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Alkaline Hydrolysis of Waste Nitrocellulose for Recovery of Pure Cellulose

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Abstract: Due to wide usage of nitrocellulose in civilian and non-domestic industries, massive amount of waste residues is generated. The waste has to be treated with an environmental friendly process. Historically, methods for decomposition of waste materials have been open burning or open explosion may not be suitable or safe disposal. Alkaline hydrolysis of nitrocellulose seems to be a simple and inexpensive method for cleavage of its structure to non-energetic materials that can be directly disposed or further biologically deteriorated. Furthermore having a valuable product is desired for making the process to be profitable. In this work, a simple method for alkaline decomposition of waste nitrocellulose to cellulose was used. The effect of sodium hydroxide solution and temperature on decomposition of nitrocellulose was investigated. In such circumstances the optimum conditions that achieved were 1.5 M sodium hydroxide, at 55°C. The identification and characterization of product was carried out by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscope (SEM). The obtain results showed that hydrolysis occurred and the product was completely denitrified and its characterization compatible and similar to pure cellulose.

Key words: Nitrocellulose · Alkaline hydrolysis · Cellulose · Fourier Transform Infrared Spectroscopy · Scanning Electron Microscope

INTRODUCTION

Nitrocellulose is a polymer; which is a nitrated cellulose ester; the chemical structure is shown in Figure 1. Physical, chemical characterizations and industrial application of nitrocellulose is strongly depended on its nitrogen content. Theoretically, the maximum nitrogen content of nitrated cellulose is estimated to be, 14.1%; the fully nitrated nitrocellulose is attained by nitration of all alcohol hydroxyl groups per dehydrated glucose monomer [1, 2]. Low nitrogen content of nitrocellulose is widely used in variety of industries such as pharmaceuticals, varnishes, ink bases, adhesives, artificial leather and printing purposes. In contrary, the high nitrogen content of nitrocellulose (more than 12.5 wt%) may be used as explosives and ammunitions [1, 3].

Aged nitrocellulose is not appropriate for the stated industrial applications because of its nitrogen content reduced under stored conditions [1]. Due to wide application of nitrocellulose in civilian and non domestic industries, immense amount of waste residues and aged nitrocellulose fines have to be treated with an environmentally suitable process. For the removal of waste nitrocellulose and aged nitrocellulose fines in

industrial wastewater process, large variety of physicochemical and biological processes has been developed. These physicochemical removal processes include microfiltration, coagulation, sedimentation, air floatation and alkaline or acid hydrolysis [4-9]. It is also well established that nitrocellulose has resisted to direct biodegradation under either aerobic or anaerobic conditions [6, 9-13]. Among the various processes, alkaline hydrolysis is the simple, inexpensive method for the cleavage of nitrocellulose to non-energetic materials that can be directly removed or further treated via biological processes.

Effect of alkalis such as sodium, calcium, ammonium and potassium hydroxides on hydrolysis of nitrocellulose has been investigated. It has been reported that NaOH and KOH at defined concentration have produced comparable levels of hydrolysis of nitrocellulose, while weak alkaline such as $Ca(OH)_2$ and NH_4OH had less hydrolytic effect [1, 4, 14, 15]. The nitrocellulose hydrolysis may occurred in a single step chemical reaction as a result nitrates and nitrites were generated [15]. Figure 2 shows the schematic chemical reactions in two possible routes for the formation of ions from a monomer of the fully nitrated nitrocellulose: (1) nitrate produced in

