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Xiaodan Shi

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Development of biomass-based cellulose nanowhiskers and its application as catalyst support in converting syngas to biofuels

By

Xiaodan Shi

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Development of biomass-based cellulose nanowhiskers and its application as catalyst support in converting syngas to biofuels

By

Xiaodan Shi

Approved:

Fei Yu
(Major Professor)

Radhakrishan Srinivasn
(Committee Member)

Jun Liao
(Committee Member)

Rajkumar Prabhu
(Graduate Coordinator)

Achille Messac
Dean
Bagley College of Engineering

Name: Xiaodan Shi

Date of Degree: December 14, 2013

Institution: Mississippi State University

Major Field: Biological Engineering

Major Professor: Fei Yu

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Candidate for Degree of Master of Science

The objectives of this research were to develop the best method for cellulose nanowhiskers (CNWs) preparation from raw biomass materials and the feasibility to perform CNWs as Fe^{3+} catalyst support in converting syngas to biofuels.

Raw kenaf bast and switchgrass were initially pretreated with dilute NaOH followed by dilute H_2SO_4. High yields of alpha-cellulose were obtained. Hemicellulose, ash, and most lignin were removed during pretreatment. Preparation of CNWs after pretreatment was then conducted via H_2SO_4 hydrolysis. The most efficient hydrolysis condition was determined as H_2SO_4 concentration through orthogonal experiments.

In contrast with pure cellulose fibers, CNWs supported Fe^{3+} catalyst applied in converting syngas to biofuels showed shorter stabilization time and higher C4+ product selectivity. With the increase of reaction temperature to 310°C, CO and H_2 could reach their peak conversion rates of 83.4% and 72.1%, while the maximum selectivity of CO_2 was 41.1%.

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I would like to thank my major advisor, Dr. Fei Yu for his guidance and support. I would like to give my thanks to Dr. Radhakrishnan Srinivasan and Dr. Jun Liao for their advice and service as committee members. I would also like to specially thank Mr. Eugene P. Columbus for his continuous research support and Dr. Jeremiah Davis for generously offering research materials. Additionally, I would like to thank Mrs. Cathy Aultman from the Department of Animal and Dairy Sciences for her kind help in research analysis. I would like to express my thanks to everyone in the bioenergy group (especially Yongcheng Zhang and Peng Zhou for their assistance).

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TABLE OF CONTENTS

CHAPTER

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

1.1 Lignocellulosic biomass materials

1.1.1 Cotton linters

Cotton today is the most widely planted crop around the world, over 75% of the countries plant cotton (ICAC, 2010). In 2012, over 100 million bales (480-pounds bale) of cotton were produced, and the United States was the third largest producer of 16 million bales (NCC, 2012). Currently, cotton has shared one of the largest fiber consumption markets of 31.7% in the global (ICAC, 2011). The history of cotton cultivation can be traced back to over 7000 years ago (Moulherat et al., 2002). In ancient times, cotton linters were mostly manufactured into textile fabrics, which required loads of labor work due to low productivity. With the rapid development of light industry after World War II, higher added value cotton products have been discovered (Raghavendra et al., 2004); for example, bleached cotton fibers are being used as medical supplies in hospital because of their biodegradability (Ripley, 1997), and fireproof filtering materials to protect people away from high temperature hazards (Carrnthen, 1937).

Cotton linters can be considered as pure cellulose fibers with the composition of 80 ~ 90% cellulose. The rest are composed of 6 ~ 8% of moisture, 4 ~ 6% of hemicellulose, and 1.5 ~ 4% useless extractives (Raghavendra et al., 2004). Compared to other raw biomass materials such as kenaf bast and switchgrass, pretreatment is hardly needed to get rid of hemicellulose, lignin, and other extractives due to the high composition of cellulose.

1.1.2 Kenaf bast

Kenaf (*Hibiscus cannabinus*) is an agricultural crop with close relationship to cotton (Webber III et al., 2002). In the United States, many places have kenaf cultivation industries such as Mississippi, Texas, and California, especially southern states. Annually, the yields of kenaf are 6 to 8 metric tons of bast and core per acre (Kaldor et al., 1990). The advantages of kenaf fibers over other conventional fiber crops include short growing time, easy adaptability to climatic conditions, and relatively low use of herbicides and pesticides (Wang & Ramaswamy, 2003).

The historical role of kenaf was used to produce rope, twine, sackcloth and etc. (Dempsey, 1975), kenaf fibers are now widely used as a source of paper, grass mats, oil-absorbent materials, animal bedding, and textiles (Keshk et al., 2006). Due to the relatively high cellulosic contents in a range from 50 ~ 60%, kenaf bast fibers have been researched with all chemical process to hierarchically prepare cellulose fibers (Shi et al., 2011) as polymeric reinforcement (Edeerozey et al., 2007; Serizawa et al., 2006; Shi et al., 2011); Joonobi et al. (2010) also successfully extracted nanofibers from kenaf core fibers. Kenaf is considered as a commercial crop grown in the United States as well. The price of kenaf maintains at approximately \$0.44 ~ \$0.55/kg (Mohanty et al., 2000). In Europe, the consumption of kenaf fibers in automotive industry increased from 1,100 tons in 1999 to 2,000 tons in 2000 (Bledzki et al., 2002).

1.1.3 Switchgrass

Switchgrass (*Panicum virgatum*) is one of the indigenous crops planted in the Central and North America (Lewandowski et al., 2003) and once was one of the dominated grasses in tall-grass prairie of the United States (Hitchcock, 1971). Due to the high productivity, environmentally friendly benefits, low fertility needs and flexibility for multipurpose uses (McLaughlin et al., 1999), switchgrass was considered as the model of energy crop by the US Department of Energy (McLaughlin, 1992).

As a high cellulosic yield biomass, many previous studies have been conducted in paper and composites industry. Excellent mechanical properties and great potential as a reinforcement component were shown in newsprint paper (Law et al., 2001). Switchgrass was also used as a biomass source for biofuels product (McLaughlin et al., 1999; McLaughlin et al., 1996; Pimentel & Patzek, 2005). Though the applications of switchgrass in paper making or as a reinforcement component seem to be successful, how to produce high value-added product and increase the immature switchgrass market are being focused. Previous researchers have shown that cellulose fibers can be obtained from variety of agricultural byproducts (Reddy & Yang, 2005a; Reddy & Yang, 2005b; Reddy & Yang, 2005c; Reddy & Yang, 2006; Reddy & Yang, 2005d), thus raw switchgrass was applied into natural cellulose fiber product (McLaughlin et al., 2002; Pimentel & Patzek, 2005).

1.2 Pretreatment methods for lignocellulosic biomass

1.2.1 Structure of lignocellulosic biomass

Cellulose is the most abundant organic compound in the world due to the estimation that every year about 7.5×10^{10} tonnes of cellulose are consumed and regenerated (Dickey, 2005). In lignocellulosic biomass, cellulose, hemicellulose, and lignin are three major chemical components existing in plant cell walls (Jørgensen et al., 2007). Cellulose, with the formula $(C_6H_{10}O_5)n$, is the main structure of plant cell walls which consists of D-glucose subunits linked by β-(1,4)-glycosidic bonds (Updegraff, 1969). The repeat linkages of sugar units are linked together by hydrogen and van der Waals bonds to form cellulose chains. Both crystalline and amorphous forms exist in cellulose whereas crystalline cellulose dominates the major portion (Béguin & Aubert, 1994). Hemicellulose is a more complex and branched network based on C5 and C6 carbohydrates. Short lateral chains of monosaccharides such as pentoses (xylose, arabinose), hexoses (mannose, galactose) and sugar acids are the main features that differentiate hemicellulose from cellulose (Kuhad et al., 1997). The role of hemicellulose is to connect cellulose fibers and lignin due to its branched network. Lignin is the most complex, large molecular structure composed by different phenolic compounds in cell walls. The cross-linked amorphous polymer presenting holds together cellulose and hemicellulose, gives support, impermeability to the plant, and defends microbial attack (Pérez et al., 2002).

1.2.2 Pretreatment methods

In order to obtain pure cellulose fibers, variety of methods are introduced to get rid of hemicellulose and lignin. Commonly pretreatment methods can be divided into following categories: mechanical, chemical, combined mechanical and chemical, and etc.

Mechanical pretreatment methods generally refer to milling, ultrasonic, and torrefaction. Milling (chipping or grinding) is often carried out before following steps to make material easy-handling. Ultrasonic pretreatment was investigated at laboratory scale. The results concluded by Imai et al. (2004) and Bochek (2003) showed that the reaction rate of subsequent enzymatic hydrolysis was highly increased by 200%, whereas the energy required was significantly higher than to break down hydrogen bonds.

Alkaline/acid hydrolysis is the most researched chemical pretreatment method. Alkaline hydrolysis is basically a delignification process meanwhile partial of hemicellulose is solubilized as well (Fan et al., 1987; McMillan, 1994). Sodium hydroxide, calcium hydroxide, potassium hydroxide, and ammonia are four main pretreatment bases (Elshafei et al., 1991; Fox et al., 1989; MacDonald et al., 1983; Soto et al., 1994). Alkaline pretreatment can be performed at ambient temperature and pressure conditions whereas consumes hours to days period. In comparison to acid pretreatment, less sugar degradation and recovery of caustic salts are the dominance or alkaline process. However, the drawbacks of alkaline process are obvious: long time performance and high concentration bases are required. For acid pretreatment, concentrated sulfuric acid, hydrochloric acid, and phosphoric acid hydrolysis are widely used to treat lignocellulosic biomass. These powerful agents surely accelerate the pretreatment process, yet the disadvantages are manifest due to high acid concentration: reactors are required to be capable to resist corrosion, experiment hazards, toxic matters, which make the acid pretreatment process much expensive (von Sivers & Zacchi, 1995). Therefore, dilute acid hydrolysis are studied instead. Previous researches show that sulfuric acid at concentration below 4 wt. % has been effectively breaking down hemicellulose to monosaccharides and furfural by achieving high reaction rates (Esteghlalian et al., 1997; Mosier et al., 2005; Root, 1956; Zeitsch, 2000). Though hemicellulosic component can be completely removed by dilute acid hydrolysis, most of lignin remains in plant cell walls and small partial of cellulose is solubilized along with hemicellulose.

Compared with other pretreatment technologies that require expensive equipment, biological pretreatment is a safe and environmentally friendly method with low energy consumption and mild operation conditions (Okano et al., 2005). Brown-, white-, and soft-rot fungi are used as microbes to digest lignin and hemicellulose (Schurz & Ghose, 1978). However, one disadvantage is that the hydrolysis rate by microbes is usually low, up to four ~ five weeks are required for degradation (Cardona & Sánchez, 2007; Hatakka, 1983; Sun & Cheng, 2002; Tengerdy & Szakacs, 2003).

1.3 Cellulose nanowhiskers (CNWs)

Cellulose nanowhiskers have been prepared from both crops and bacterial sources (Eichhorn, 2011). Cotton linters (Roohani et al., 2008), flax bast fibers, hemp fibers, kraft pulp, and rutabaga (Bhatnagar & Sain, 2005)are major crops to obtain CNWs. Methods for cellulose nanowhiskers preparation including an enzyme treatment (Henriksson et al., 2007), an agitation culture system (Tsuchida & Yoshinaga, 1997), a shearing followed by crashing technology (Chakraborty et al., 2005), a grinder treatment (Iwamoto et al., 2005) have been conducted. All these methods to prepare cellulose nanofibers are combinations of chemical, mechanical, and other processes. Cellulose nanofibers have different morphologies because of different preparation methods, such as entangled network (Stelte & Sanadi, 2009), spherical or rod-like nanoparticles (Wang et al., 2008; Yi et al., 2008). Different terminologies have been used to designate rod-like nanofibers: such as nanowhiskers, monocrystals, nanocrystals, etc. (Siqueira et al., 2008). In this research, we use the term of cellulose nanowhiskers (CNWs).

1.4 Cellulose nanowhiskers as catalyst support in converting syngas to biofuels

1.4.1 Biofuels from syngas

Syngas is a gas mixture consisting of carbon monoxide (CO), carbon dioxide (CO_2), hydrogen (H_2) and nitrogen (N_2). Biofuels from syngas normally contain hydrogen (H_2), methanol (CH_3OH), and ethanol (C_2H_5OH). The product of biofuels from syngas can utilize the entire biomass including the uneasy-to-breakdown lignin content. Biomass based syngas can be converted to biofuels usually via metal catalysts or bio-catalysts. In case of metal catalytic method, though different metal catalysts are put into use, conversion processes are similar. Main reactions involved in the process are based on Fischer-Tropsch synthesis (FTS) (Fischer & Tropsch, 1926):

$$CO + 3H_2 \rightarrow CH_4 + H_2O\ (\Delta H_{298K} = -247KJ/mol) \qquad (1.1)$$

$$CO + 2H_2 \rightarrow \left(\frac{1}{n}\right)(C_nH_{2n}) + H_2O \qquad (1.2)$$

Currently, four main series of catalyst are considered effective in FTS, including Fe, Co, Ru, and Ni (Zhang et al., 2005a; Zhang et al., 2005b). Metal catalytic method though is reliable in conversion process, some serious challenges such as high reaction temperature and pressure requirements, heat removal duty, as well as the low selectivity and catalyst poisoning are not ignorable (Dunleavy, 2006).

An alternative route to obtain biofuels from syngas is the bio-catalytic method. This promising technology avoids catalyst poisoning in virtue of its high tolerance for syngas contaminants of some microbial catalysts (Ahmed et al., 2006; Ragauskas et al., 2006). Just as all other methods have advantages and disadvantages of their own, bio-catalytic conversion process has superb operation temperature and pressure, which are both easily to achieve, whereas requires longer reaction time suffers from slow microbe-growth (Wolfrum & Watt, 2002). A good bioreactor to deal with gas mass transfer limitations and low ethanol productivity is necessary (Worden et al., 1997).

