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Autohydrolysis processing as an alternative to enhance cellulose solubility and preparation of its regenerated bio-based materials

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HIGHLIGHTS

- Autohydrolysis temperature is negatively correlated to cellulose molecular weight.
- Cellulose solubility and viscosity are improved after cellulose pretreatment.
- Autohydrolysis improved the properties of regenerated cellulose materials.

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ABSTRACT

Kenaf core pulp has been successfully autohydrolysed using an autoclave heated in oil bath at various reaction temperature at 100, 120 and 140 °C. Membranes, hydrogels and aerogels were then prepared from autohydrolysed kenaf in urea/alkaline medium by casting on the glass plate, by using epichlorohydrin (ECH) as cross-linker via stirring and freeze-drying method, respectively. The autohydrolysis process reduced the molecular weight of cellulose and enhanced cellulose solubility and viscosity. Structure and properties of the regenerated products were measured with Field emission scanning electron microscope (FESEM), X-ray diffraction (XRD), Ultraviolet–visible (UV–Vis) spectrophotometer and swelling testing. As the autohydrolysis temperature increased, the porosity of cellulose membranes (as seen from the morphology) increased. The autohydrolysis process improved the swelling porperties and transparency of regenerated cellulose hydrogels. This finding is expected to be useful in reducing molecular weight of cellulose in order to produce regenerated bio-based cellulose materials.

1. Introduction

Lignocellulosic biomass material is cheap, abundant and renewable feedstock applicable for biochemical and biofuel production. The lignocellulosic biomass material attracts a lot of attention as sustainable and renewable energy source due to it is a non-edible part of the plant [1]. Cellulose, hemicelluloses and lignin are the three main components consist in plant cell wall from the agro based materials [2]. Cellulose is an organic polymer with natural production at approximately 1.5×10^{12} tons in a year and it is increasing from time to time due to the higher demand on environmentally friendly and biocompatible products [3]. Nowadays, the cellulose is processed massively in industry to the regenerated material (such as films, sponges, food casings, fibers, membranes, paper and so forth) and cellulose derivatives (which include ether and ester) [4].

Cellulose can be obtained from various kinds of natural resources such as kenaf. Kenaf is known as Hibiscus cannabinus L. (Malvacae) plant and consists of 45–57 wt% cellulose, 21.5 wt% hemicellulose, 8–13 wt% lignin, and 3–5 wt% pectin [5]. The properties of kenaf fiber is comparable with wood fibers in producing textiles, paper, pressed wood materials and so on [6]. However, the specific structure in cellulose tends to arrange the polymer chains into tightly pack and highly crystalline structure which is water insoluble and resistant to depolymerisation [7]. Water molecules are able to penetrate into cellulose structure and

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swell the fibers but it cannot dissolve the cellulose [8]. It can be concluded that cellulose is hardly dissolved in common solvent due to its high molecular weight, high degree of crystallinity and the presence of strong inter- and intra-hydrogen bonding between hydroxyl groups in the fibril of cellulose [9]. Therefore, the pretreatment on cellulose is required to reduce the molecular weight of cellulose, interrupt the hydrogen bonding present among cellulose chains and dislocate the crystalline structure of cellulose.

Autohydrolysis is a process that involves treatment with hot water under elevated temperatures and high pressures to maintain its liquid form [10]. It is a type of pretreatment on lignocellulosic materials which is water only media and chemical-free. This has offered a low-cost, simple, limited equipment corrosion problems and environmental friendly pretreatment technology [11,12] especially carry out in sealed autoclave that provides a more homogeneous reaction [13]. There are several reports have investigated autohydrolysis pretreatment on a diversity of lignocellulosic materials. Lee, Shi, Venditti and Jameel [11] reported on autohydrolysis pretreatment on Coastal Bermuda Grass to enhance the enzyme hydrolysis, whereas Garrote, Domi and Parajo [14] investigated the kinetic assessment of autohydrolysis on corncobs which can be used subjected for the production of xylooligosaccharides. Generally, the autohydrolysis (the water and feedstock are the only reagents) results in selective hemicelluloses solubilisation, producing the liquors containing sugar oligomers, sugars, sugar-decomposition products and to a solid phase enriched in lignin and cellulose, which can be used for further processing [14]. However, the investigation and further utilization on cellulose (solid fraction) obtained from autohydrolysis process were limited.

The severity of autohydrolysis pretreatment differs in a broad range of temperatures (130–230 °C) [11]. In addition, Chen, Lawoko and Heiningen [15] determined the intrinsic kinetics of hemicellulose dissolution in autohydrolysis using continuous mixed flow reactor. Furthermore, Pu, Treasure, Gonzalez, Venditti and Jameel [16] studied on autohydrolysis pretreatment on mixed hardwoods in which the sugar of the extracted liquid was analyzed and the woody residuals can be converted into fuel, or paper etc. The autohydrolysis is normally used to extract hemicelluloses from wood before the pulping process for the preparation of co-products such as acetic acid and ethanol besides pulp [15]. Recently, the autohydrolysis process has been used to get rid of the hemicelluloses from wood after pulping process and bleaching the cellulose pulp with a high purity in cellulose.