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Babol, Iran. E-mails: najafpour@nit.ac.ir & najafpour8@yahoo.com.
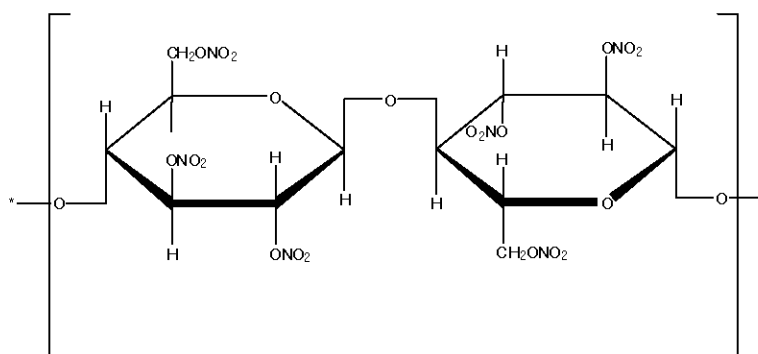
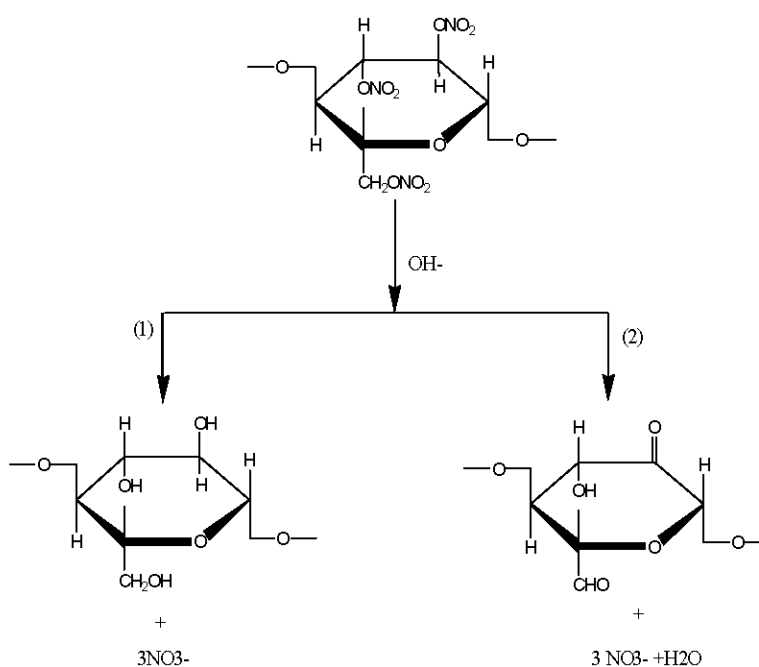Fig. 1: Chemical structure of the fully nitrated Nitrocellulose

Fig. 2: Schematic diagram of possible reactions for alkaline hydrolysis of nitrocellulose from a fully nitrated monomers

a simple ester hydrolysis or (2) formation of carbonyl groups at the substitution site produced nitrite. The nitrated sites on the surface of nitrocellulose fibers have initially been attacked by alkaline ions; resulted destruction of polymeric structure of nitrocellulose. Once the top surface layer of nitrocellulose has been removed, the new one exposed to hydrolytic alkaline ions. The process continued till the entire solid matrix of nitrocellulose is completely hydrolyzed [15].

Extensive research has been conducted on effect of certain variables such as type of bases, concentration of alkaline solution, temperature and reaction time for the hydrolysis [7, 9, 13]. There were no solid procedures available for decomposition of nitrocellulose. An investigation may be required to define a suitable

hydrolysis of nitrocellulose as eco-friendly and economically desired process. Destruction of polymeric material is required for denitrification of nitrocellulose, while pure cellulose is resulted. It has been noticeable that one of the most important products of destruction of nitrocellulose fines is denitrated nitrocellulose that can be classified as pure cellulose. Cellulose is a natural polymer of glucose monomers as widely used as raw material. According to denitrified cellulose properties, it can be further treated by microorganisms for synthesizing biodiesel or it can be further treated as a pure cellulose [16].

The purpose of present research was to investigate alkaline hydrolysis of nitrocellulose. The concentration of alkaline solution and decomposition temperature for

hydrolysis of nitrocellulose was extensively studied. The optimum conditions for hydrolysis of nitrocellulose to produce cellulose were determined. The optimization method for defining the optimum conditions was based on one at the time variable.