1.4.2 Catalyst support

Carbons, ranging from diamond through graphite to fullerene (C_{60}), have been attracting people's attention to conduct researches as catalyst supports for decades (Furimsky, 2008). Low cost, high surface area, electrical conductivity, the modification of pore size distribution, and the ability for active metals' recovery are discovered as carbons' most promising properties for catalyst supports (Auer et al., 1998; Jüntgen, 1986). Among all various carbon types, porous carbons are known to be suitable as catalyst supports in virtue of their much higher surface area than conventional carbon black, and their pores are often used as catalytic reactors (Kim et al., 2012). Currently, there are two main techniques to synthesize porous carbon, one is to use silica or zeolite as the carbonization template which leads to the product of porous carbon (Lee et al., 2004; Ma et al., 2001; Titirici et al., 2007); the other one is based on block copolymers as structure-directing agents for the synthesis of ordered porous carbons (Wan et al., 2006). However, both techniques have many complex steps and require special materials to control pore size and shape. Zhang et al. (2008) used biomass materials to produce porous carbon. Kim et al. (2012) conducted a research for CO_2 reforming of CH_4 using natural cellulose fibers-based (specifically henequen fibers) porous carbon supported Ni catalyst (Ni/cellulose). A high and porous surface of cellulose support was displayed. Higher catalytic activity and long-term stability in comparison to conventional Ni/Al_2O_3 model catalyst were shown.

1.5 Objectives

The objectives of this study are: (1) to develop the best methods for cellulosic fibers preparation from pure cellulose fibers, cotton linters, raw kenaf bast and switchgrass; (2) to investigate catalytic performance of CNWs supported Fe^{3+} catalyst in converting pure syngas to biofuels.

CHAPTER II

CELLULOSE NANOWHISKERS DERIVED FROM PURE CELLULOSE, COTTON LINTERS, KENAF BAST AND SWITCHGRASS

2.1 Materials

Pure cellulose (fibers, medium) was obtained from Sigma-Aldrich with original moisture of 5.6%. Cotton linters, kenaf bast fibers and switchgrass fibers were harvested from Mississippi State University in 2010 and 2012, and then ground up into powders with length of ~ 5 mm. Moisture contents of cotton linters, kenaf bast and switchgrass were 7.7%, 10.2% and 11.8%, respectively. Sulfuric acid (ACS reagent, 95.0 ~ 98.0 wt. %, Sigma-Aldrich) and sodium hydroxide (ACS reagent, 97.0 wt. %, pellets, Sigma-Aldrich) were diluted into desired low concentrations as pretreatment agents. Higher concentrations (50 ~ 65 wt. %) diluted sulfuric acid were applied as hydrolysis agents.

2.2 Methods

The flowchart of the procedure of biomass pretreatment and cellulose nanowhiskers preparation is shown in figure 2.1.

2.2.1 Biomass pretreatment

Kenaf bast and switchgrass were ground to ~ 5 mm long. A sealed reactor with mechanical stirring was used for retting and bleaching processes. In order to fully immerse solid samples, a ratio of solid (g) to solution (ml) 1:50 was selected for all pretreatment processes. Each sample was first retted with 5 wt. % NaOH at 160°C for 1 hour. The retted fibers with basic solution were washed with distilled water to remove chemicals and neutralized to pH 6 ~ 7. Then the retted fibers were bleached with dilute H_2SO_4. For optimal different levels of period (20, 40 and 60 minutes), optimal temperature of three different levels (80, 100, and 120°C) were applied to three acid concentration levels (3, 3.5, and 4 wt. %). The acidic liquid with bleached fibers was then centrifuged at a rotation speed of 4,050 rpm for five minutes. Repeated centrifugation to remove supernatant and fresh distilled water was added until pH 6 ~ 7. Neutral pretreated fibers were obtained for following chemical content analysis and cellulose nanowhiskers (CNWs) preparation.

2.2.2 Preparation of cellulose nanowhiskers

Pure cellulose fiber, cotton linters and pretreated biomass were all treated via sulfuric acid hydrolysis at four sulfuric concentrations (50, 55, 60 and 65 wt. %). For optimal concentration level, four period levels (2, 3, 4 and 5 hours) were applied to four temperature levels (50, 55, 60 and 65°C). After hydrolysis, acidic sample solutions were centrifuged with a rotation speed of 4,050 rpm to remove supernatant and washed to neutral by fresh distilled water.

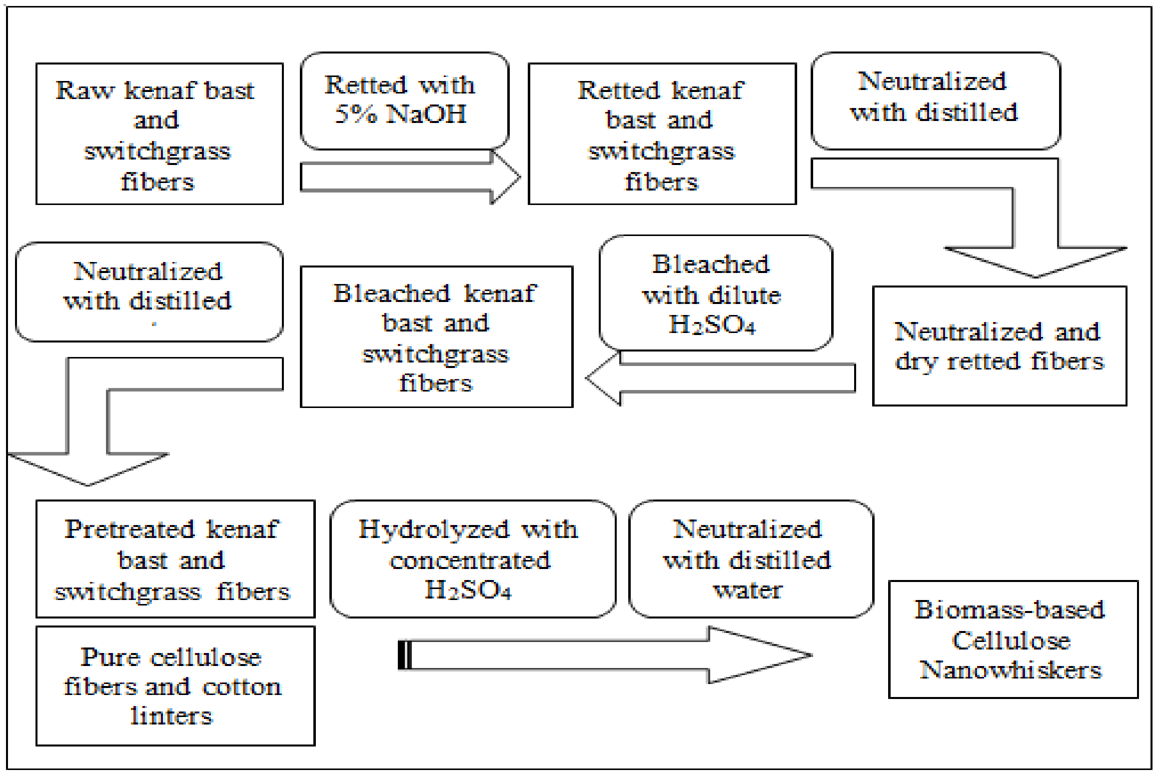


Figure 2.1 Flowchart of biomass pretreatment and cellulose nanowhiskers preparation

2.2.3 Determination of product yields and chemical components analysis

Yields of target product were calculated based on the ratio of oven-dry weight to the original weight of biomass.

α-Cellulose, hemicellulose, Klason lignin, and ash contents were considered as main chemical components in biomass materials. In this study, chemical contents in raw material fibers, retted fibers, and bleached fibers were tested following NREL standard methods. The determination of α-cellulose, hemicellulose and Klason lignin followed NREL/TP-510-42618 standard (Sluiter et al., 2008). Extractives in biomass were determined by NREL/TP-510-42619 standard (Sluiter et al., 2005b). Ash contents were measured using the NREL/TP-510-42622 standard (Sluiter et al., 2005a). Three replications were done for each analysis and the average was reported.

2.2.4 Morphology analysis

Samples of non-pretreated fibers, retted fibers, and bleached fibers were coated with 5 nm platinum in order to provide electrical conductivity. Scanning electron microscope (SEM, Supra TM 40, Zeiss) with an accelerating voltage of 15 kV was used to analyze fiber structure and dimensions. CNWs samples for atomic force microscope (AFM, ScanAsyst-Air, Bruker) analysis were obtained by placing a drop of dilute CNWs suspension onto a glass slide and drying in air at ambient temperature.

2.3 Results and discussion

2.3.1 Optimization of pretreatment conditions of biomass

Table 2.1 shows the fiber yields and chemical components in raw kenaf bast and switchgrass before and after being retted with 5% NaOH at 160°C for 1 hour. NaOH retting removed most of the Klason lignin and over half of the hemicellulose in both kenaf bast and switchgrass. All extractives were removed by retting as well. 60.8% and 46.2% yields of retted kenaf bast fibers and switchgrass fibers were obtained, in which 89.0% and 82.0% were α-cellulose.

Table 2.1 Chemical component contents of kenaf bast and switchgrass before/after retting with 5% NaOH at 160°C for 1 hour

	Fiber yield	α-cellulose	Hemicellulose	Klason lignin	Ash
Raw kenaf bast		56.9	21.6	12.0	4.9
Retted kenaf bast fibers	60.8	89.0	6.9	0.3	1.8
Raw switchgrass		38.1	30.1	19.0	6.3
Retted switchgrass fibers	46.2	82.0	13.2	1.1	2.0

2.3.1.1 Results for kenaf bast pretreatment

Figure 2.2 and 2.3 show the yields of bleached kenaf fibers and chemical component contents after bleaching with 3 wt. % H_2SO_4 at 80°C for three different periods (20, 40, and 60 minutes). With the bleaching time increased from 20 minutes to 40 minutes, α-cellulose content in bleached kenaf bast fibers increased by 2.3% from 94.4% to 96.7% but only slightly increased by 0.6 % with 20 more minutes bleaching. The contents of hemicellulose, Klason lignin and ash with longer bleaching time from 40 minutes to 60 minutes also show slight decrease. Thus, bleaching time of 40 minutes was selected as the most efficient of the three tested.

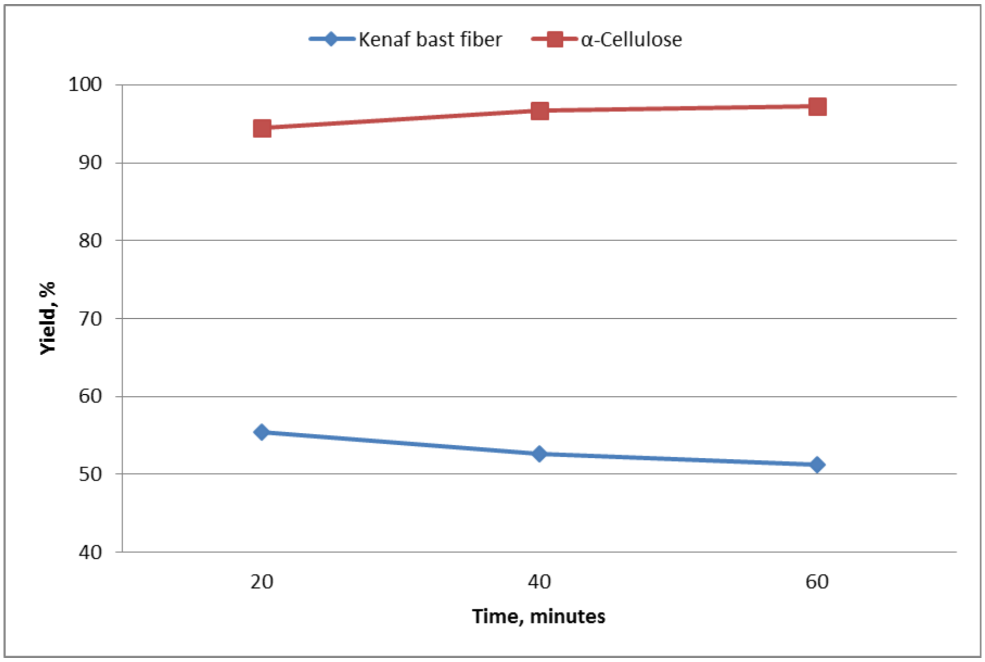


Figure 2.2 Yields of kenaf bast fibers and α-cellulose for different bleaching periods (20, 40, and 60 minutes) at 80°C with 3 wt. % H_2SO_4

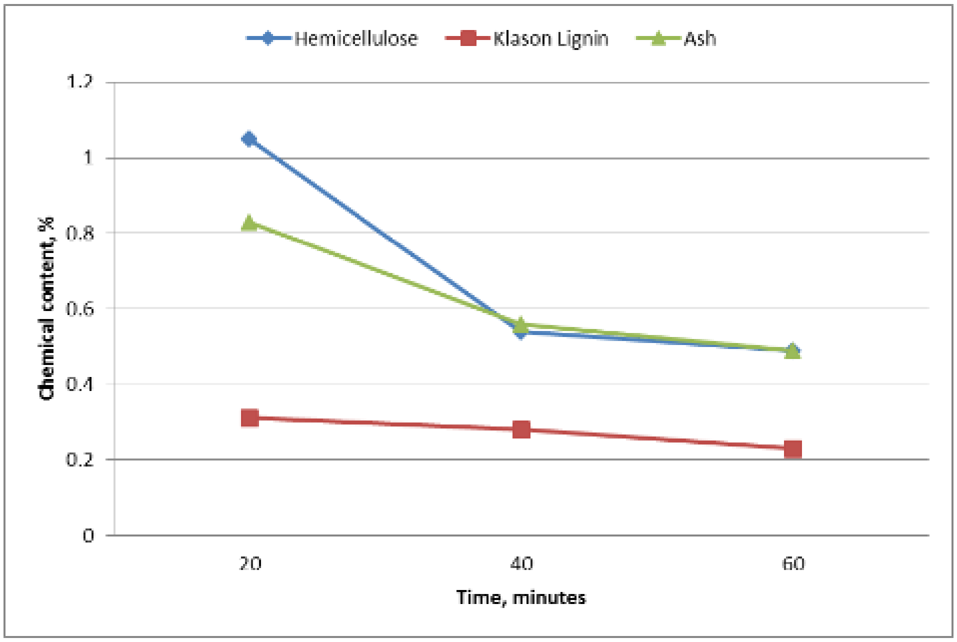


Figure 2.3 Chemical contents of hemicellulose, Klason lignin and ash in kenaf bast fibers for different bleaching periods (20, 40, and 60 minutes) at 80°C with 3 wt. % H_2SO_4

Figures 2.4 and 2.5 show the yields of kenaf bleached fibers and chemical component contents of hemicellulose, Klason lignin and ash after bleaching with 3 wt. % H_2SO_4 for 40 minutes at three different temperatures (60, 80, and 100°C). Contents of hemicellulose and Klason lignin bleached at 80°C were slightly lower than that at 60°C, but got decreased largely when the temperature was 100°C at which ash was also mostly removed and α-cellulose had a maximum content percentage of 98.5%.Therefore, bleaching temperature at 100°C was selected with 3 wt. % H_2SO_4 for 40 minutes as best conditions.

