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Optimization of cellulose nanofibrils carbon aerogel fabrication using response surface methodology

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ABSTRACT

This research investigated the simultaneous effects of processing parameters in the making of carbon aerogel from cellulose nanofibrils (NFC). Variables such as peak temperature and heating rate at different levels were systematically investigated with the goal of parameter optimization using response surface methodology (RSM). A face-centered central composite design (CCF) was used to evaluate the feasible range of process conditions where the levels of peak temperature and heating rate were varied at levels ranging from 230 °C to 320 °C. Results indicated that the quadratic model developed for the response surface was adequate for the prediction of optimal parameters. Response surface predictions were developed to explore the integrated and feasible operating space. Optimum conditions were: 300 °C peak temperature and a heating rate of 8.00 °C/min. The carbon aerogel achieved approximately 90.10 g/g of the normalized oil absorption capacity despite a weight reduction percentage of 82%.

1. Introduction

Oil recovery from oil spills using absorbent materials has recently attracted extensive scientific and practical interest. Among numerous materials, absorbents from natural precursors are of the most interest. Despite the fact that conventional nature absorbent materials are widely used for large-scale oil spill cleanup, the hydrophilic nature of these materials drastically hampers the oil absorption efficiency. As a result, new absorption materials with hydrophobic properties are of great interest. Examples include carbon foams, graphene aerogel, carbon nanotube aerogel, carbon fiber aerogel, and carbon microbelts aerogel [1–7].

Nanocellulose is a promising new material not only because it is a bio-based, sustainable, nontoxic, abundant, and renewable resource; but it also has unique intrinsic properties [8–11]. In particular, cellulose nanofibrils (NFC) consists of long, flexible fibers cleaved from the hierarchy of plant or wood cellulose by mechanical processes [12–14]. Among these superior properties, thermal stability is of great interest [15]. Since the development of the carbon structures from this potential green alternative, numerous promising applications are in development, ranging from electrochemical energy storage, hydrogen storage, to super capacitors, etc. [16–18]. The mechanism and the structure–properties relationships of carbonaceous material have been studied [19–21]. For cellulose material, the carbonization is mainly dominated by two reactions including degradation and depolymerization [22]. In addition, heating temperature, and heating rate during carbonation have been

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demonstrated as key factors that influence the mechanical properties [23]. However, the effect of these two parameters on the porous and adsorption properties is limited. Our previous study successfully developed a super-light, hydrophobic carbon aerogel with highly oil absorption properties using microfibril cellulose as the raw material [24]. We demonstrated a green synthesis approach involves freeze-drying and carbonization process to achieve 3D porous network structure and hydrophobic properties. In addition, in order to achieve maximum oil absorption capacity and increase the final carbon yield, research attention is focused on two factors: 'peak temperature' and 'heating rate' during carbonization.

There are some disadvantages of studying the influence of the factor on the response one-factor at a time, e.g., it is time consuming involving many experiments and does not allow for the examination of interaction effects. Design of experiments (DOE) is a tool that allows for parameter optimization, especially in cases where many factors are involved and varied simultaneously. Among the different methods of experimental design, Response Surface Methodology (RSM) is an effective statistical modeling tool. It can be used in studies including biochemical systems, biotechnology, nanotechnology, etc. [25]. RSM allows for: expanded inference; the study of interactions; and parameter optimization. RSM is considered a formal experimental design technique that maximizes inference while minimizing the number of experimental runs.

The research focus of this study was to estimate the effect of key factors on the response of oil absorption and weight reduction, and to determine the optimal values for processing carbon aerogel. This approach quantified the relationship between NFC aerogel carbonization processing conditions and carbon aerogel's physical properties. The RSM used two variables, 'peak temperature' and 'heating rate' on the oil absorption capacity and final weight reduction of carbon aerogel. In addition, physical properties, internal morphology, and thermal properties of carbon aerogel were investigated.

2. Materials and methods

2.1. Material

Cellulose nanofibrils with a solid content of 5% were obtained from commercial sources (University of Maine, USA). Cross-linker Kymene™ resin was commercially available (Ashland Hercules Inc., USA).

2.2. Preparation of NFC aerogel and carbon aerogel

NFC suspension with concentration of 1.5 wt% and cross linker resin (5 wt% of dry NFC) was mixed and poured into open-ended copper pipes (1.50 in. in length and 0.81 in. in diameter) and sealed with aluminum foil. The samples were then placed into liquid nitrogen for one minute for rapidly freezing, following which the aluminum foil was removed and the samples were freeze-dried in a vacuum lyophilizer (Labconco, Inc., Kansas City, MO) at −51 °C for three days. Ultralight sponge-like aerogel was obtained. Samples were oven-heated at 120 °C for 3 h to promote cross-linking in order to form a three-dimensional network. Carbonized on NFC aerogel was carried out under flowing nitrogen (20 ml/min) using a tube furnace (Thermo Scientific) by heating the sample from room temperature to 180 °C with a heating rate of 10 °C/min, followed by increasing the temperature from 180 to 230 °C at a rate of 5 °C/min, and increasing the temperature from 230 to 320 °C at different heating rates ranging from 0.20 to 5 °C/min. Finally, samples were further heat treated by increasing the temperature from 320 °C to peak temperatures of 400 °C, 700 °C and 1000 °C respectively at a rate of 5 °C/min in nitrogen and holding for 15 min. Samples were then cooled to room temperature.

2.3. Oil sorption experiments

Oil absorption experiments were carried out using paraffin oil (BP PLC gas station). Carbon aerogel sponges were weighed first and immersed into oil. After the immersion, the sponge was taken out, drained for 30 s to wipe away the excess oil, and immediately transferred to a tarred pan. Sample was measured by weight and this process was repeated until carbon aerogels reached sorption saturation. The oil absorption capacity could be defined as the ratio between the weight of absorbed carbon aerogel and the weight of dried carbon aerogel.

2.4. Structure characterization of NFC aerogel and carbon aerogel

The inner structures of NFC aerogel and carbon aerogel were imaged using scanning electron microscopy (SEM, Zeiss Auriga SEM/FIB crossbeam workstation). NFC aerogel was coated with a thin layer of gold to provide conductivity and to protect the sample from electron beam damage. The ultrastructure of the carbon aerogel was characterized by transmission electron microscopy (TEM, Zeiss Libra 200 MC). Carbonized aerogel was ground into powder and dispersed into distilled water. TEM samples were prepared by depositing suspension drops (0.001% w/v in water) on amorphous lacey carbon-coated electron microscope grids and were then allowed to dry. The TEM was operated at a 200 kV accelerating voltage. Thermal stability and carbonization yield were determined using thermogravimetric analyzers (TGA; Perkin–Elmer 7 series; Perkin–Elmer Cetus Instruments, Norwalk, CT). The heating program was set up exactly the same to mimic the carbonization process.