MATERIALS AND METHODS

All the chemicals used were supplied by Merck (Darmstadt, Germany). Characterization of raw material as waste nitrocellulose is summarized in Table 1. Waste nitrocellulose was analyzed for chemical composition and the nitrogen content was determined using Ferrous sulfate method. The experiments were carried out in a flask stirred by a magnet using hot-plate magnetic stirrer Model (VELP, SCIENTIFICA, Germany). The flask temperature was controlled by a precision digital thermocouple (VELP, SCIENTIFICA, Germany) and also pH was defined by a pH meter (HANNA instruments, Romania). Experiments were carried out in temperature ranges (25, 45, 55, 65 and 85). These temperatures were chosen based on reported data in literatures which is in the range of 60 to 150°C. It worth to note that the desired product may be decomposed at high temperatures [9, 17]. Sodium hydroxide solutions were prepared with 0.5, 1, 1.5, 2 and 2.5 M and preheated prior to any experimental run. In a typical experiment, approximately 0.1 g of nitrocellulose was introduced into a batch reactor with defined concentration of sodium hydroxide at constant temperature. The concentrations of total nitrogen released were monitored in every 15 min; the reaction time was prolong for duration of 150 min. Nitrogen content measurements were in triplicates with well established standard reagents of sulfanilamide and N-(1-naphthyl) ethylenediamine [18]. When the experiment was over, the solution was neutralized with 40% phosphoric acid solution. The obtained sediments were filtered for the residual cellulose recovery. In order to assure all nitrates were detached from the cellulose fibers, the residue was filtered by nonwoven poly pyrrolidine cloths and then the cloths were washed with distilled water and acetone for

Table 1: Characterization of Waste Nitrocellulose

Color	White
Phase	Solid
Physical appearance	Fine powders
Density	0.2111 (g/cm³)
Water absorbance	26.46%
Nitrogen content	8.330%
Cellulose	91.67%

purification of recovered fibers. The characterization of obtained fibers was determined by Fourier Transform Infrared Spectroscopy (FTIR) and the morphological criteria were investigated with the aid of Scanning Electron Microscope (SEM). The sample was fixed on an aluminum stub and coated with gold-palladium by a polaron machine (EMITECH, model K350, Cambridge, UK) at 3-5 nm coating thickness. Finally, the surface image of the sample was examined under scanning electron microscope by a stereoscan (model VEGA\TESCAN, Czech Republic).

RESULTS AND DISCUSSION

A defined amount of waste nitrocellulose was introduced into a preheated alkaline solution. The waste nitrocellulose was decomposed in 1.5 M NaOH solution at several temperatures, in the range of 25-85°C. The concentrations of total nitrogen released were determined in a time interval of 15 min for the duration of 150 min. The released nitrogen from decomposition of the waste nitrocellulose was measured through the developed standard methods. Typical obtained results from the nitrocellulose hydrolyzates are illustrated in Figure 3. At high temperature, the rate of decomposition of nitrocellulose appeared to be faster than the decomposition at low temperature. This means the decomposition process was increasing trend as temperature increased. At room temperature (25°C) the decomposition reaction was very slow; while the decomposition of nitrocellulose at 55 °C was reasonably resulted high yield. The concentration of liberated nitrogen at 25 and 55°C were 11.2 and 73.6 mg/L, respectively. Even though, at high temperature the reaction was fast but the cleavage of cellulose chain in alkaline condition would be possible. Therefore, experiments were performed at 55°C.