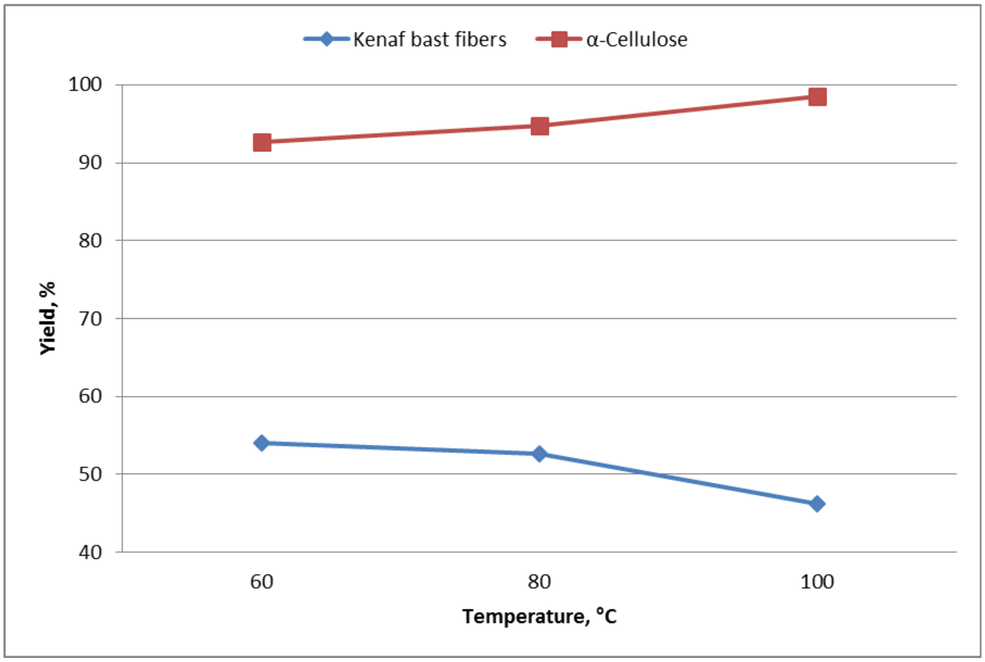


Figure 2.4 Yields of kenaf bast fibers and α-cellulose at different bleaching temperatures (60, 80, and 100°C) with 3 wt. % H_2SO_4 for 40 minutes

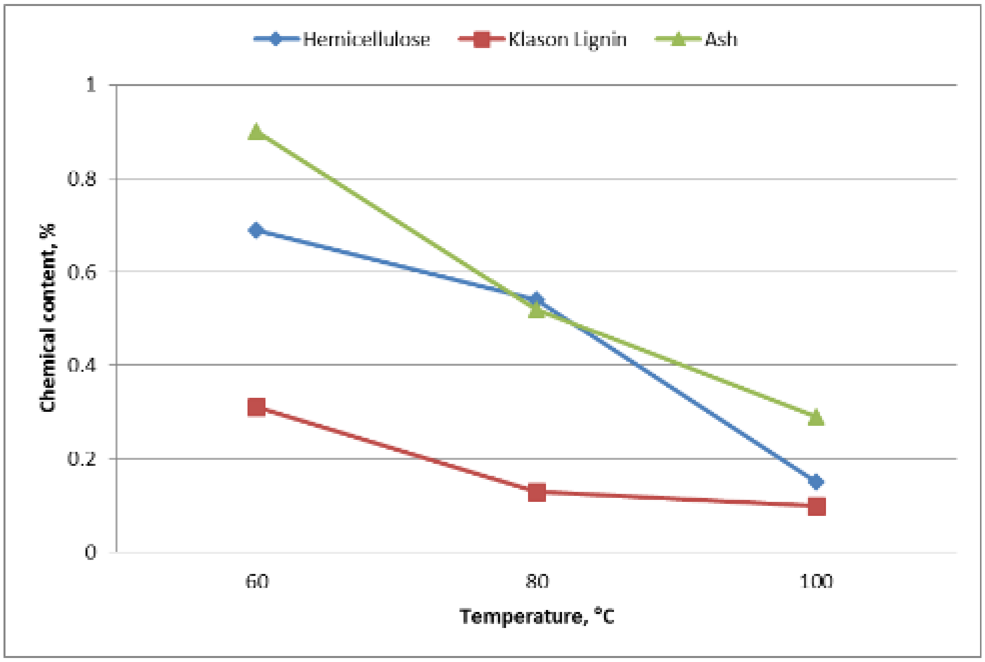


Figure 2.5 Chemical contents of hemicellulose, Klason lignin and ash in kenaf bast fibers at different bleaching temperatures (60, 80, and 100°C) with 3 wt. % H_2SO_4 for 40 minutes

Figures 2.6 and 2.7 show the yields of bleached kenaf bast fibers and chemical component contents of hemicellulose, Klason lignin and ash after bleaching with three different sulfuric concentrations (3, 3.5, and 4 wt. %) at 100°C for 40 minutes. In contrast with lower acid concentrations, the content of α-cellulose reached 99.2% with 4 wt. % H_2SO_4, which is the maximum of all bleaching concentrations. Meanwhile the complete removal of hemicellulose, Klason lignin and ash with the 4 wt. % H_2SO_4 gives the most efficient bleaching acid concentration. Thus, 4 wt. % of H_2SO_4, 100°C of temperature and 40 minutes of time were selected as the optimal bleaching conditions to obtain the highest content of α-cellulose and best removal effect of hemicellulose, Klason lignin and ash.

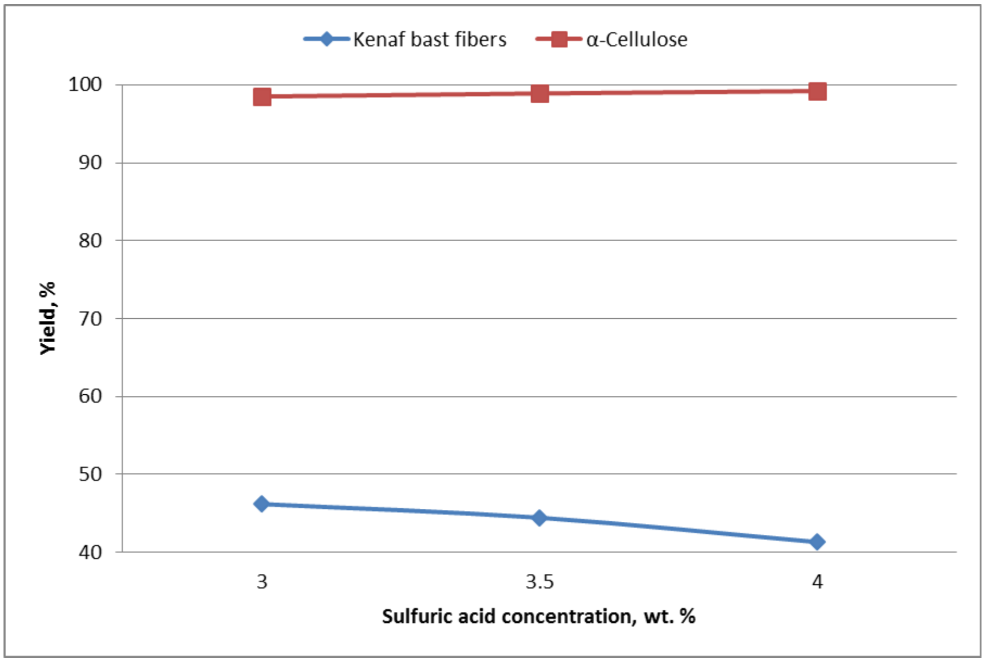


Figure 2.6 Yields of kenaf bast fibers and α-cellulose with different bleaching sulfuric acid concentrations (3, 3.5, and 4 wt. %) at 100°C for 40 minutes

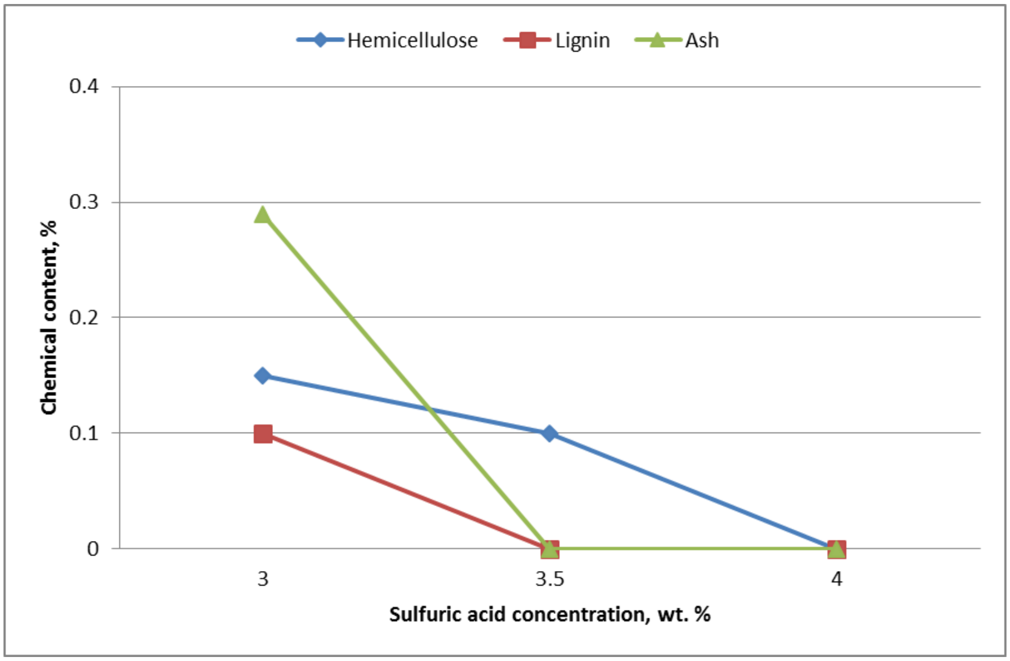


Figure 2.7 Chemical contents of hemicellulose, Klason lignin and ash in kenaf bast fibers with different bleaching sulfuric acid concentrations (3, 3.5, and 4 wt. %) at 100°C for 40 minutes

2.3.1.2 Results for switchgrass pretreatment

Figures 2.8 and 2.9 show the fiber yield of switchgrass and contents of α-cellulose, hemicellulose, Klason lignin and ash after bleaching with 3.5 wt. % H_2SO_4 for 80°C at three different periods (20, 40, and 60 minutes). With the increase of bleaching time from 20 minutes to 60 minutes, the yield of bleached switchgrass fibers decreased to 35.5%, including 94.1% of α-cellulose. The removal of hemicellulose, Klason lignin and ash had best effect when bleached for 60 minutes. Since the increase content of α-cellulose and removal of hemicellulose, Klason lignin and ash kept steadily, bleaching time of 60 minutes was selected as the best to ret switchgrass fibers.

