and CNC yield. The CCD has been developed in the vein of RSM, building on initial screening results from related studies to establish a design space and integrating subsequent experimentation for process optimization (Vining, 2011). In light of the sequential nature of RSM, this initial study encompasses a broad design space and its objectives are to 1) identify significant factors and factor interactions and 2) delineate a narrowed design space for subsequent experimentation. Because of its technological importance, the sulfate group density is included in this study as a second response variable.

2. Materials and methods

2.1. Materials

Cellulose, in the form of dissolving-grade softwood sulfite pulp (Temalfa 93), was provided by Tembec, Inc. Sulfuric acid (96.4%, certified ACS plus), sodium chloride (ACS certified), and sodium hydroxide (0.02 N, certified) were purchased from Fisher Scientific. The water used in the experiments was deionized (DI) water from a Millipore Direct-Q 5 ultrapure water system with 18.2 MΩ-cm resistivity at 25 °C.

2.2. Methods

2.2.1. Experimental design and data analysis

A three-factor, rotatable CCD with six center runs was generated with JMP statistical data analysis software (SAS Institute Inc., v8.0x). In this experimental design, the factor *a,* defining the radius of the circumscribed sphere, is 1.682. The levels for each factor ($-a$, -1, 0, 1, a) are listed in Table 1 and the design matrix is shown in Table 2. Factor levels were selected on the basis of literature values used for CNC production (Revol et al., 1992; Revol et al., 1994; Revol et al., 1998; Wang et al., 2012). Measured responses (output variables) are the CNC yield and the sulfate group density. Experiments were conducted in randomized order, generated by the software.

It is important to note in Table 1 that the $-a$ level of the hydrolysis time (x_3), called for in Run 7 (Table 2), corresponds to a negative hydrolysis time that is experimentally not feasible. The goal of this CCD experiment is to minimize variable limitations and encompass the largest possible design space, enabling further optimization through subsequent experimentation around a smaller, refined design space. To this end, the hydrolysis times of 30 and 180 min were maintained as the -1 and 1 levels respectively, and only one run is impacted by the infeasible $-a$ level. Model analysis in subsequent sections accounts for the discrepancy.

Response values were analyzed using the least squares method to fit the data to Eq. (1).

$$y = \beta_0 + \sum_{i=1}^{n} \beta_i x_i + \sum_{i=1}^{n} \beta_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \beta_{ij} x_i x_j + \varepsilon \quad (1)$$