The experiments were carried out at constant temperature (55°C) with variable NaOH concentrations. The obtained results are shown in Figure 4. Nitrocellulose seems to decompose quite fast at high concentration of NaOH. Maximum nitrogen released at 1.5 M NaOH solution. According to linkage of $O-NO_2$, the nitrocellulose structure was attacked by hydroxyl group. Increase in alkaline concentration may activate the sites selected by alkaline ions, a protection layer was formed and the beneath layers of nitrocellulose did not expose to hydroxyl attacked, as a result the released nitrogen decreased. In fact such cases were observed when the solid particle sizes were large and non-uniform.
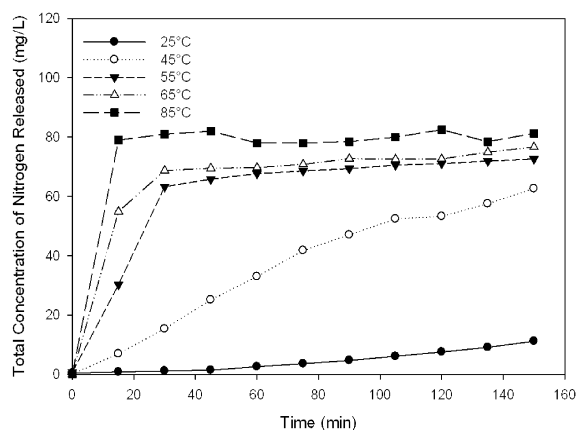
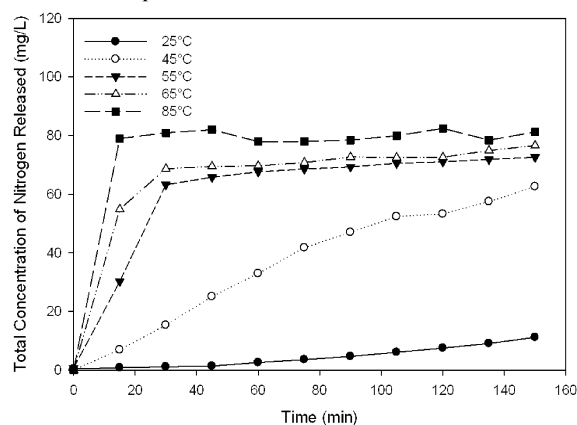Fig. 3: Total Nitrogen released form waste nitrocellulose decomposition at 1.5 M NaOH solution

Fig. 4: Total Nitrogen released during NC decomposition at 55°C and various sodium hydroxide concentrations

Fig. 5: Rate of nitrocellulose hydrolysis in 0.1 M dosage of NaOH

Fig. 6: The rate constant temperature dependency

Table 2: Final amount of cellulose at various experiments

T (°C)	NaOH Solution (M)	Final Cellulose (mg)
25	1.5	5.37
45	1.5	1.20
55	0.5	1.32
55	1.0	1.26
55	1.5	1.16
55	2.0	0.98
55	2.5	0.94
65	1.5	0.63
85	1.5	0.34

The generated masses of cellulose fibers in experimental runs were determined; the results are summarized in Table 2. As the concentration of NaOH increased, nitrocellulose was decomposed to cellulose; then cellulose structure may be affected by the alkaline solution and reduced to glucose monomers. The same phenomena may happen at elevated temperature.
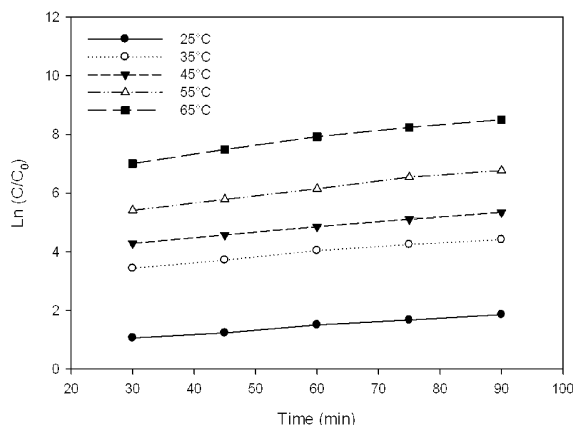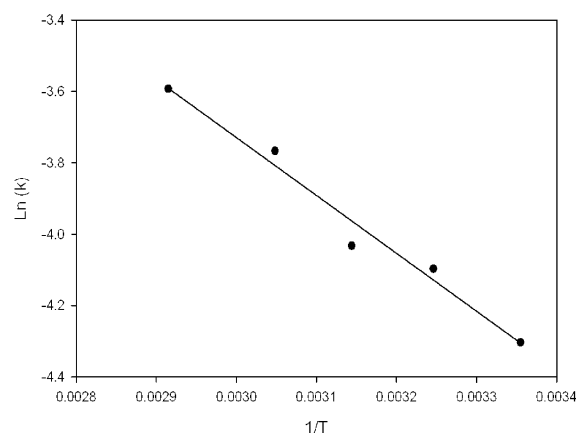
It is apparent that thermal decomposition of cellulose may be more effective than hydrolysis under alkaline conditions. Maximum amount of cellulose was obtained at 25°C. In contrary, at low temperature the reaction was slow; therefore optimum temperature should be defined. The obtained results with respect to temperature were compared with data at 55°C; the data indicated that the most effective parameter on degradation of cellulose was temperature. At fixed temperature (55°C) variation of alkaline concentration had no significant effect on cellulose cleavage. At optimum temperature (55°C) and 1.5 M NaOH, the hydrolysis was faster than other alkaline dosages. Maximum nitrogen was released and reasonable amount of cellulose was obtained.