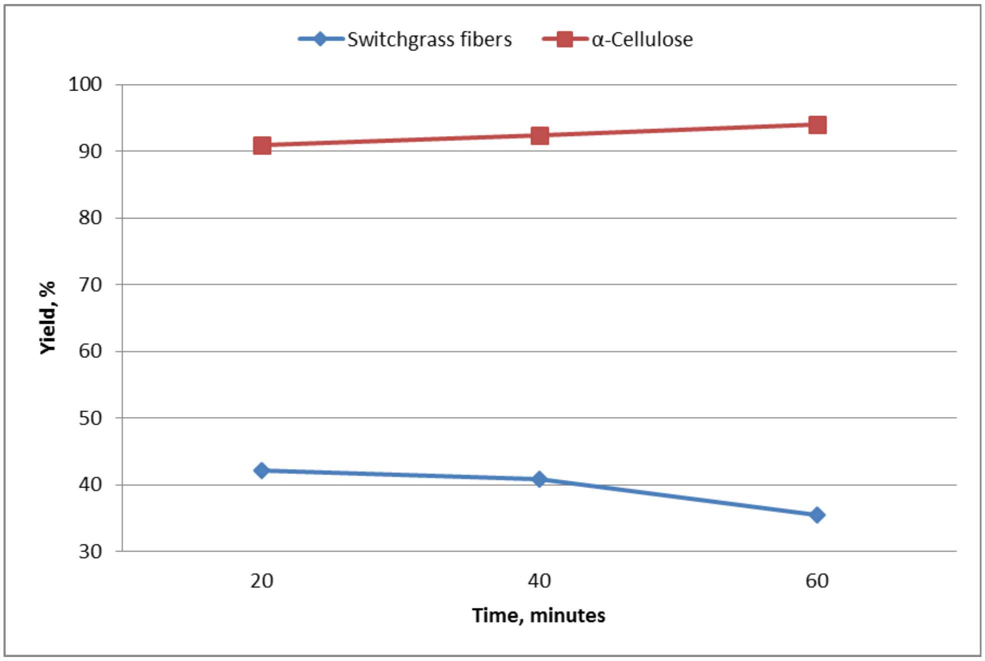


Figure 2.8 Yields of switchgrass fibers and α-cellulose for different bleaching periods (20, 40, and 60 minutes) at 80°C with 3.5 wt. % H_2SO_4

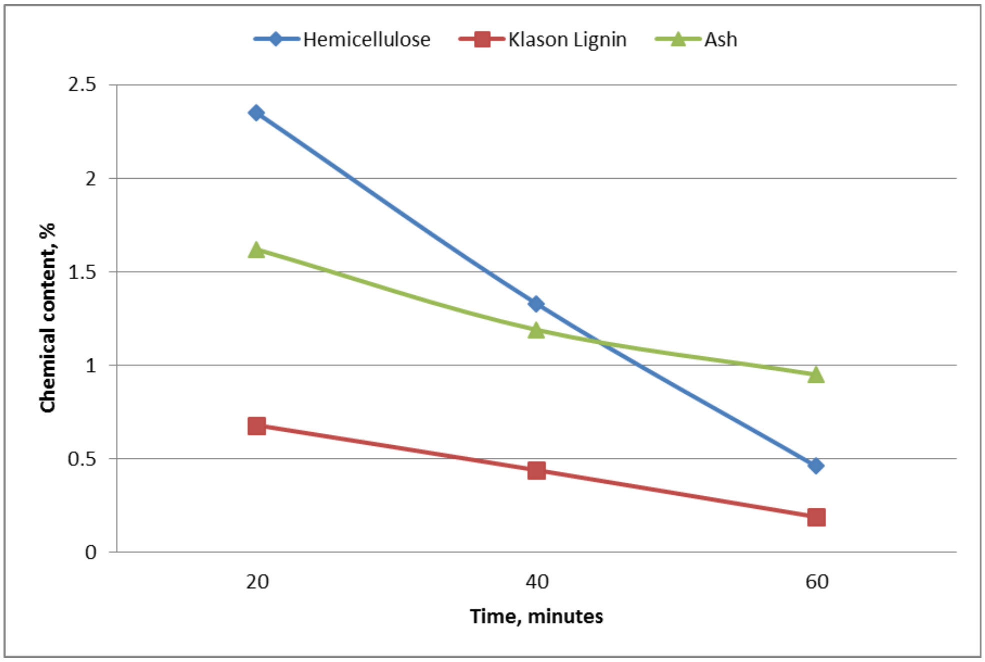


Figure 2.9 Chemical contents of hemicellulose, Klason lignin and ash in switchgrass fibers for different bleaching periods (20, 40, and 60 minutes) at 80°C with 3.5 wt. % H_2SO_4

Figures 2.10 and 2.11 show the fiber yield of switchgrass fibers and contents of α-cellulose, hemicellulose, Klason lignin and ash after bleaching with 3.5 wt. % H_2SO_4 at three temperatures (60, 80, and 100°C) for 60 minutes. The contents of α-cellulose increased significantly from 88.7% to 94.1% with the temperature went up from 60°C to 80°C, meanwhile hemicellulose and Klason lignin decreased largely. But there were slight changes in the content of target α-cellulose, removal of hemicellulose and Klason lignin, when the temperature was up to 100°C. Hence, though ash content steadily went down with each increasing temperature, 80°C was selected as the optimal bleaching temperature of three tested.

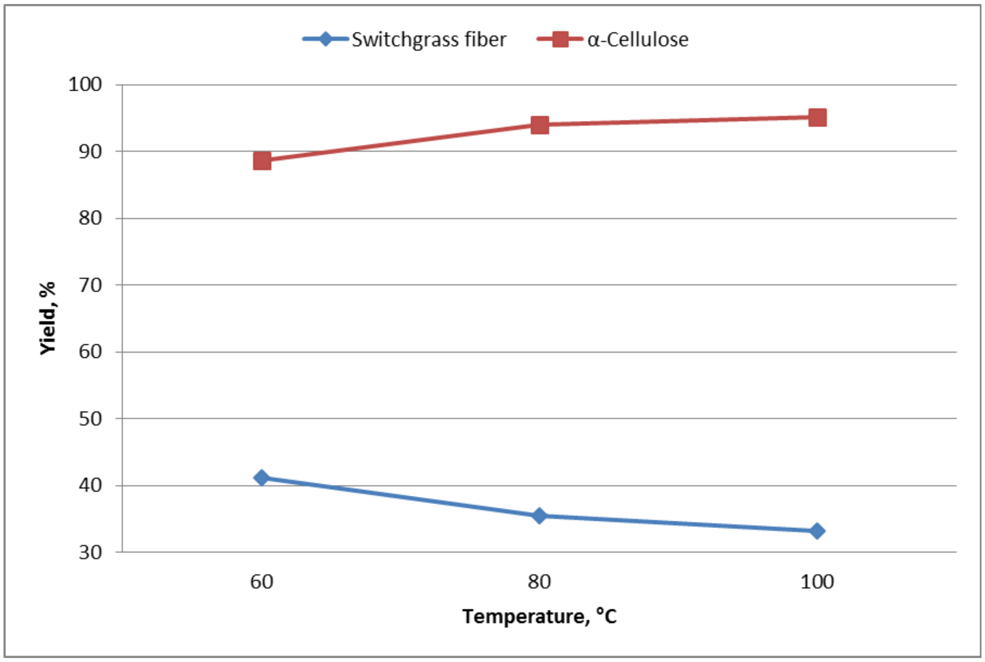


Figure 2.10 Yields of switchgrass fibers and α-cellulose at different bleaching temperatures (60, 80, and 100°C) with 3.5 wt. % H_2SO_4 for 60 minutes

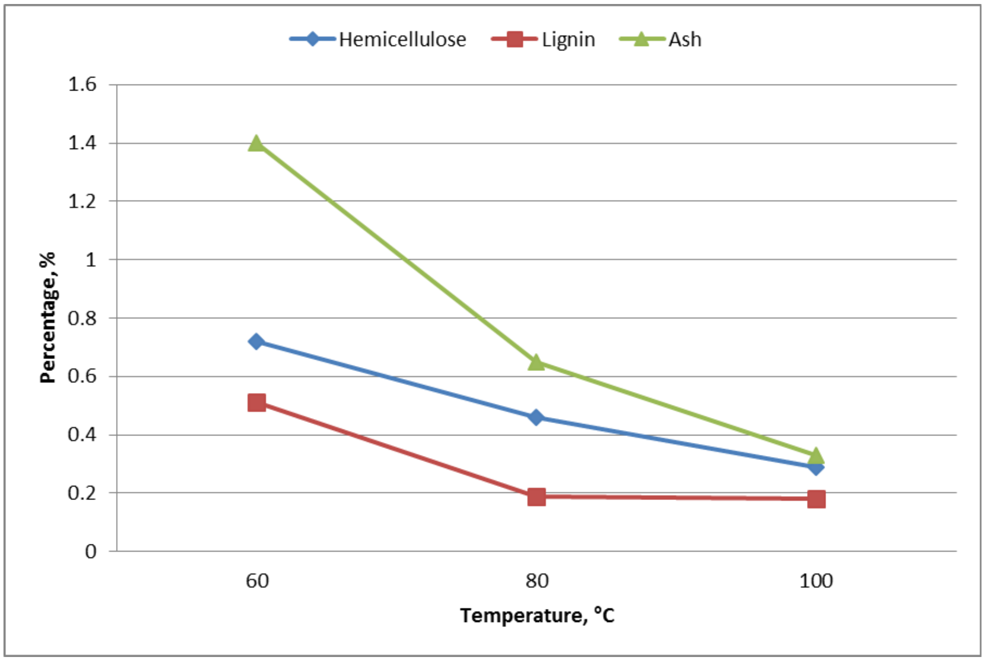


Figure 2.11 Chemical contents of hemicellulose, Klason lignin and ash in switchgrass fibers at different bleaching temperatures (60, 80, and 100 °C) with 3.5 wt. % H_2SO_4 for 60 minutes

Figure 2.12 and 2.13 show the fiber yield of switchgrass fibers and contents of α-cellulose, hemicellulose, Klason lignin and ash after bleaching at 80°C for 60 minutes with three different acid concentrations (3, 3.5, and 4 wt. %). In contrast to lower acid concentrations, hemicellulose and ash were completely removed with 4 wt. % H_2SO_4 bleaching, and the content of Klason lignin was decreased to the lowest of 0.1%. Target α-cellulose reached its highest yield of 97.2%. Thus, bleaching H_2SO_4 with 4 wt. % was considered to be the optimal concentration of all three tested.

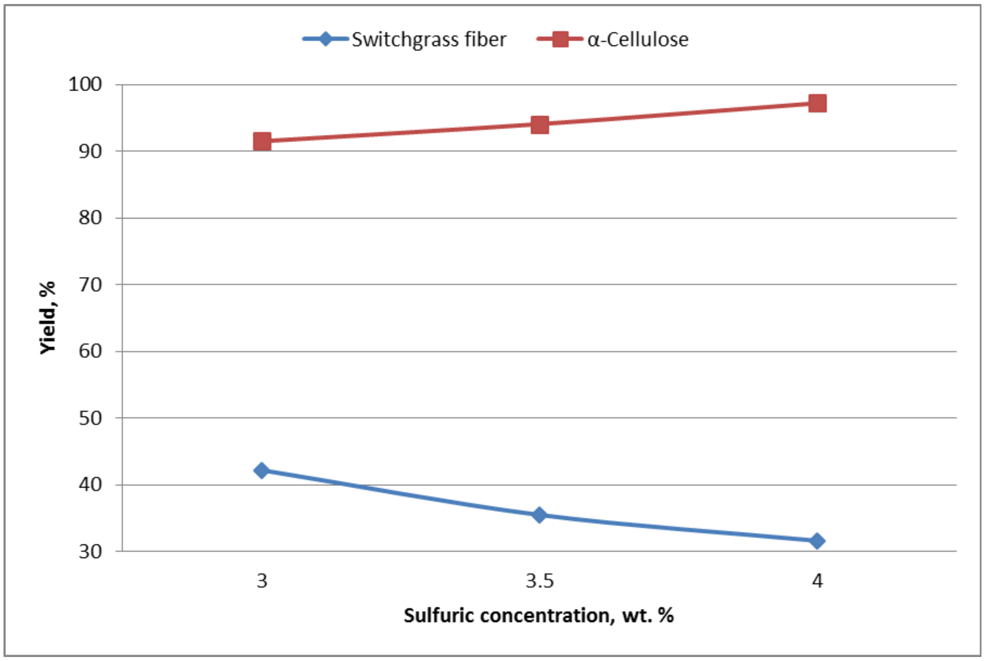


Figure 2.12 Yields of switchgrass fibers and α-cellulose with different bleaching acid concentrations (3, 3.5, and 4 wt. %) at 80°C for 60 minutes

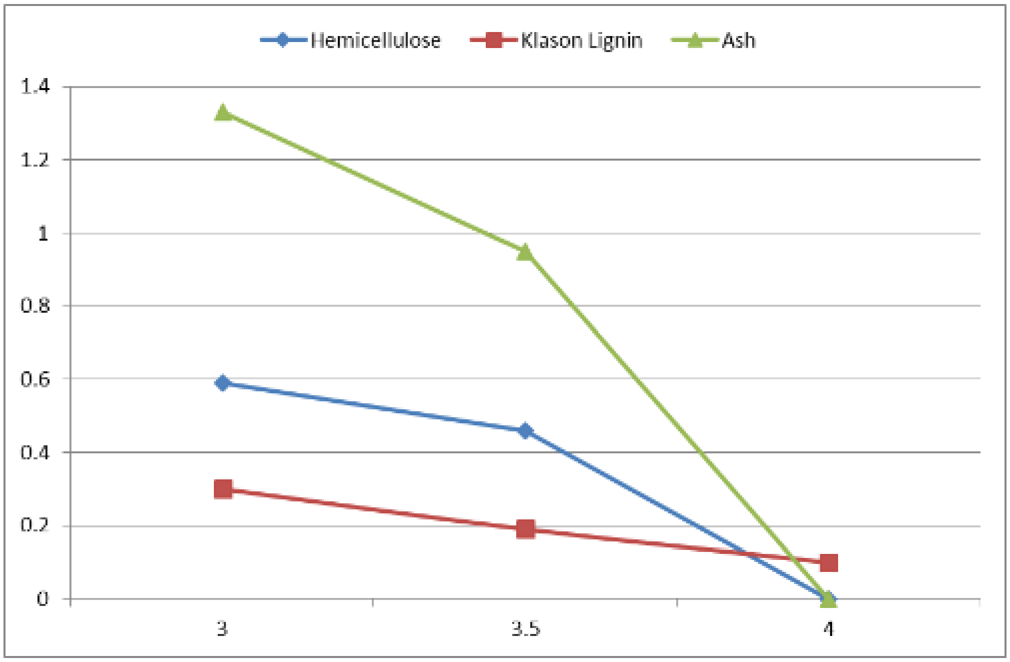


Figure 2.13 Chemical contents of hemicellulose, Klason lignin and ash in switchgrass fibers with different bleaching acid concentrations (3, 3.5, and 4 wt. %) at 80°C for 60 minutes

2.3.2 Optimization of preparation of cellulose nanowhiskers (CNWs)

The main objective of this part was to determine optimal acid hydrolysis conditions for biomass to increase cellulose nanowhiskers (CNWs) yields. After removing hemicellulose, lignin and ash from kenaf bast fibers and switchgrass fibers, all four raw materials were treated by sulfuric acid with limited acid concentration, temperature and period levels to obtain maximum yields of CNWs.

