

Electronic Thesis and Dissertation Repository

8-3-2016 12:00 AM

Fractionation of cornstalk into cellulose and lignin for the production of sodium carboxymethyl cellulose

Tao Shui, *The University of Western Ontario*


Supervisor: Charles(Chunbao) Xu, *The University of Western Ontario*

Joint Supervisor: Takashi Kuboki, *The University of Western Ontario*

A thesis submitted in partial fulfillment of the requirements for the Master of Science degree in Chemical and Biochemical Engineering

© Tao Shui 2016

Follow this and additional works at: <https://ir.lib.uwo.ca/etd>

 Part of the [Bioresource and Agricultural Engineering Commons](#), [Other Chemical Engineering Commons](#), and the [Polymer Science Commons](#)

Recommended Citation

Shui, Tao, "Fractionation of cornstalk into cellulose and lignin for the production of sodium carboxymethyl cellulose" (2016). *Electronic Thesis and Dissertation Repository*. 3959.
<https://ir.lib.uwo.ca/etd/3959>

This Dissertation/Thesis is brought to you for free and open access by Scholarship@Western. It has been accepted for inclusion in Electronic Thesis and Dissertation Repository by an authorized administrator of Scholarship@Western. For more information, please contact wlsadmin@uwo.ca.

Abstract

This thesis project aimed to fractionate cornstalk into cellulose and lignin, and utilize the crude cornstalk-derived cellulose for the production of sodium carboxymethyl cellulose and the lignin for the synthesis of bio-based phenol-formaldehyde resole resins as wood adhesives. In this thesis work, cornstalk was efficiently fractionated into crude cellulose and crude lignin in mixed solvents of acetic acid, formic acid and water at a solid/agent ratio of 1:5 (g/mL) at 80-100 °C for 120-240 min. The best conditions for organosolv fractionation of cornstalk among the test conditions were determined as follows: mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v), HCl as the catalyst, 90 °C and 180 min residence time, where the yield (and purity) of crude cellulose and lignin products were approximate 53% (85%) and 38% (44%), respectively, on the basis of mass of oven-dried cornstalk, and the obtained crude cellulose products have very low residual lignin contents (<4%). The crude cellulose fractionated from cornstalk was further used, after bleaching, as feedstock for the synthesis of sodium carboxymethyl cellulose (CMC). The best molar ratio of the reaction reagents (NaOH/ClCH₂COOH /cellulose) among the test conditions were investigated and determined to be 4.0:2.5:1 and 4.6:2.8:1, or the molar ratio of NaOH/ClCH₂COOH being 1.6-1.64. The CMC products obtained at the best reactants molar ratios have relatively high water solubility and reasonably high viscosity and molecular weights. The average degree of substitution (DS) of these two CMC products obtained at the best molar ratios among the test conditions are 0.57 and 0.85, respectively.

Keywords

Cornstalk, organosolv fractionation, acetic acid, formic acid, crude cellulose, organosolv lignin, bleaching, etherification, sodium carboxymethyl cellulose, water solubility, degree of substitution (DS) .

Acknowledgments

I would like to express my most sincere and special gratitude to my supervisors, Profs. Charles Xu and Takashi Kuboki, as well my colleagues, Dr. Shanghuan Feng and Dr. Yuan, who provided me great guidance and assistance in the course of my thesis project, and I would cherish the two-year wonderful time spent at the Institute for Chemicals and Fuels from Alternative Resources (ICFAR). I want to thank Mr. Gang Chen and Ms. An Li for their assistance in some experimental work of the thesis project. My sincere thanks also go to all of my friends and family members who have supported me with their huge motivation and encouragement throughout my thesis study. Moreover, the funding from Ontario Ministry of Agriculture, Foods and Rural Affairs (OMFRA), Natural Sciences and Engineering Research Council of Canada (NSERC), and Western Engineering Scholarship is gratefully appreciated.