Kinetic studies for the hydrolysis reaction were conducted to define reaction rate. For the rate studies, all experiments were carried out in 0.1 M NaOH. Low alkaline concentration was selected in order to control reaction rate in long duration (90min). The rate of nitrocellulose hydrolysis was proposed as pseudo-first order chemical
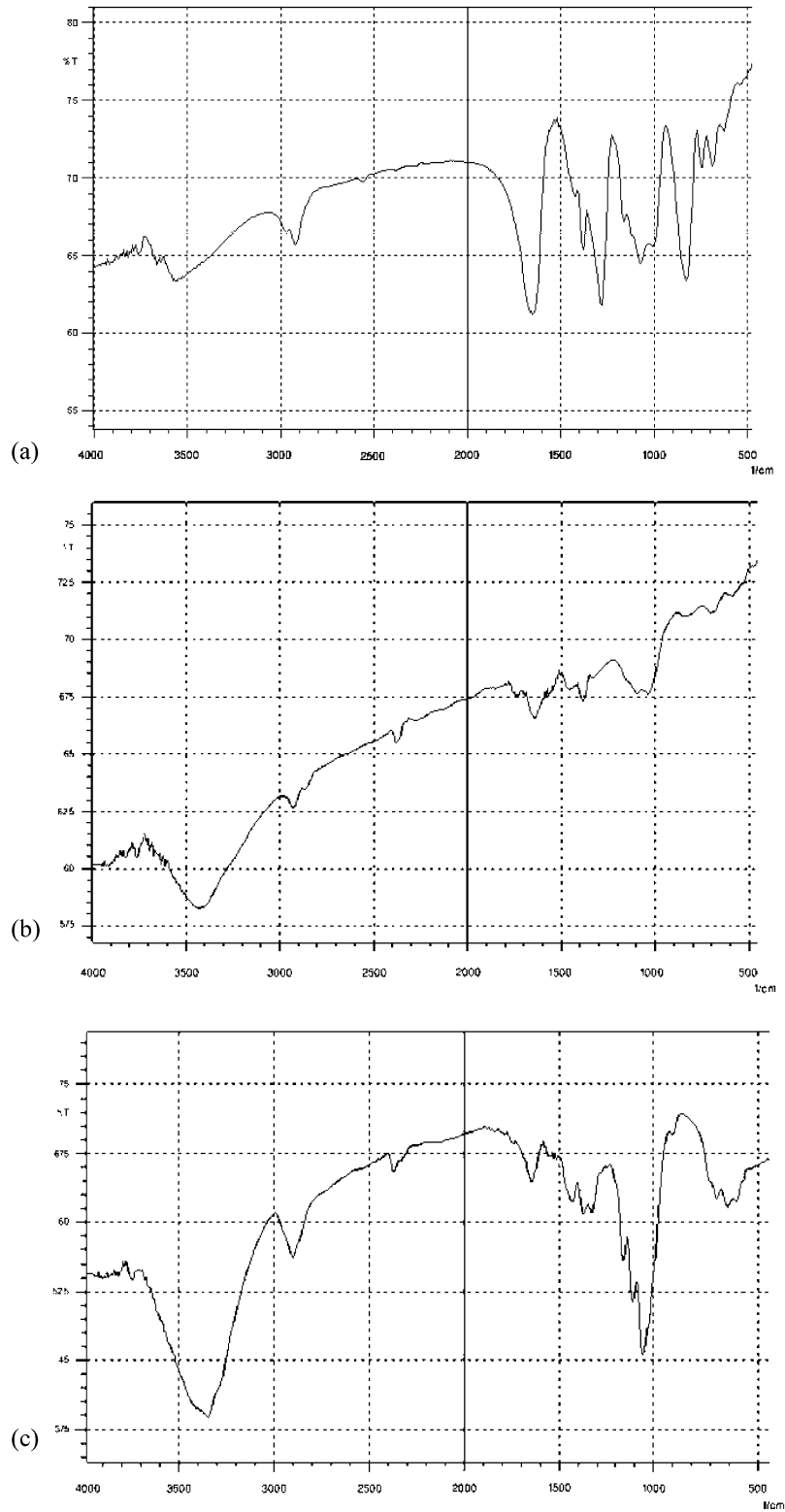
Fig. 7: FTIR spectrum: (a) Parent Nitrocellulose, (b) Final residues, (c) Commercial cellulose