Figure 2.14 shows CNWs yields of four materials affected by acid concentration levels. Pure cellulose fibers, cotton linters, pretreated kenaf bast fibers and switchgrass fibers were treated with four different sulfuric acid concentrations (50, 55, 60, and 65 wt. %) at 55°C for 3 hours. CNWs derived from pure cellulose fibers and cotton linters both had their maximum yields of 83.4% and 65.7% when the sulfuric concentration was 55 wt. %. For pretreated kenaf bast fibers and switchgrass fibers, CNWs had the maximum yields of 34.7% and 26.4% with 60 wt. % H_2SO_4. After reaching the maximum yields of CNWs, a magnificent decrease occurred due to the degradation of major cellulose to glucose led by concentrated acid homogeneous. Thus, 55 wt. % H_2SO_4 of was selected as the most efficient hydrolysis treatment for pure cellulose fibers and cotton linters, and 60 wt. % H_2SO_4 for pretreated kenaf bast fibers and switchgrass fibers.

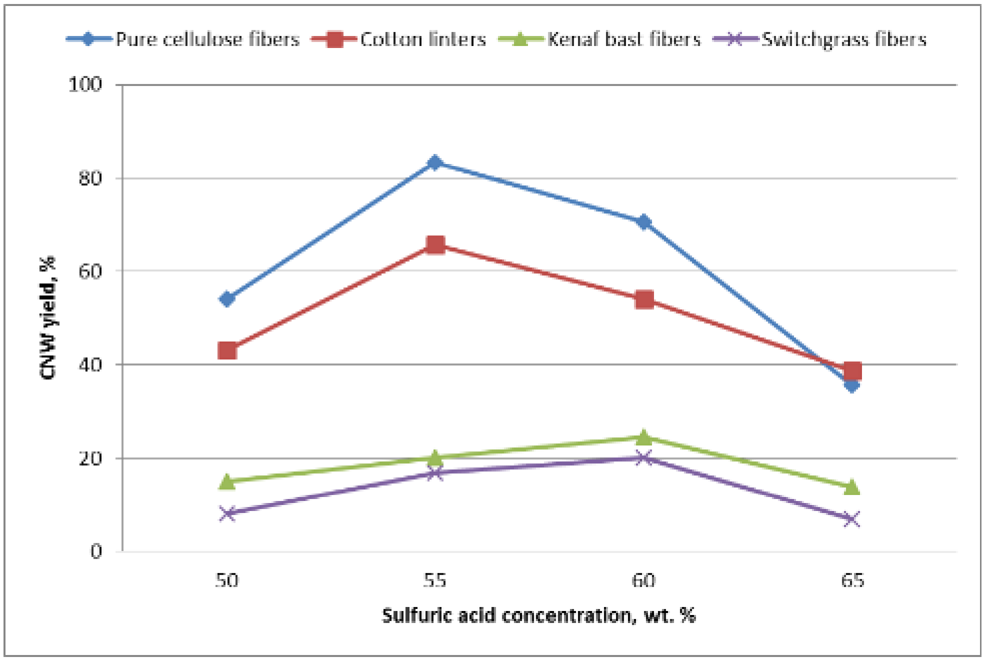


Figure 2.14 CNWs yields of four materials (pure cellulose fibers, cotton linters, kenaf bast fibers, and switchgrass fibers) treated at 55°C for 3 hours with different sulfuric concentrations (50, 55, 60, and 65 wt. %)

Figure 2.15 and 2.16 show the yields of CNWs of four materials affected by hydrolysis period levels. Four raw materials samples mentioned above were treated with four different hydrolysis periods (2, 3, 4, and 5 hours) at 55°C. Acid concentrations of 55 wt. % and 60 wt. % were applied separately to each material. Figure 2.15 shows that

CNWs yields of pure cellulose fibers and cotton linters reached their maximum of 83.4% and 76.7% when hydrolyzed for 3 hours and 4 hours.

CNWs yields of kenaf bast fibers and switchgrass fibers were shown in figure 2.16. Maximum of 31.2% from kenaf bast fibers and 23.6% from switchgrass fibers were obtained for 4 hours hydrolysis. Therefore, 55 wt. % H_2SO_4 for 3 hours and 4 hours were selected for pure cellulose fibers and cotton linters to obtain maximum CNW yields. For kenaf bast fibers and switchgrass fibers, maximum yield of CNWs could be obtained with 60 wt. % H_2SO_4 hydrolysis for 4 hours.

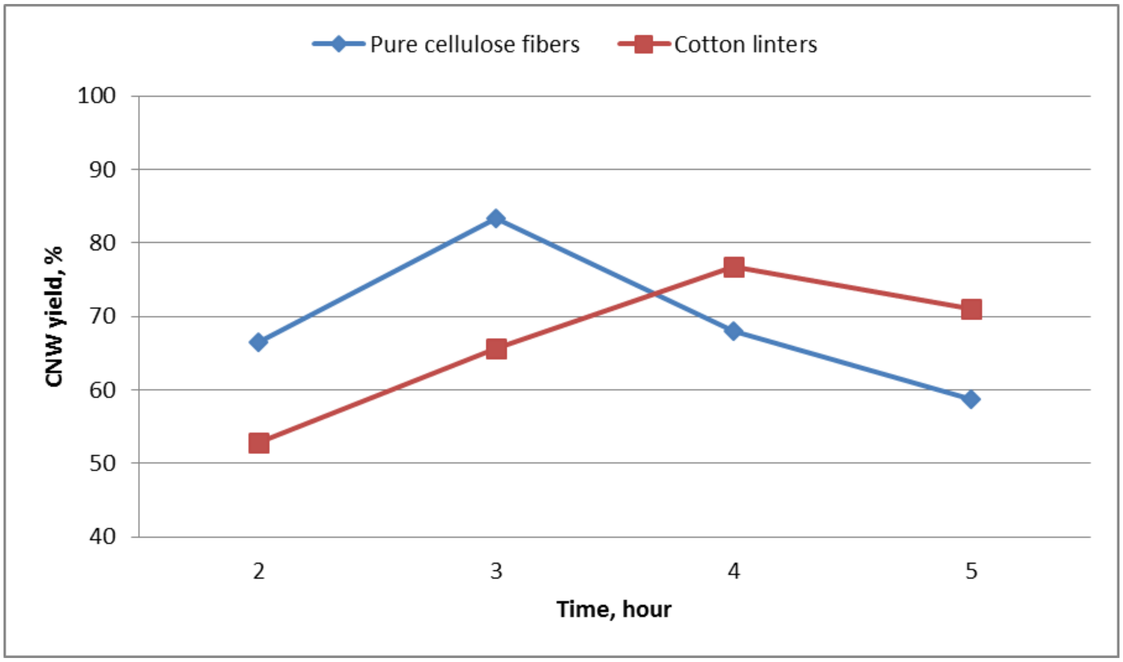


Figure 2.15 CNWs yields of pure cellulose fibers and cotton linters treated with 55 wt. % H_2SO_4 at 55°C for different periods (2, 3, 4, and 5 hours)

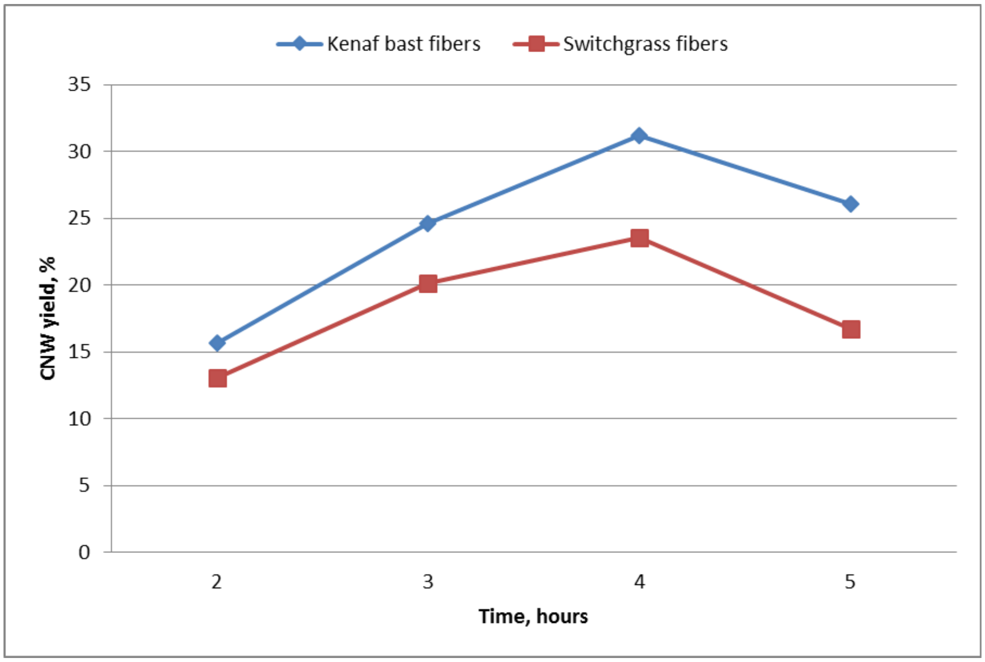


Figure 2.16 CNWs yields of kenaf bast fibers and switchgrass fibers treated with 60 wt. % H_2SO_4 at 55°C for different periods (2, 3, 4, and 5 hours)

Figures 2.17, 2.18 and 2.19 show the yields of CNWs affected by hydrolysis temperature levels. Shown in figure 2.17, CNW yield of pure cellulose fibers reached maximum from 75.5% to 83.4% with the increase of temperature from 50°C to 55°C, and then the yield got decreased when temperature kept continuously increasing. Shown in figure 2.18, cotton linters had maximum CNWs yield of 80.8% with higher temperature of 60°C compared to pure cellulose fibers. After increasing the hydrolysis temperature of cotton linters to 65°C, only 42.8% CNW yield was obtained. Shown in figure 2.19, maximum CNWs yields of kenaf bast fibers (34.0%) and switchgrass fibers (25.3%) were obtained when the temperature was at 55°C, and then two yields decreased to 18.1% and 14.9% with the increase of temperature up to 60°C and 65°C. Thus, in order to have maximum CNWs yields, temperature of 55°C was selected for pure cellulose fibers, kenaf bast fibers and switchgrass fibers, while temperature of 60°C was considered as the optimal for cotton linters.

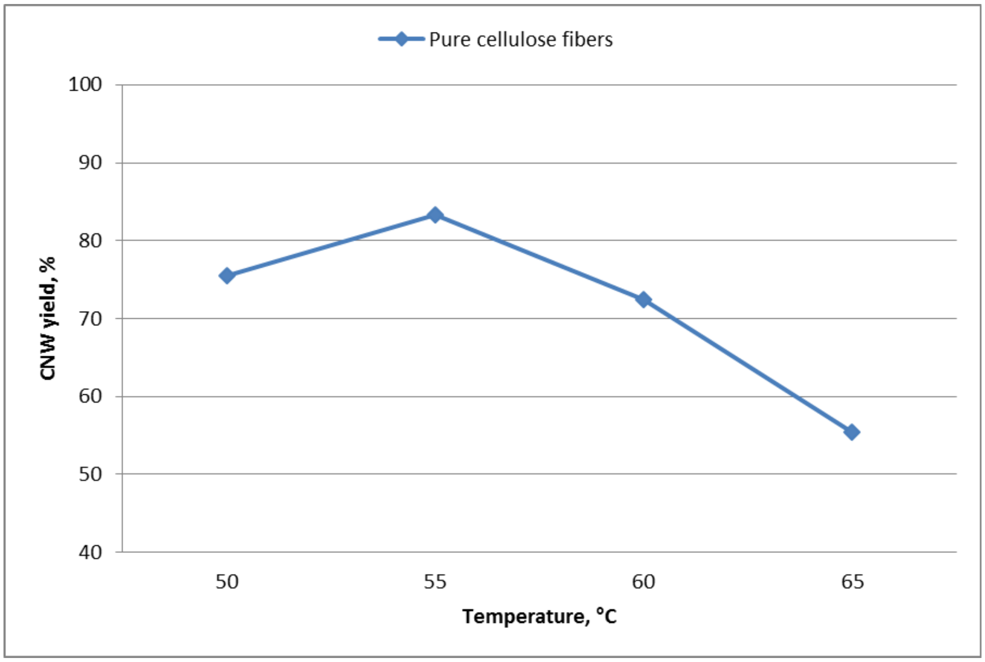


Figure 2.17 CNWs yield of pure cellulose fibers treated with 55 wt. % H_2SO_4 for 3 hours at different temperatures (50, 55, 60, and 65°C)