Table of Contents

Abstract.....	i
Acknowledgments.....	ii
Table of Contents.....	iii
List of Tables.....	vi
List of Figures.....	vii
1 Introduction.....	1
1.1 Background.....	1
1.2 Literatures review.....	2
1.2.1 Biomass Fractionation Process.....	2
1.2.2 Applications of cellulose for sodium carboxymethyl cellulose (CMC) ...	11
1.2.3 Use of lignin for bio-based phenol–formaldehyde resole resin.....	14
1.2.4 Summary of the literature.....	15
1.3 Objectives.....	16
2 Organosolv fractionation of the cornstalk in to lignin and cellulose.....	18
2.1 Materials.....	18
2.2 Methods.....	19
2.2.1 Fractionation procedure.....	19
2.2.2 Characterizations of crude cellulose and lignin products.....	20
2.3 Results and discussions.....	23
2.3.1 FTIR spectra of cornstalk and crude cellulose derived from the cornstalk.....	23
2.3.2 Effects of fractionation solvent composition.....	24
2.3.3 Effects of catalysts.....	27
2.3.4 Effects of temperature.....	29

2.3.5	Effects of residence time.....	32
2.4	Project summary	34
3	Synthesis of the sodium carboxymethyl cellulose by using bleached cellulose	37
3.1	Materials and Methods.....	37
3.1.1	Materials	37
3.2	Methods.....	37
3.2.1	Cornstalk fractionation.....	37
3.2.2	Crude cellulose bleaching	38
3.2.3	CMC synthesis	38
3.3	Characterizations.....	40
3.3.1	Characterizations of crude cellulose	40
3.3.2	Characterizations of CMC products.....	41
3.3.3	Water solubility of the CMC products.....	41
3.3.4	Structure, viscosity and molecular weight of the CMC products	42
3.3.5	Average degree of substitution for the CMC products	42
3.4	Results and discussion	43
3.4.1	Characterizations of bleached crude cellulose	43
3.4.2	Effects of the reactants molar ratio on water solubility of the CMC products.....	44
3.4.3	FT-IR analysis of the CMC products.....	47
3.4.4	SEM micrographs of the CMC products	50
3.4.5	¹ H-NMR spectra of the CMC products.....	51
3.4.6	Physical and chemical properties of the CMC products.....	52
3.5	Project Summary.....	56
4	Conclusions and Recommendation for future works	57
4.1	Conclusions.....	57

4.2 Recommendation for Future works	58
References.....	60
Curriculum Vitae	71

List of Tables

Table 1.1: Comparisons of lignosulfonates, Kraft lignin and organosolv lignin.....	5
Table 1.2: Conditions for typical organosolv processes	6
Table 1.3: Properties of CMC from different types of cornstalks	13
Table 2.1: Proximate composition and chemical components in oven-dried cornstalk feedstock	18
Table 2.2: Comparison the invented process and the existing organosolv fractionation process employing organic acid(s) as the reaction medium	35
Table 3.1: Yield and composition of oven-dried bleached crude cellulose	43
Table 3.2: Appearance and viscosity of the CMC products	53
Table 3.3: Molecular weight and DS of the bio-based CMC	54

List of Figures

Fig. 1.1: Molecular structure of sodium carboxymethyl cellulose (DS=1)	12
Fig. 2.1: Block diagram of the experimental procedures for organosolv fractionation of Cornstalk	20
Fig. 2.2: FTIR spectra of cornstalk and various crude cellulose products	23
Fig. 2.3: Effects of fractionation solvent composition on the yields of crude cellulose and crude lignin products from the operations without catalyst at 90 °C for 180 min (The ratio as shown on the horizontal axis is the volumetric ratio of acetic acid/formic acid/water)	25
Fig. 2.4: Effects of fractionation solvent composition on the purities of crude cellulose and crude lignin products, as well as contents of α -cellulose, hemicellulose and residual lignin in the crude cellulose products from the operations without catalyst at 90 °C for 180 min (ratio on the horizontal axis is the volumetric ratio of acetic acid/formic acid/water).....	26
Fig. 2.5: Effects of catalysts on the yields of crude cellulose and lignin products from the fractionation operations at 90 °C for 180 min in mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v).....	27
Fig. 2.6: Effects of catalysts on the purity of crude cellulose and lignin, contents of α -cellulose, hemicellulose and residual lignin in the crude cellulose products from the fractionation operations at 90 °C for 180 min in mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v).....	29
Fig. 2.7: Effects of temperature on yield and purity of the crude cellulose products obtained the fractionation operations in mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v) for 180 min with HCl catalyst.....	30
Fig. 2.8: Effects of temperature on the purity of the crude cellulose and crude lignin products, contents of α -cellulose, hemicellulose and residual lignin in the crude cellulose	