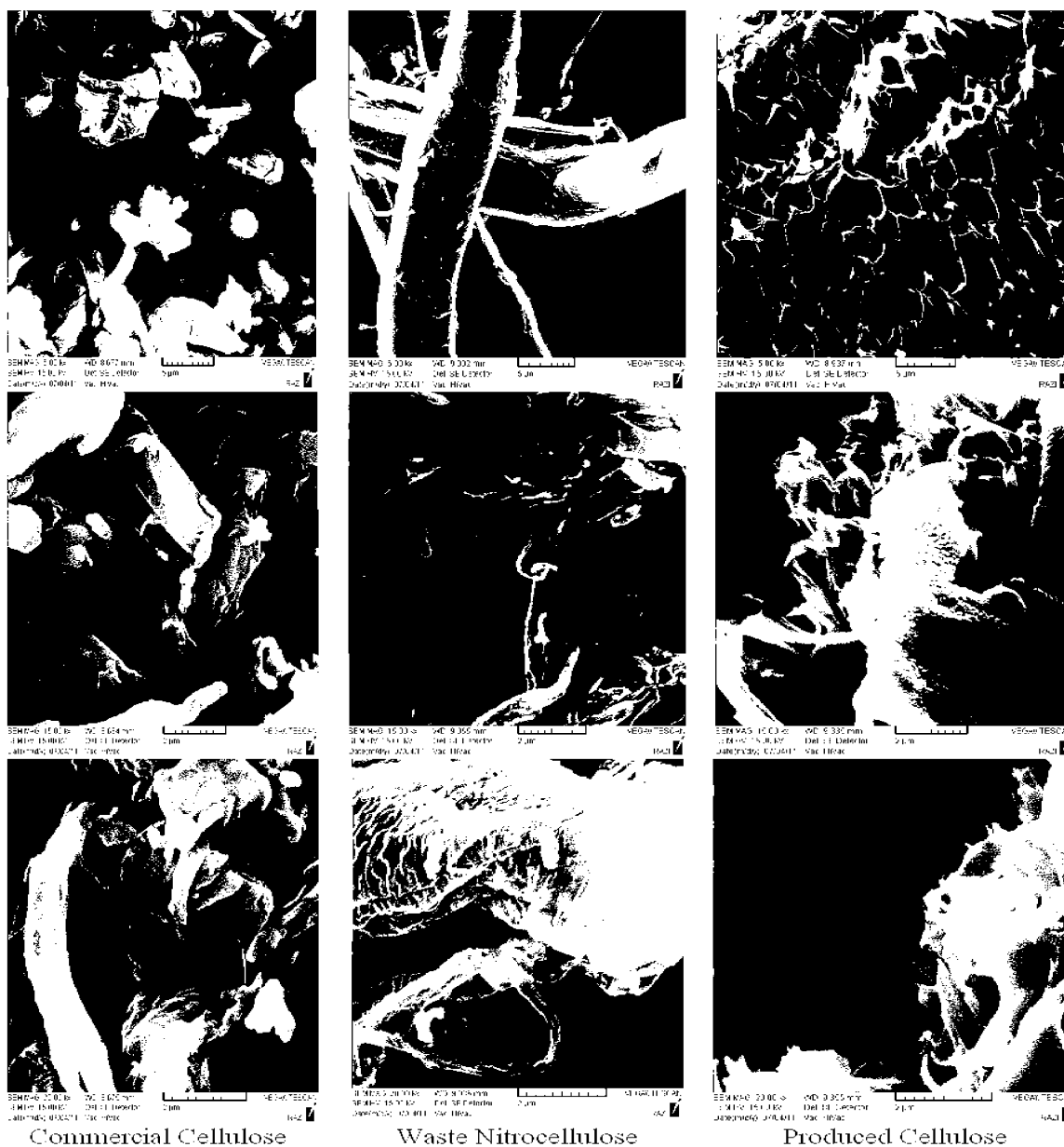Commercial Cellulose   Waste Nitrocellulose   Produced Cellulose

