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Optimization of cellulose phosphate synthesis from oil palm lignocellulosics using wavelet neural networks

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ABSTRACT

Cellulose phosphate was synthesized from microcrystalline cellulose derived from oil palm lignocellulosics via the $H_3PO_4/P_2O_5/Et_3PO_4$/hexanol method. The influence of process variables (*viz.* temperature, reaction time, and the H_3PO_4/Et_3PO_4 ratio) on the properties of the resulting cellulose phosphate was investigated using a wavelet neural network model with the goals of ascertaining which factors were critical and of determining optimized reaction parameters for this synthesis. The experimental results corroborated the good fit of the wavelet neural network model. The prediction errors were quite small (less than 7%), and the regression values (R^2 greater than 0.99) were also satisfactory.

1. Introduction

The goals of chemical process optimization are to obtain a solid understanding of how to maximize the efficiency and economics of the process while maximizing the throughput and quality and minimizing the energy and chemical consumption. Optimization problems can be viewed as multivariate interpolations in which the underlying relationships between the operational variables and the process outputs are derived, producing a model that offers a reliable approximation of the process response when experimental data are input into the model.

A number of designs have been developed to establish an accurate mathematical model to determine the intrinsic interactions between the governing operating conditions and the process response, and these designs can be categorized into two primary approaches: (i) theoretical/parametric models that require a highly detailed understanding of the fundamental process mechanism and (ii) empirical/nonparametric models that are derived from observations instead of fundamental theory (Khayet et al., 2011).

Artificial neural networks (ANNs), being one of the most popular types of empirical models, possess the unique attention-grabbing ability of self-learning. These methods use simple computational operations to solve highly complex nonlinear problems, enabling successful implementation in optimization problems (Haykin, 1999; Johan and Ibrahim, 2012; Zainuddin et al., 2011). ANNs are particularly useful when a priori knowledge on the exact mathematical expression of the process under investigation is unavailable. A more remarkable characteristic of ANNs is that the variables can be kept in strict conformity with the dynamic experimental environment despite changes to the physical process. ANNs can be continuously updated with new data, which is a significant advantage over theoretical models that require new rules or new assumptions to be introduced when the process under study is altered.

The integration of wavelet decomposition with ANNs yielded the wavelet neural network (WNN) model (Zhang and Benveniste, 1992). This method has been found to be superior for alleviating the deficiencies of conventional multilayer perceptrons, which (i) have difficulties converging when significant nonlinearities exist, (ii) tend to become trapped in local minima in a complex search space, and (iii) require large amounts of time for training. The WNN model has been proven to be reliable and generally applicable in diverse fields (Amina et al., 2012; Chen, 2011; Zainuddin and Ong, 2011a,b; Zainuddin et al., 2011; Zhang and Benveniste, 1992), and the list of applications is still growing. The present study focused on employing WNNs in the phosphorylation of cellulose, where the main concerns are predicting the characteristics of the resulting cellulose phosphate and identifying the optimal operational conditions for the phosphorylation process. While WNNs have been proven useful in various real-world problems, they have not yet been utilized in this context.

Cellulose phosphate, a new form of cellulose derivative that is produced from the substitution of free hydroxyl groups on a cellulose backbone with phosphate functional groups, has received

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renewed research interest due to its swelling ability and the renewable nature of the raw material (Wanrosli et al., 2011a,b). Cellulose phosphate was first formulated as a flame retardant additive for textiles due to its inherent flame resistance (Reid and Mazzeno, 1949). Since then, the number of applications for this material has increased. Due to its excellent ion exchange properties, cellulose phosphate has been used extensively for the separation of trace metals (Li et al., 2002; Rocha et al., 1997). Its biocompatibility and bioactivity have also generated substantial attention for the potential applications of cellulose phosphate in biomedical research. The ion exchange ability of phosphorylated cellulose and its strong affinity for divalent cations means that it can inhibit the absorption of dietary calcium, which is beneficial for kidney stone treatment (Pak et al., 1971). While cellulose is not capable of osteoinduction, the phosphorylation of cellulose can promote the ingrowth of calcium phosphate, giving it great promise as an implantable orthopedic biomaterial (Fricain et al., 2002; Granja et al., 2001a,b). Incorporation of phosphorylated cellulose in hemodialysis membranes can prohibit the activation of detrimental blood proteins in hemodialysis (Suflet et al., 2006).

The feedstock for cellulose phosphate synthesis is purified fluffy cellulose extracted by deconstructing refined wood pulp. However, the devastation of indigenous forests and woodlands to facilitate urban use of the area, industrialization, and commercial logging has created pressure on these sources of lignocellulose. Nonwoody cellulosic raw materials are favored due to their abundance, inexpensiveness, and ready accessibility (they are widely available in agricultural residues). Malaysia is the world's second largest producer of palm oil, generating more than 77 million tons of biomass annually, including fronds, trunks, oil palm empty fruit bunches (OPEFB), kernel shells, and mesocarp fibers (Ng et al., 2011). The massive amount of OPEFB (6.93 million tons on a dry weight basis in 2009) and its high cellulose content of 60.6% (Wanrosli et al., 2004) suggest the viability of converting these renewable oil palm lignocellulosics into value-added products, particularly cellulose phosphate, and this possibility has been assessed (Wanrosli et al., 2011a,b).