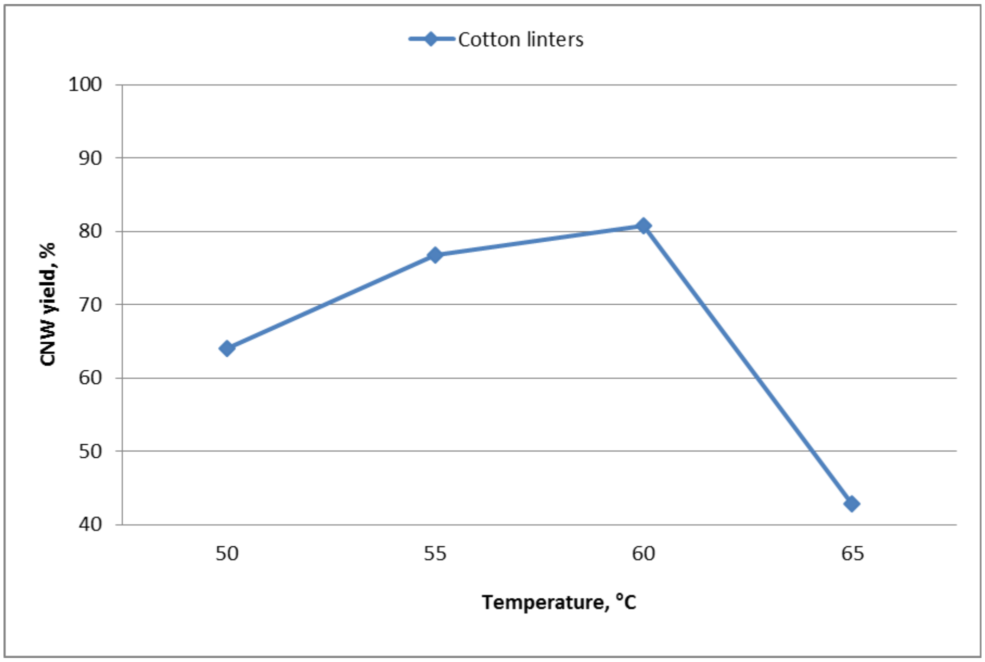


Figure 2.18 CNWs yield of cotton linters treated with 55 wt. % H_2SO_4 for 4 hours at different temperatures (50, 55, 60, and 65°C)

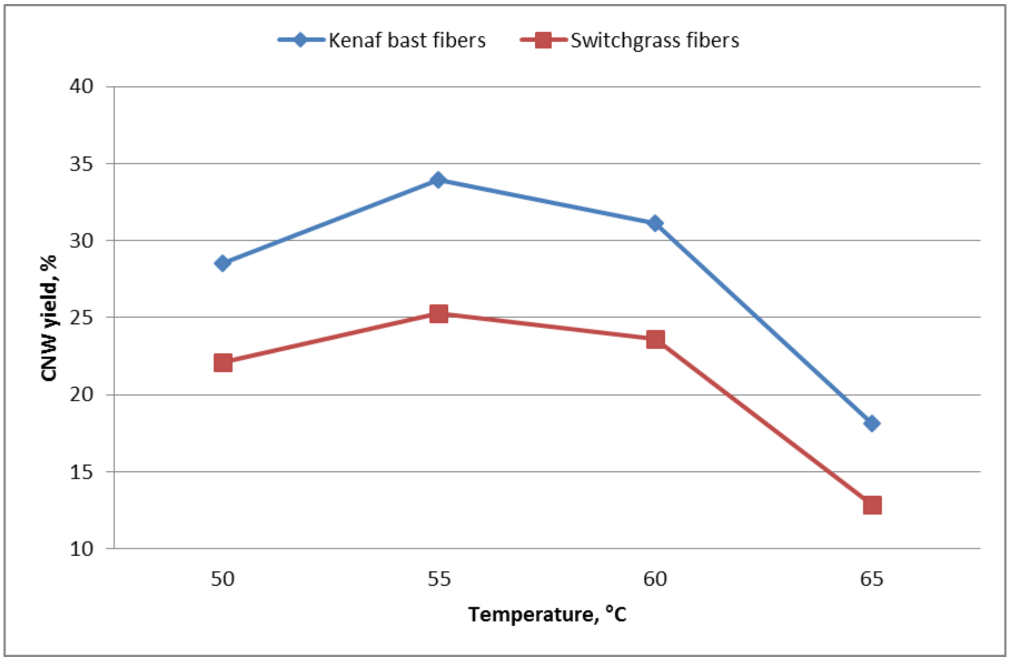


Figure 2.19 CNWs yield of kenaf bast fibers and switchgrass fibers treated with 60 wt. % H_2SO_4 for 4 hours at four different temperatures (50, 55, 60, and 65°C)

2.3.3 Orthogonal experiments

In order to further optimize experiment parameters, orthogonal experiments were introduced to test the influence of hydrolysis conditions on CNWs yields which were derived from cotton linters, pretreated kenaf bast fibers and switchgrass fibers.

According to the previous results of single factor experiments on CNWs yields, it is known that cotton linters had the highest CNWs yield when hydrolyzed with 55% H_2SO_4 at 60°C for 4 hours; for pretreated kenaf bast fibers and switchgrass fibers, the conditions were hydrolyzed with 60% H_2SO_4 at 55°C for 4 hours.

For each factor that affected CNWs yield, three levels were tested in the experiment. Three replicas were applied to each sample and average results were recorded. The results of orthogonal experiments on CNWs yields derived from cotton linters, kenaf bast fibers and switchgrass fibers were shown table 2.2, table 2.3, and table 2.4.

Table 2.2 Results of orthogonal experiment on CNWs yield derived from cotton linters

No.	Sulfuric acid/ %	Period/ h	Temperature/ °C	CNWs yield/ %
1	52	3.5	57	85.4
2	52	4	60	72.2
3	52	4.5	63	52.1
4	55	3.5	60	60.6
5	55	4	63	48.3
6	55	4.5	57	62.3
7	58	3.5	63	45.9
8	58	4	57	43.4
9	58	4.5	60	40.3
k_1	69.913	63.980	63.710	
k_2	57.073	54.667	57.720	
k_3	43.217	51.557	48.773	
R	26.696	12.423	14.937	

NOTE: Parameters k_1, k_2, k_3, and R represent the same concepts in table 2.3 and table 2.4.
k_1, k_2, k_3: Average results of CNWs yields based on 52, 55, and 58 wt. % sulfuric acid in each row.
R: Range of k_1, k_2, k_3 in each column

In table 2.2, CNWs yield had its maximum value of 85.4% when the hydrolysis condition was with 52 % H_2SO_4 at 57°C for 3.5 hours. The results indicate that sulfuric acid concentration has the strongest effect on cotton-based CNW yield; though hydrolysis temperature and period show much influence on CNWs yields as well, these two factors are weaker compared to that of acid concentration.

Table 2.3 Results of orthogonal experiment on CNWs yield derived from kenaf bast fibers

No.	Sulfuric acid/ %	Period/ h	Temperature/ °C	CNWs yield/ %
1	57	3.5	52	24.4
2	57	4	55	33.8
3	57	4.5	58	34.1
4	60	3.5	55	33.0
5	60	4	58	26.6
6	60	4.5	52	22.1
7	63	3.5	58	15.5
8	63	4	52	14.8
9	63	4.5	55	11.2
k_1	30.750	24.287	25.383	
k_2	27.237	25.047	26.010	
k_3	13.827	22.480	20.420	
R	16.923	2.567	5.590	

Table 2.3 gives the maximum CNWs yield of 34.1% from pretreated kenaf bast fibers when hydrolyzed with 57% sulfuric acid at 58°C for 4.5 hours. Table 2.4 shows that the optimal conditions to obtain switchgrass-based CNWs are to hydrolyze with 57% H_2SO_4 at 55°C for 4 hours. Both ranges (R) in table 2.3 and 2.4 state clearly that among three factors, acid concentration has the most significant influence on biomass-based CNWs yields, while reaction temperature and period play less important roles.

Table 2.4 Results of orthogonal experiment on CNWs yield derived from switchgrass fibers

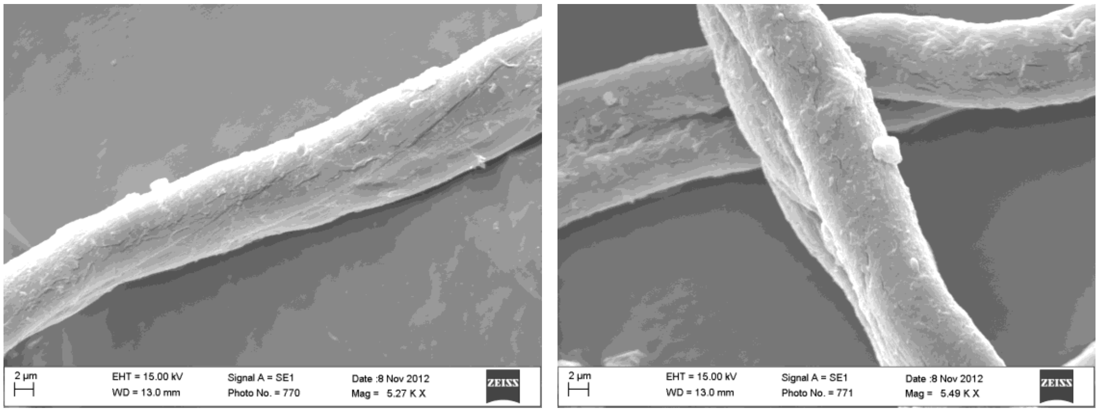
No.	Sulfuric acid/ %	Period/ h	Temperature/ °C	CNWs yield/ %
1	57	3.5	52	19.8
2	57	4	55	26.8
3	57	4.5	58	20.7
4	60	3.5	55	19.3
5	60	4	58	23.4
6	60	4.5	52	17.9
7	63	3.5	58	10.4
8	63	4	52	9.3
9	63	4.5	55	7.4
k_1	22.447	16.507	15.653	
k_2	20.200	19.940	17.823	
k_3	9.017	15.317	18.187	
R	13.430	4.523	2.534	

2.3.4 Morphology analysis

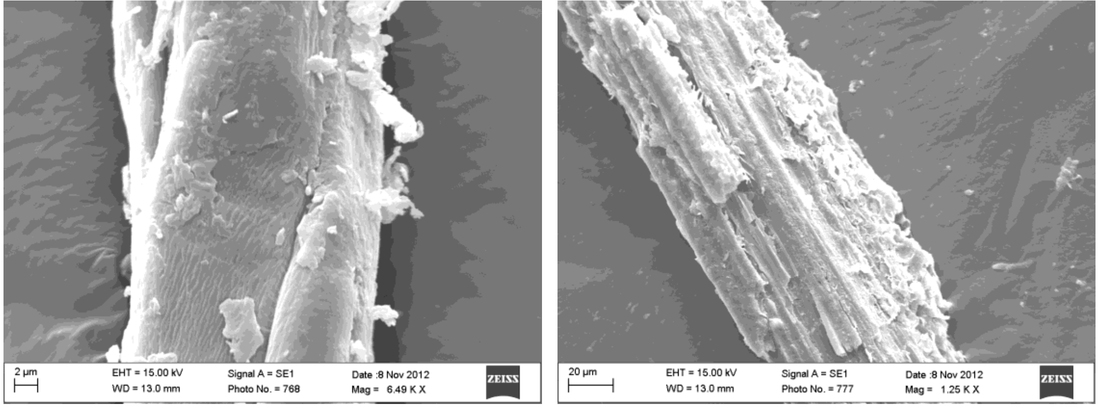
SEM (Scanning Electron Microscope) images of pure cellulose fiber, cotton linter, raw kenaf bast and switchgrass were shown in figure 2.19. SEM images of pretreated kenaf bast fiber and switchgrass fiber were shown in figure 2.20. AFM (Atomic Force Microscope) images of CNWs obtained from all materials were shown in figure 2.21.

For both kenaf bast and switchgrass, raw fibers had rougher surfaces and larger diameters than pretreated fibers. Fiber surface became smoother with the removal of lignin, hemicellulose and ash; small fibers in bundles were released due to the broken-down of cell wall which was mainly composed of lignin.

The lengths of CNWs were in a range from 100 ~ 300 nm, and the diameters ranged from 10 ~ 30 nm. The aspect ratios ranged from 10 ~ 100, with an average value of 10.

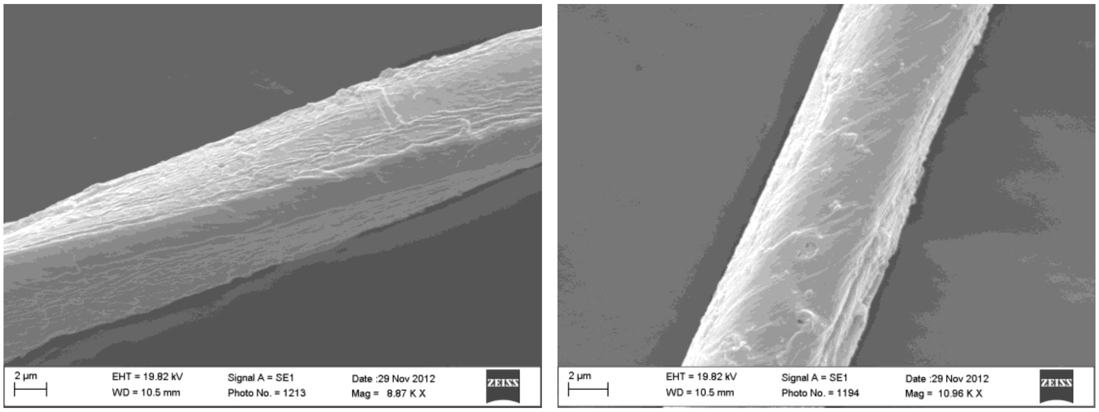


(a) Pure cellulose fiber (b) Cotton linter



(c) Raw kenaf bast fiber (d) Raw switchgrass fiber

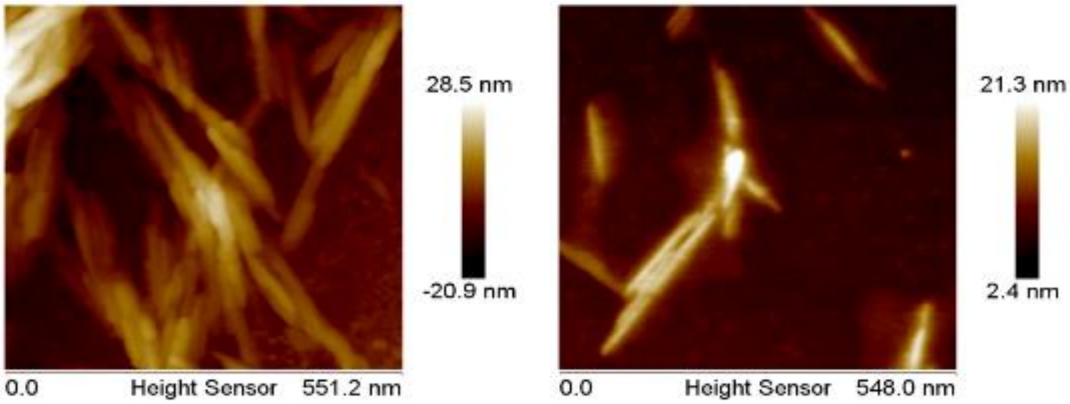
Figure 2.20 SEM images of (a) pure cellulose fiber, magnification = 5.27K X; (b) cotton linter, magnification = 5.49K X; (c) raw kenaf bast fiber, magnification = 6.49K X; (d) switchgrass fiber, magnification = 1.25K X