products obtained the fractionation operations in mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v) for 180 min with HCl catalyst.....	31
Fig. 2.9: Effects of residence time on the yields of crude cellulose and crude lignin products obtained the fractionation operations in mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v) at 90°C with HCl catalyst.....	33
Fig. 2.10: Effects of residence time on purity of the crude cellulose and crude lignin products, and the contents of α -cellulose, hemicellulose and residual lignin in the crude cellulose products obtained the fractionation operations in mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v) at 90°C with HCl catalyst	34
Fig. 3.1: Block diagrams of the experimental procedure for synthesis of CMC with bleached cornstalk-derived cellulose	39
Fig. 3.2: Effects of the alkali agent (NaOH) on water solubility of the CMC products obtained at various molar ratios of NaOH/ClCH ₂ COOH/cellulose in the range of (4~5): 2: 1.	45
Fig. 3.3: Effects of etherifying agent (ClCH ₂ COOH) on water solubility of the CMC products obtained at various molar ratios of NaOH/ClCH ₂ COOH/cellulose in the range of 4: (2.0~3.0): 1 (a) or 4.6: (2.0~2.8): 1 (b).....	46
Fig. 3.4: FTIR spectra of the CMC products obtained at various molar ratios of NaOH/ClCH ₂ COOH/cellulose in the range of (4~5): 2: 1 (a), 4: (2.0~3.0): 1 (b) and 4.6: (2.0~2.8): 1 (c).	49
Fig. 3.5: SEM micrographs of powders: (a) CMC products at the feedstock molar ratio of 4.0:2.5:1; (b) CMC products at the feedstock molar ratio of 4.6:2.8:1; (c) bleached crude cellulose	50
Fig. 3.6: ¹ H-NMR spectra of the CMC products	52
Fig. 3.7: Dependency of viscosity of the CMC-water solution on the CMC concentration (wt%) measured at 25 °C, 101.3 kPa and 100 s ⁻¹ shear rate	54

1 Introduction

1.1 Background

Corn has become one of the largest agricultural products in Canada. In 2015, around 2035000 acres of grain corn were harvested in Ontario (about 8.8 tons), Canada¹. As a crop residue with limited applications as an organic fertilizer, silage for livestock and energy source for heat and electricity, cornstalk has received less attention by far. Cornstalk is a typical lignocellulosic biomass, consisting of lignin (16-20%), cellulose (30-35%), hemicellulose (25-30%), ash, extractives and protein. Lignin is a complex amorphous polymer consisting of phenylpropanes, while cellulose, the dominant structural polysaccharide in cornstalk cell walls, is a linear polymer of β (1 \rightarrow 4)-linked D-glucopyranoside monomer units. Cellulose has degrees of polymerization with 5000-7000 glucose monomer units in general cell walls. However, hemicellulose only has a polymerization degree of 200, and it is a heterogeneous polymer of pentoses (xylose, arabinose), hexoses (mannose, glucose, galactose), and sugar acids². Lignin, due to its phenolic nature can be a source of bio-based phenols or polyols for the production of various bio-based materials such as bio-based phenol formaldehyde resins and polyurethane resins^{3,4}. Cellulose can be directly modified for the production of sodium carboxymethyl cellulose or cellulose acetate. Thus, fractionation of lignocellulosic biomass for the production of its chemical components (mainly lignin and cellulose) has attracted increasing interest.