There are limited literature reported about effect of autohydrolysis on cellulose (solid fraction) solubility in cellulose solvent and properties of its regenerated bio-materials. Most of the literature discussed on the conversion of lignocellulosic materials into fermentable sugars (liquid fraction) that were usually obtained from different type of hydrolysis such as physical pretreatment, physico-chemical treatment, chemical treatment or enzymatic hydrolysis. The reasons of the applied pretreatment are reducing cellulose crystallinity, removing hemicellulose and lignin, and increasing the porosity of the fibers [17]. Hence, in this study, we focus on effect of autohydrolysis temperature on cellulose to reduce the viscosity average molecular weight (Mv) and degree of polymerization (DP) of cellulose instead of lignocellulosic materials and liquid fraction that usually consists of fermentable sugars. This is to improve the solubility of cellulose in the urea-alkaline solvent with lower reaction temperature in order to prepare its regenerated cellulose materials. The crystallinity index, morphology, transparency and swelling properties of the regenerated cellulose biomaterials prepared from the cellulose solution are also investigated.

2. Experimental

2.1. Materials

Raw kenaf core in this study was taken from the Malaysian Agricultural Research and Development Institute (MARDI). The lithium hydroxide monohydrate ($LiOH \cdot H_2O$) (98%), sulphuric acid (H_2SO_4) (98.8%) and epichlorohydrin (ECH) were purchased from Sigma Aldrich. The sodium chlorite (80%) was obtained from Acros Organics. The urea and analytical grade sodium hydroxide were obtained from R & M Chemicals. All the chemicals were used without further purification. The raw kenaf core was undergone soda pulping in Forest Research Institute Malaysia (FRIM) using digester with 25% NaOH for 2 h and 30 min at 170 °C. The bleaching process of kenaf core pulp involved four stages (D-E-E-D) of bleaching which has been described in our previous work [18]. The scheme of pulping and bleaching process was described in Fig. 1.

2.2. Autohydrolysis process

The autohydrolysis on cellulose was prepared using autoclave and oil bath. The bleached KCP was mixed with distilled water and stirred in room temperature for 30 min to produce a well dispersed cellulose solution. The cellulose solution was then filled into the autoclave and was closed tightly before immersed into oil bath. The reaction time for this study is fixed at 3 h whereas the temperatures are applied as following: 100 °C, 120 °C and 140 °C. Whenever the reaction time reached, the autoclaves were taken out from oil bath and immersed in a water bath to stop the reaction immediately. The autohydrolysis kenaf (AK) sample was solid fraction from the autohydrolysis treatment and the weight of solid fraction samples recovered was in the range of 83 wt% to 92 wt%. The AK sample was washed with distilled water several times with the aid of vortex shaker. Follow by centrifugation process to get rid of the excess chemical on the sample. The AK samples were dried in a vacuum oven at 80 °C for 12 h and stored in a dried place. These synthesized AK samples are labelled as AK100, AK120, and AK140.

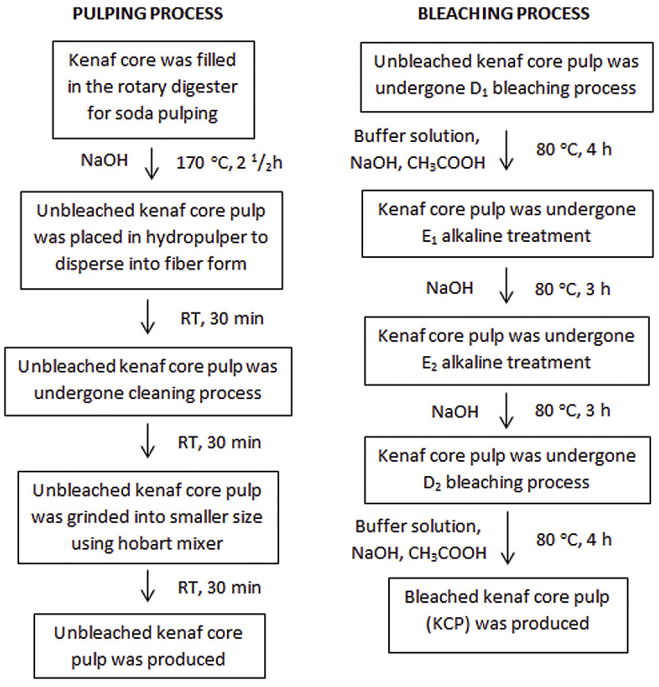

Fig. 1. Scheme of pulping process and bleaching process.