The present study will focus on simulating the synthesis of cellulose phosphate from OPEFB using WNNs. The two objectives of the study are (i) to construct a predictive model based on WNNs to identify the phosphorylation process parameters (*viz.* temperature, reaction time, and the H_3PO_4/Et_3PO_4 ratio) that influence the properties of the resulting cellulose phosphate from OPEFB (*viz.* phosphorus content, yield, and swelling capacity) and (ii) to maximize the performance of cellulose phosphate synthesis using WNNs.

2. Materials and methods

2.1. Preparation of oil palm empty fruit bunch microcrystalline cellulose

OPEFB cellulose was prepared using water prehydrolysis prior to a soda-anthraquinone pulping process, as described by Wan Rosli et al. (2003) and Leh et al. (2008). The unbleached pulp underwent an environmentally benign totally chlorine-free (TCF) bleaching process based on the OZP sequence (Oxygen–Ozone–Peroxide), yielding pulp with a kappa number of 1.4.

The bleached pulp was then acid hydrolyzed with dilute 2.5 M HCl, with the solid-to-liquor ratio controlled at 1:20, and refluxed at $105 \pm 2\,^{\circ}C$ for 15 min. Following hydrolysis, the pulp was washed well with distilled water and air-dried. The sample was ground by a ball mill to produce oil palm empty fruit bunch microcrystalline cellulose (OPEFB-MCC) in powder form and stored in a desiccator over phosphorous pentoxide before use in subsequent experiments.

2.2. Synthesis of oil palm empty fruit bunch cellulose phosphate

Phosphorylated cellulose was synthesized according to the method described by Granja et al. (2001b) because this technique is able to eliminate any biologically hazardous compounds, which is crucial if this cellulose derivative is to be used as a biomaterial. Powdered OPEFB-MCC (4.0 g) was successively swollen for 24 h each in distilled water, ethanol, and hexanol to activate the cellulose surface. The reaction of cellulose with phosphorus acid was carried out in a four-neck round-bottom flask equipped with a nitrogen inlet, condenser, thermometer, and mechanical stirrer. Following the dispersion of the OPEFB-MCC in 29 mL of 1-hexanol, a solution of 50 g of phosphorous pentoxide in 37 mL of triethylphosphate and 42 mL of 85% phosphoric acid was gradually added to the suspension. The phosphorylation reaction was allowed to proceed under constant stirring and in a nitrogen atmosphere for various reaction times and temperatures, in accordance with the design matrix shown in Table 1. The obtained oil palm empty fruit bunch cellulose phosphate (OPEFB-CP) was then rinsed thoroughly with hexanol and ethanol to remove excessive reagents and air-dried at room temperature. The OPEFB-CP was kept in a desiccator over phosphorous pentoxide before analysis.

2.3. Determination of the phosphorus content

The phosphorus content was quantified according to the Kjeldahl digestion procedure. The sample was left in a concentrated sulfuric–nitric acid mixture until it was fully digested, and subsequently analyzed using the ascorbic acid colorimetric method (Csuros, 1997). In the colorimetric analysis, the ammonium molybdate and antimony potassium tartrate were reacted in an acid medium with a dilute solution of phosphorous to form an antimony–phosphomolybdate complex. The reaction of the converted phosphorous in phosphomolybdate form with ascorbic acid resulted in the formation of a blue complex that was proportional to the phosphorous concentration, and the concentration of this blue complex could be determined by spectrophotometry at 760 nm.

2.4. Determination of the swelling capacity

The samples were soaked in water in polyethylene centrifuge tubes for 30 min, followed by centrifugation at 5000 rpm for 15 min. The sample weights were measured before and after the removal of the excess water. The swelling capacity was thus defined as the difference in weight before and after swelling, which is given by:

$$\text{Swelling capacity}\,(\%) = \frac{w_i - w_0}{w_0} \times 100\%, \quad (1)$$

where w_i and w_0 are the weights of the dry and swollen samples, respectively.

2.5. Wavelet neural network modeling

WNNs have more compact topologies than other ANNs and fast learning speeds because they consist of localized wavelet activation functions. Thus, WNNs have been applied in various research areas to improve the generalization capability and reduce the complexity of the modeling approach (Zhang and Benveniste, 1992). In this work, the relationships between the operational variables and the properties of the resulting OPEFB-CP will be investigated using the WNN model, such that the variability of the OPEFB-CP characteristics can be defined as the nonlinear mapping between