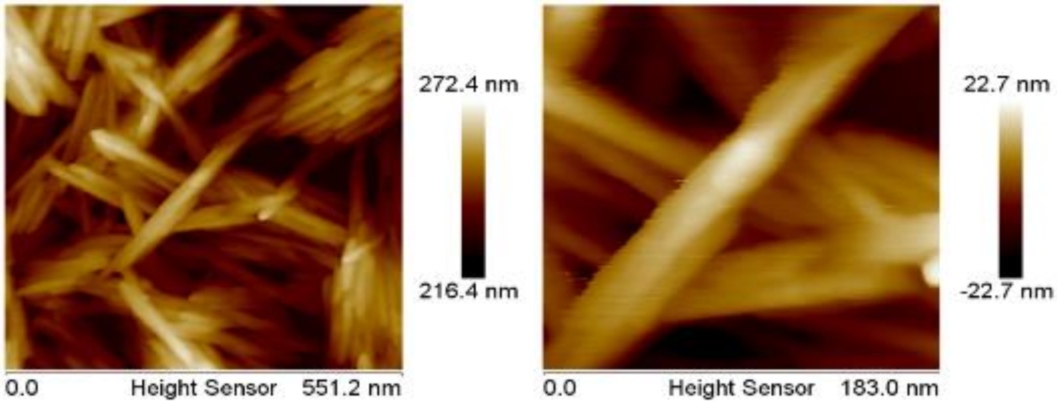
(a) Pretreated kenaf bast fiber (b) Pretreated switchgrass fiber

Figure 2.21 SEM images of pretreated kenaf bast fiber and pretreated switchgrass fiber.

(a) magnification = 8.87K X; (b) magnification = 10.96 KX



(a) CNWs obtained from pure cellulose fibers (b) CNWs obtained from cotton linters



(c) CNWs obtained from kenaf bast fibers (d) CNWs obtained from switchgrass fibers

Figure 2.22 AFM images of CNWs contained from pure cellulose fibers, cotton linters, kenaf bast and switchgrass

2.4 Conclusions

Best pretreatment conditions of raw kenaf bast fibers and switchgrass fibers were determined in order to obtain high yields of α-cellulose. For raw kenaf bast fibers, 99.2% of α-cellulose was obtained after retting with 5 wt. % NaOH at 160°C for 1 hour followed by bleaching process with 4 wt. % H_2SO_4 at 100°C for 40 minutes, which removed all hemicellulose, Klason lignin and ash. For raw switchgrass fibers, a highest yield of 97.2% α-cellulose was obtained with the same retting conditions, and 4 wt. % H_2SO_4, 80°C and 60 minutes beaching, where only 0.1% Klason lignin remained.

After pretreatment, a research of best hydrolysis conditions combined with sulfuric concentration, temperature and period was conducted to obtain maximum yields of CNWs from different materials. For pure cellulose fibers, 55 wt. % H_2SO_4 at 55°C for 3 hours was determined, which produced 83.4% CNWs. For cotton linters, 55 wt. % H_2SO_4 at 60°C for 4 hours was selected to produce 80.8% yield of CNWs. As regards of kenaf bast fibers and switchgrass fibers, 34.0% and 25.3% of raw materials were converted into CNWs when hydrolyzed with 60 wt. % H_2S0_4°C at 55 for 4 hours.

To further maximize biomass-based CNWs yields from discussed sources, orthogonal experiments were conducted. A maximum CNWs yield of cotton linters was determined as of 85.4% with 52 wt. % H_2SO_4 hydrolysis at 57°C for 3.5 hours; 34.1% for kenaf bast fibers and 26.8% for switchgrass fibers were obtained respectively with 57 wt. % H_2SO_4 at 58°C for 4.5 hours and 57 wt. % H_2SO_4 at 55°C for 4 hours.

The most efficient hydrolysis conditions were accomplished by orthogonal experiments as well. Sulfuric acid concentration pays the most tribute to affect CNWs yields, and reaction temperature and period contribute less. Due to different sources of materials, the optimal value of each factor varies.

CHAPTER III

CATALYTIC PERFORMANCE OF CELLULOSE NANOWHISKERS AS CATALYST SUPPORT IN CONVERTING SYNGAS TO BIOFUELS

3.1 Background

People today rely on fossil fuels for modern world's industrialization and motorization in many aspects. However, as a nonrenewable energy source, increasing energy demand has led to the exhaustion of fossil fuels. By combusting fossil fuels, many negative effects to the environment have also been found including land desertification, melting glaciers, rise of sea level and etc. (Gullison et al., 2007). In order to fulfill the requirement of rapid energy consumption, hunting for alternative, renewable, and environmental friendly energy sources is becoming an imminent challenge. In this case, biofuels, as one of the most promising resource with their renewability, biodegradability, and acceptable exhaust gas, have caught global attention to replace fossil fuels in the recent decade (Bhatti et al., 2008).

Biofuels converted from syngas usually refer to value-added mixed alcohols, such as ethanol, propanol and butanol, and higher-value chemicals (Street & Yu, 2011). Both noble metals, such as Rh, and non-noble metals have been studied as heterogeneous catalysts to convert syngas to biofuels (Fan et al., 2009; Fang et al., 2009; Mei et al., 2010; Mo et al., 2009; Subramanian et al., 2010). Though noble metals-based catalysts show good catalytic performance, they are not available for industrial applications due to commercial reasons. However, major non-noble metal-based catalysts including Cu, Fe, Mo, and Co are also used for biofuels conversion from syngas (Lu et al., 2012). In this study, we choose the most widely used Fe as the catalyst of conversion process.

As it is elaborated in Chapter I, porous carbons have been researched as one of the most desirable catalyst supports in virtue of their higher surface area (Kim et al., 2012). Several biomass materials were used to produce porous carbons (Zhang et al., 2008). For example, natural cellulose fibers as catalyst support were researched in CO_2 reforming of CH_4 and resulted in high catalytic activity and long-term stability (Kim et al., 2012).

3.2 Materials

Cellulose nanowhiskers (CNWs), prepared from four different varieties of raw materials (pure cellulose fibers, cotton linters, kenaf bast, and switchgrass) in Chapter II, were used as experimental catalyst supports. Pure cellulose fibers prepared catalyst support was studied as the control group. Concentrated sulfuric acid (H_2SO_4, 95 ~ 98 %, ASC reagent, Sigma-Aldrich) and nitric acid (HNO_3, 70%, ASC reagent, Sigma-Aldrich) were appropriately diluted and used as surface oxidation chemicals. Commercially available Iron(III) nitrate nonahydrate [$Fe(NO_3)_3 \cdot 9H_2O$, ≥98%, ASC reagent, Sigma-Aldrich] was applied as a *Fe* precursor. Pure syngas of 1:1 (v/v) CO/H_2 was injected to react with catalyst.

3.3 Methods

3.3.1 Catalyst preparation

CNWs or cellulose fibers were first carbonized in a tube installed muffle furnace at 900°C for 3 hours. The furnace was heated up at a speed of 1°C/min. Next, for surface oxidation, carbonized CNWs or cellulose fibers were immersed in a 1:1 (v/v) H_2SO_4 (98 wt. %) and HNO_3 (60 wt. %) mixed solution for 1 hour. Mixed solution was then washed to neutral with distilled water using a centrifuge machine. Dried the resultant carbonized samples in an oven for 12 hours at 110°C.

For carbonized samples to be prepared as catalyst supports, a conventional wet-impregnation method was introduced. Immigrated Fe^{3+} [$Fe(NO_3)_3 \bullet 9H_2O$] as a precursor in the carbonized samples solution and dispersed the solution using ultrasound treatment for 30 minutes. The loading of Fe^{3+} was 20% (w/w). After the ultrasound treatment, carbonized samples with Fe^{3+} were filtered and dried in oven at 60°C. Catalyst supports and precursor were finally calcined in a N_2 atmosphere at 450°C for 6 hours to obtain CNWs or pure cellulose fibers supported Fe^{3+} catalyst (Kim et al., 2012).

3.3.2 Catalytic activity

The catalytic activity of catalysts was performed in a stainless tube (12.7 mm inner diameter) using a fixed-bed reactor. Before each reaction, each catalyst was reduced using flowing pure syngas [1:1 (v/v) CO/H_2] at ambient pressure. Heated up the reactor to 350°C at 1°C/min, held the temperature at 350°C for 10 hours, and then lowered the temperature to 100°C. The syngas flow rate was set up to 50ml/min throughout the reduction process.

Gradually increased the reactor pressure to 300 psi within 1 ~ 2 hours, and then heated the system up to target temperatures at a speed of 1°C/min. A gas hourly space velocity (GHSV) of 1000 h^{-1} was maintained (Lu et al., 2012).

Conversion rate is calculated as the mole percentage of consumed CO and H_2 converted to products (3.1 and 3.2). Selectivity is the percentage of given product converted from total CO (3.3).

$$CO\ conversion\ rate = \frac{CO_{in} - CO_{out}}{CO_{in}} \times 100\% \tag{3.1}$$

$$H_2\ conversion\ rate = \frac{H_{2\,in} - H_{2\,out}}{H_{2\,in}} \times 100\% \tag{3.2}$$

$$Selectivity = \frac{Given\ product\ converted\ from\ CO}{Total\ CO} \times 100\% \tag{3.3}$$

3.4 Results and discussion

Catalytic performance of carbonized CNWs supported Fe^{3+} was measured for converting syngas to biofuels. The result was compared with that obtained by using a cellulose fibers supported Fe^{3+} model catalyst. Conversion rates of CO and H_2, and selectivity of CO_2, CH_4, C2-C3 product, and C4+ product were analyzed by a gas chromatograph (GC, 7890A, Agilent) connected to the outlet of the reactor. Each test was repeated three times and the average value was recorded as the experiment result.

3.4.1 Catalytic performance of cellulose supported Fe^{3+} catalyst

Figure 3.1 shows the conversion rates of carbon monoxide (CO) and hydrogen (H_2) obtained from non-treated cellulose fibers supported Fe^{3+} catalyst over different periods at 280°C. The initial conversion rates at 10th hour were about 21.2% of CO and 10.5% of H_2, and catalytic activity slowly increased by 2% of CO conversion and 1% of H_2 conversion over 60 hours reaction time.

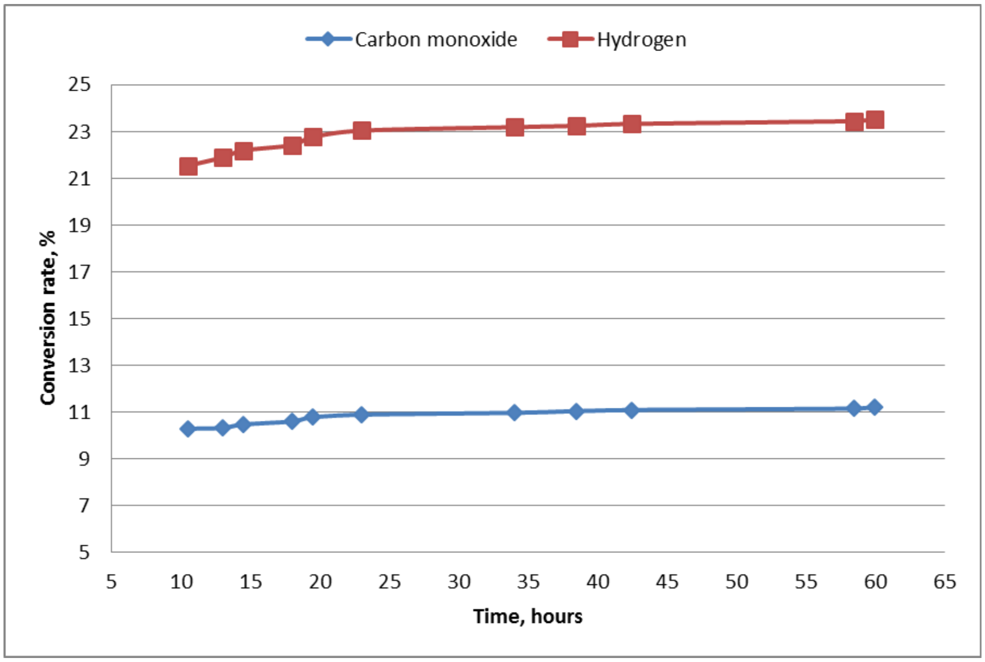


Figure 3.1 Conversion rates of carbon monoxide and hydrogen via non-treated cellulose fibers supported Fe^{3+} catalyst at different periods

Figure 3.2 shows the selectivity of CO_2, CH_4, C2-C3 product and C4+ product obtained by non-treated cellulose fibers supported Fe^{3+} catalyst over different periods. With the increasing of reaction time, the selectivity of CH_4 and C2-C3 product slowly increased by about 2% from initial over 60 hours reaction. For C4+ product, though the maximum selectivity of 59.7% occurred at 40th hour, there was no significant change due to 1% increase with 40 hours reaction.