Cornstalk derived cellulose can be a potential cellulose source for carboxymethyl cellulose (CMC), which can be applied as surfactant and thickener in food industry and other necessities (such as toothpaste, laxatives, papers and diet pills). CMC is highly recommended due to the properties of non-toxicity, high water solubility as well as the outstanding light and thermal stability. Nevertheless, the considerable cost of the traditional feedstock (purified cotton cellulose) somewhat restricts the growth of CMC market, hence various inexpensive feedstocks recognized as potential substitutes such

as cornstalk-derived cellulose comes to people's horizon because of their abundant and inexpensive features.

In addition to a potential cellulose source for CMC, cornstalk can be a promising feedstock for the production of lignin, which has long been considered as phenol substitute for preparation of bio-based phenol formaldehyde (BPF) resins/adhesives or bio-polyols for the synthesis of bio-based polyurethane resins/foams. PF resole resin is a highly crosslinked, three-dimension aromatic polymer, linked by C-C or ether bonds. Due to its superb resistance to moisture, excellent heat and light stability, and considerable strength, PF resoles have been widely used as adhesives for manufacture of exterior-grade plywood panels, oriented strand board (OSB) panels and particleboards ⁶. However, high cost of phenol results in high price of the PF resins. Accordingly, exploration for phenol substitute has been attracting increasing academic and industrial interests in recent years. With aromatic structure, free reactive site on ortho positions and hydroxyl group on the C3 side-chain of its molecular structure, lignin has demonstrated to be an active substitute for phenol in the production of BPF resins ⁷.

1.2 Literatures review

1.2.1 Biomass Fractionation Process

By far, various lignocellulosic biomass fractionation processes have been developed, including physical treatment (ball-mill, hydro-thermolysis), chemical treatment (using acids, alkali, organic solvents) and physico-chemical treatment (e.g., steam explosion, ammonia fiber explosion) ⁸. Milled wood lignin (MWL), which is also called Bjorkman lignin, is the product of prolonged milling of wood, followed by extraction in solvents like co-solvents of dioxane and water ⁹. Generally, the addition of solvent during wood milling could prevent changes to the lignin structure ¹⁰. Drawbacks of MWL preparation include a low yield and long isolation duration ¹¹. Regardless of these drawbacks, MWL is still considered to be a representative source of native lignin and

has been widely applied in lignin structure analysis^{12,13}. Recently, cellulolytic enzymes or enzymatic mild acidolysis treatment of wood has become another pathway for native lignin preparation¹⁴. Some studies demonstrated that lignin of this type is more preferred over MWL due to the higher yield and purity^{15,16}.

Acid is also widely applied in lignocellulosic biomass fractionation. Klason method is the most typical lignin quantity determination procedure and the amount of Klason lignin is generally used as the reference to judge the lignin isolation efficiency of other methods. Klason lignin is obtained by depolymerization of cellulose and hemicelluloses in 72% sulfuric acid for 2 hr at 30 °C, followed by hydrolysis of the dissolved polysaccharides in diluted sulfuric acid (3.0%) for 1 hr at 120 °C. The main part of lignin is isolated as an acid insoluble material, which is gravimetrically determined. Acid-insoluble Klason lignin content varies from ca. 29% to ca. 39% in softwoods and from ca. 16% to ca. 22% in hardwoods¹⁷. The other small portion of lignin is sulfuric acid soluble, which is generally determined by UV spectrophotometric measurement using the absorption at 200-205 nm or 280 nm^{18,19,20,21}. As for other dilute acid treatments, large amount of acidic medium results in the decomposition of cellulose, thus those treatments are restricted to lignin production by sacrificing cellulose with sugars as a by-product.

Steam explosion process is a rapid process in which lignocellulose releases individual chemical components through steam impregnation under pressure, followed by rapid pressure release²². However, a large amount of steam usage (16-34 bar) and a high operating temperature (up to 240°C) make this process expensive. Other processes like ionic liquid dissolution are also limited by their high operation costs due to the use of expensive ionic liquids (can be as costly as \$600-1000/kg).