Fig. 8: SEM images of commercial cellulose, waste nitrocellulose and produced cellulose at magnifications of 5kx, 10kx and 20kx

reaction. The rate of nitrogen released is illustrated in Figure 5. The plotted data for all hydrolysis at variable temperatures were straight lines; that has indicated the first-order kinetics and fitted data were reasonably proved the proposed the rate model. The reaction rate constant (k) was calculated based on slope of the best fitted data.

The temperature dependency of the chemical reaction rate was investigated. Figure 6 depicts the value of ln (k) versus (1/T). The slope of the line resulted in a precious value. Base on plotted data Arrhenius law was applied

and activation energy was obtained. The exact value for the activation energy was 13195.8 (J/mol.K). Reaction with high activation energy showed to be very temperature sensitive; that means nitrocellulose was decomposed fast at high temperature as it was temperature dependent [19].

The characteristic of obtained cellulose was compared with parent nitrocellulose and commercial cellulose by Fourier Transform Infrared Spectroscopy (FTIR). The FTIR spectra are shown in Figure 7. The absorption peak of nitrocellulose with two sharp peaks

located between 1390-1300 and 1600-1500 cm^{-1} are assigned to the stretching vibration of nitrite bounds [20]. The FTIR results showed that the waste nitrocellulose was completely denitrated and the new product was nitrite free. The major peak for pure cellulose centered between 3500-3250 cm^{-1} was corresponds to the stretching vibration of OH [20]. Comparing the resulted cellulose product and commercial cellulose, the -OH stretching vibration in the product was shifted to the high region. It was obvious that, there was no considerable difference between final residue's structure and commercial cellulose's; this may prove the purity of the obtained cellulose.

Figure 8 shows SEM images of commercial cellulose, waste nitrocellulose and obtained cellulose product. The SEM images in 3 rows are categorized based on magnification of images in 5, 10 and 20kx, respectively. In the left column, commercial cellulose images are shown with defined morphological strips of fibers. The middle column images are related to waste nitrocellulose; as the surfaces of the image may be slightly extended due to presence of nitrite groups. The right column is allocated to product cellulose. Hollow fibers of product cellulose and reacted nitrocellulose at alkaline condition shows decomposition of nitrocellulose certainly occurred. The unique images of product cellulose were found.

CONCLUSION

A new method for decomposition of waste nitrocellulose with alkaline was developed. Results showed that high temperature may decompose nitrocellulose and degrade cellulose structure. The optimum condition for nitrocellulose decomposition was identified at 55°C, with 1.5 M NaOH. The morphology of parent nitrocellulose, commercial cellulose and product cellulose were compared by SEM images. The final residue was filtered and characterized with the aid of FTIR spectra. The result indicated that the product was relatively pure cellulose. According to enormous variety of cellulose usage, this process is economically desirable for the conversion of waste nitrocellulose to pure cellulose.

ACKNOWLEDGMENT

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