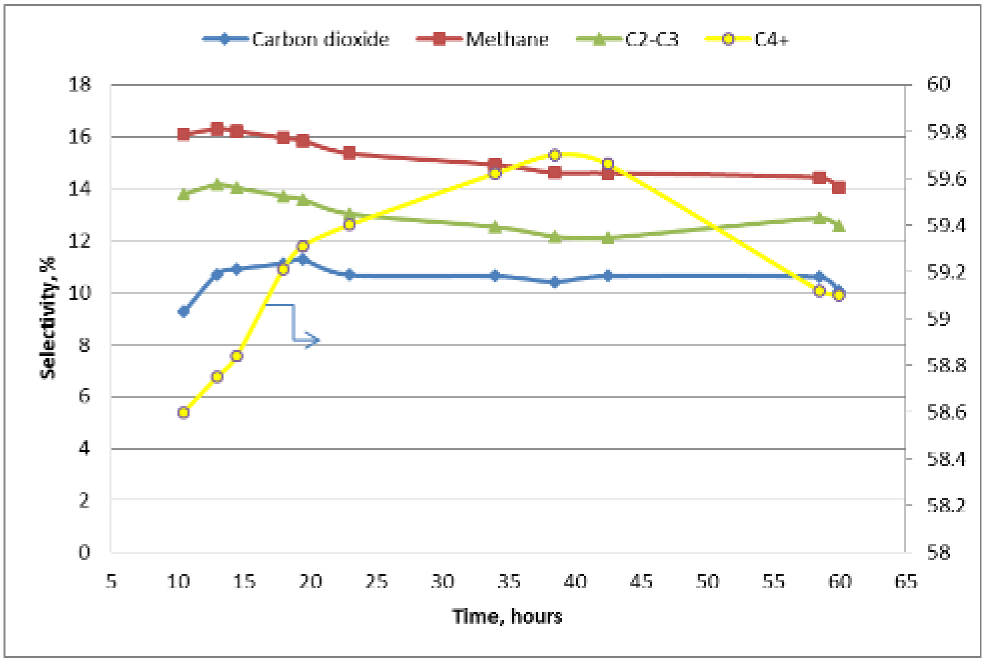


Figure 3.2 Selectivity of carbon dioxide, methane, C2-C3 product, and C4+ product via non-treated cellulose fibers supported Fe^{3+} catalyst

3.4.2 Catalytic performance of CNWs supported Fe^{3+} catalyst

In the case of catalytic performance of CNWs supported Fe^{3+} catalyst over different periods, conversion rates and selectivity are shown in figures 3.3 and 3.4. The initial CO conversion rate was about 21%, and increased by 6% after 12 hours reaction. For the conversion rate of H_2, 2% was increased from its initial of 9.6%. Meanwhile the selectivity of CO_2 slightly increased by 1.5 ~ 2%, CH_4 and C2-C3 products slightly decreased by less than 1%, and C4+ product reached 61% selectivity.

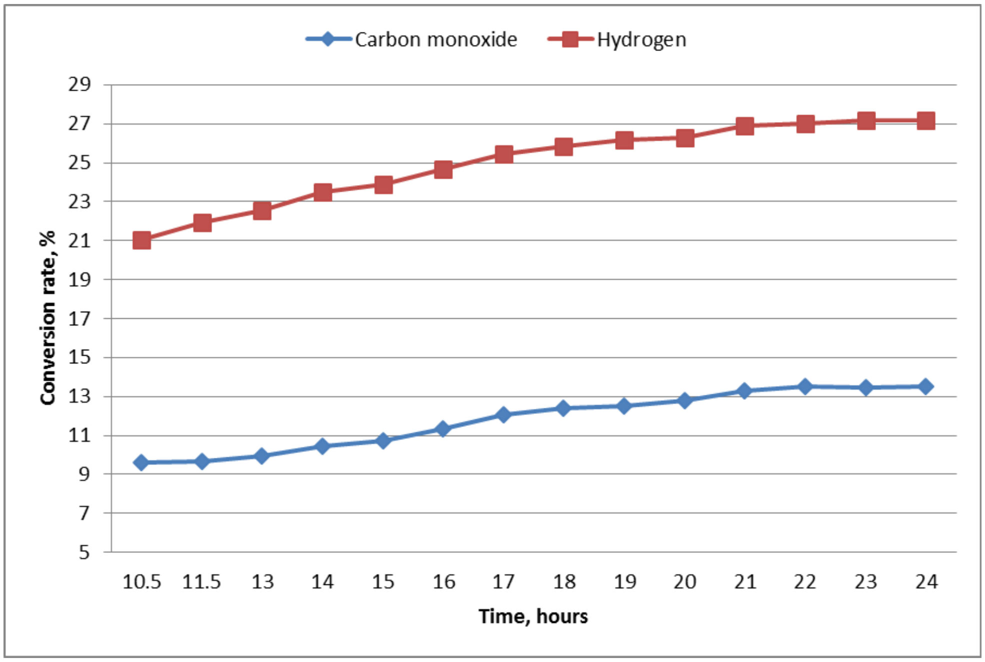


Figure 3.3 Conversion rates of carbon monoxide and hydrogen via CNWs supported Fe^{3+} catalyst

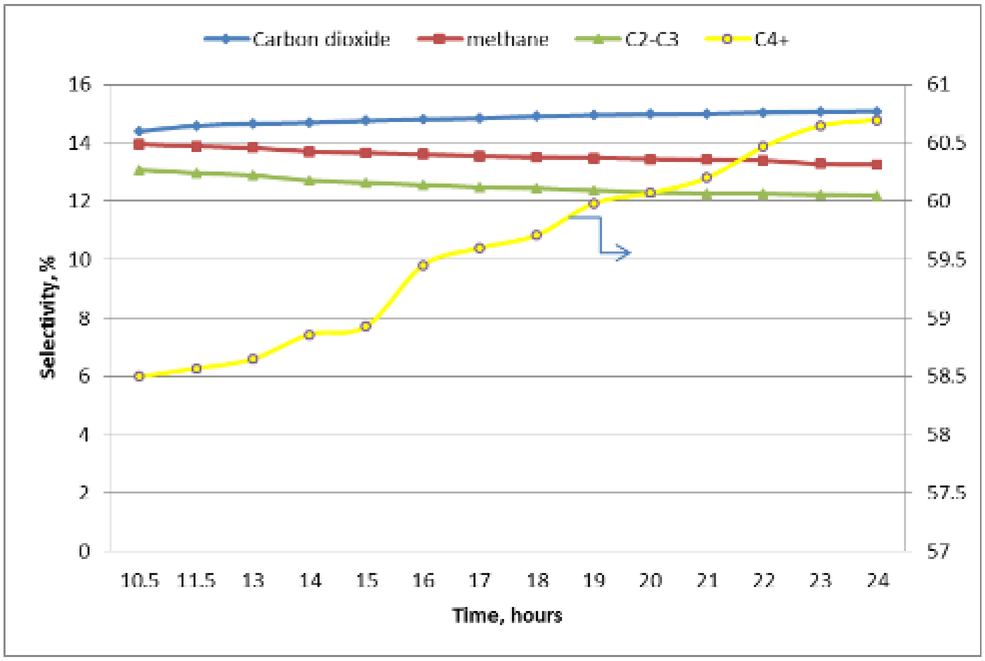


Figure 3.4 Selectivity of carbon dioxide, methane, C2-C3 product, and C4+ product via CNWs supported Fe^{3+} catalyst

Since there were no significant variations for conversion rates and selectivity with reaction periods change, temperature effect was conducted. Four reaction temperatures (280, 290, 300, and 310°C) were chosen. Figure 3.5 shows the conversion rates of CO and H_2 at different reaction temperatures obtained from carbonized CNWs supported Fe^{3+} catalyst. CO conversion increased by over 60 % from initial of 22.5% at 280°C to 83.37% at 310°C, while H_2 conversion increased from 37.4% to 72.1%. Figure 3.6 indicated that reaction temperatures also exert an obvious influence on the selectivity of CO_2 and C4 products. CO_2 selectivity increased by over 20% from initial 19% through 280°C to 300°C, and C4+ product decreased by about 15% during this temperature interval. With the increasing of temperature to 310°C, only slight changes were observed. For methane and C2-C3 product, only slight influence of selectivity (1.5% and 3%) occurred when the temperature was increased from 280°C to 290°C, then selectivity remained steady as temperature went up.

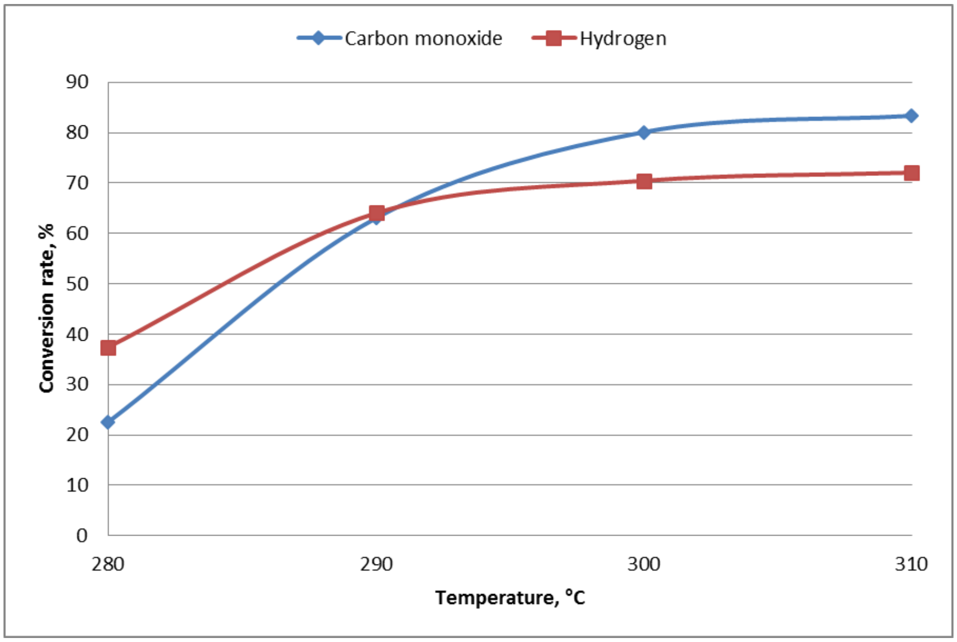


Figure 3.5 Conversion rates of carbon monoxide and hydrogen at different temperatures (280, 290, 300, and 310°C) via carbonized CNWs supported Fe^{3+} catalyst

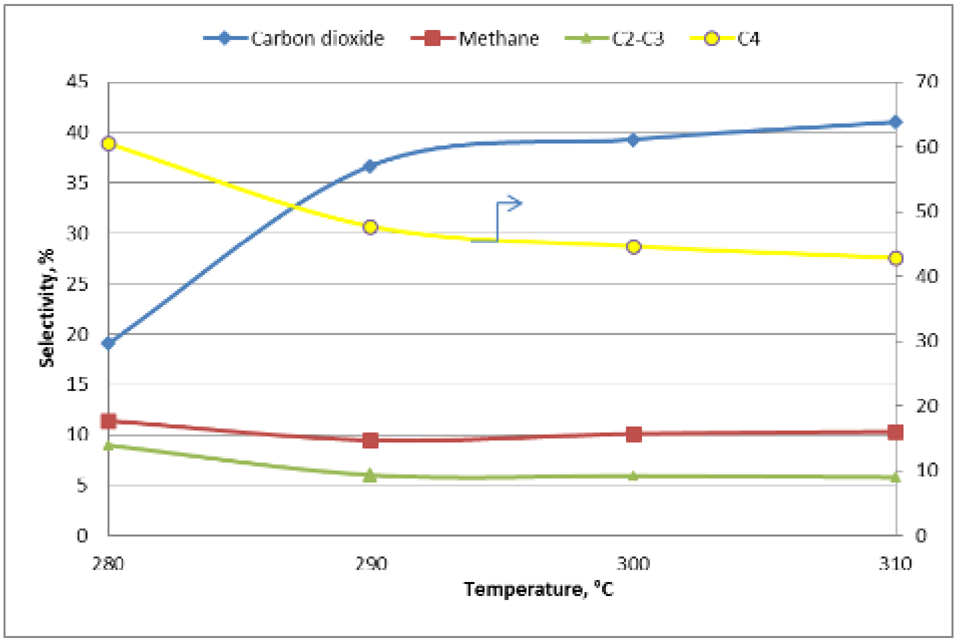


Figure 3.6 Selectivity of carbon dioxide, methane, C2-C3 product, and C4+ product at different temperatures (280, 290, 300, and 310°C) via carbonized CNWs supported Fe^{3+} catalyst

3.5 Conclusions

Catalytic performance of carbonized CNWs supported Fe^{3+} catalyst was studied with reaction period and temperature variation. In contrast with cellulose fibers supported Fe^{3+} catalyst at the same reaction temperature of 280°C; it took shorter time, 21 hours, for CNWs supported Fe^{3+} catalyst to stabilize. The selectivity of C4+ product performed by CNWs supported Fe^{3+} catalyst was kept at a higher level of over 60% for longer time; however cellulose supported catalyst got inactivated quickly after reaching its peak.

Temperature influence at four levels (280, 290, 300, and 310°C) for CNWs supported Fe^{3+} catalyst was conducted as well. At 310°C, CO and H_2 could reach their peak conversion rates of 83.4% and 72.1%, while the maximum selectivity of CO_2 was 41.1%.

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