Kraft lignin, liginosulfonates, soda lignin and organsolv lignin are four typical technical lignin that have been commercialized around the world. Kraft pulping is currently the dominant chemical pulping process in the world. Kraft pulping is operated in water under a high pH condition with alkaline reagent such as NaOH or Na₂S at 150-180°C. It

is fairly effective for delignification of lignocellulosic biomass to produce cellulose (pulp) as the main product^{23,24}. Kraft lignin is recovered from the “black liquor” along with most of the hemicelluloses. In a forest bio-refinery, Kraft lignin may be recovered from the black liquor by lowering the pH, which is typically accomplished by bubbling the black liquor with CO₂ captured from the boiler’s flue stack or with mineral acids via the patented processes such as Lignoboost and LignoForceTM. While lowering the pH, a substantial portion of the Kraft lignin in black liquor is precipitated and recovered by filtering and washing²⁵. Currently, Kraft lignin is mainly used as a fuel in recovery boilers to recover the pulping chemicals and supply part of the energy requirement for the pulping process.

Sulfite pulping is carried out between pH 2-12, depending on the cationic composition of the pulping liquor. Most sulfite processes are acidic and use calcium and/or magnesium as the counter-ions. Sulfite lignin is generally soluble throughout the entire pH range so it cannot be readily isolated by simple pH adjustment like Kraft lignin. Thus, recovery of sulfite lignin is commonly done through concentration of the waste liquor after stripping and recovery of the sulfur. Precipitation of calcium lignosulfonate with excess lime (Howard process) is the simplest recovery method where up to 95% of the liquor’s lignin could be recovered. Compared with Kraft lignin, sulfite lignin has a higher average molecular weight (M_w ranging from 1,000 to 140,000 g/mol, and more commonly $M_w = 5,000-20,000$), higher polydispersity, and higher sulfur content (3 - 8 wt%). The high content of sulfonic acid groups makes the sulfite lignin surface-active with binding properties. Due to the nature of the sulfite process, the isolated lignin contains considerable sulfur in the form of sulfonate groups present in the aliphatic side chains. However, the sulfite pulping process is still a potential source of forest bio-refinery lignin because in contrast to Kraft pulping, sulfite pulping generally does not recover pulping chemicals, which makes a lignin-rich black liquor stream more available for utilization of the lignin for chemicals²⁵.

In the recent years, organosolv pulping (fractionation) has become a hot research topic as this process is environmentally friendly and requires relatively mild conditions.

Comparisons of liginosulfonates, Kraft lignin and organosolv lignin are as illustrated in Table 1.1.

Table 1.1: Comparisons of liginosulfonates, Kraft lignin and organosolv lignin

Properties	Liginosulfonates	Kraft lignin	Organosolv lignin
Molecular weight	20, 000-50, 000	2, 000-3, 000	<1, 000
Empirical formula	$C_9H_{8.5}O_{2.5}(OCH_3)_{0.85}(SO_3H)_{0.4}$	$C_9H_{8.5}O_{2.1}S_{0.1}(OCH_3)_{0.8}(CO_2H)_{0.2}$	$C_9H_{8.53}O_{2.45}(OCH_3)_{1.04}$
Average monomer M_w	215-254	180	188
Polydispersity	6-8	2-4	2.4-6.4
Sulfonate (meq/g)	1.25-2.5	0	0
Organic sulphur (%)	4-8	1-1.5	0
Color	Brown	Brown	Brown
Solubility	Soluble in H_2O (at all pH's), Insoluble in organics	Soluble in alkali (pH > 10.5), DMF, methyl cellosolve	Insoluble in water, soluble in alkali and many organics

Different from the processes using inorganic chemicals, organosolv processes employ organic solvents such as dioxane, methanol, ethanol, ethylene glycol, glycerol, acetone, acetic acid or formic acid^{23, 26, 27, 29, 30}. Organosolv processes could retain much of lignin's original structure linked by β -O-4 inter-unit and the lignin can be easily separated from the pulping solvents either by solvent extraction, or precipitation accompanied by distillation to recover the solvents. The obtained organosolv lignin is sulfur-free, of high-purity and low molecular weight (M_w) with relatively narrow M_w distributions, which favor its industrial applications for polymers. Organosolv fractionation involves mixing a lignocellulosic feedstock such as wood chips with an aqueous organic solvent at temperatures ranging from 90 to 220 °C. This causes lignin to break down by hydrolytic cleavage of alpha aryl-ether links into fragments that are soluble in the solvent system. Organosolv fractionation has also demonstrated to be an

effective approach for lignocellulosic biomass pretreatment for hydrolysable and fermentable substrates for bio-ethanol production because of its advantages such as being environment-friendly, low capital investment and high solvent recovery^{31, 32, 33, 34}. Higher boiling-points alcohol solvents can also be used since they have the superiority of lower process pressure, but recovery of the solvents by distillation would be a challenge³⁵. Ethanol has commonly been as the preferred solvent due to its easy recovery. For instance, Pan recovered 79% of the lignin from a woody biomass at 170 °C, with 1.1% w/w H₂SO₄ as catalyst and ethanol-water solvent (65% v/v) for 60 minutes³⁶. Besides, a wide variety of processes using mixed solvents have been developed for organosolv fractionations, including ethanol based Alcell process (aqueous ethanol), acetic acid based Acetosolv process (with the catalysis of an inorganic acid) and Acetocell process, acetic and formic acid based Formacell process, and formic acid and hydrogen peroxide (peroxide acid) based Milox process. Typical organosolv processes and their operating conditions are as listed in Table 1.2.

Table 1.2: Conditions for typical organosolv processes

Organosolv process	Conditions condition				
	Extracting agents	Catalyst	Temp.	Pressure	Time
Alcell ²⁷	50% aqueous ethanol	H ₂ SO ₄ (depends)	160-200 °C	Compressed	120 min
Acetosolv ^{37, 38}	Acetic acid	HCl 0.1%-0.8% based on liquor phase	Boiling point or 120 °C	Atmospheric pressure	180 min
Acetocell ^{39, 40}	80-90% Acetic acid	None	170-190 °C	0.8-1.5 MPa	120-180 min
Formacell ^{41, 42, 43}	75-76.5% acetic acid	formic acid 5-10%	150-175 °C	in autoclave	75-120 min

	and 8.5-10% formic acid				
Milox ²⁷	80-88% Formic acid	H ₂ O ₂ or peroxyformic acid 2%-4% based on feed weight	Boiling point	Atmospheric pressure	60-270 min
Other process ^{44, 45}	Formic acid/acetone (7:3)	None	150 °C	Atmospheric pressure	5-100 min
	50-80% aqueous acetone or phenol	None	150- 200 °C	Atmospheric pressure	30-120 min

Alcell process is an aqueous ethanol based auto-catalyzed pulping technology. In a typical Alcell process, extraction time generally ranges from 40 to 120 min, cooking temperature is from 170 to 200 °C with the aqueous ethanol concentration of 30-70 vol% under compressed pressure^{46, 47}. Cleavage of β -O-4 linkages and ester bonds (acetyl and coumaryl residues) are the major mechanisms of delignification¹². The solubility of Alcell lignin in aqueous ethanol varies with ethanol concentration, specifically it increases significantly as ethanol concentration increases up to 50% or 65%, then increases slowly until the maximum solubility is reached at the ethanol concentration of about 70%, whereas a further increase in the ethanol concentration would result in a slight decrease in the lignin solubility⁴⁸. Although aqueous ethanol with an ethanol concentration over 50% is favorable for solubilizing lignin, 50% aqueous ethanol is generally preferred because aqueous ethanol with a lower or higher ethanol concentration than 50% may cause lignin precipitation on the fiber surface^{49, 50} which make the lignin recovery difficult. Alcell process produces a large amount of

high quality lignin, which is relatively pure, with a low molecular weight and abundant reactive groups, primarily unaltered and less condensed than other types of lignin⁵¹. Temperature exerts important effects on the Alcell delignification process, followed by pressure, and the best results with respect to delignification extent were obtained with 50% aqueous ethanol at 190 °C and 16 MPa⁵². Alcell pulping process had been industrially demonstrated at the New Castle facility in Canada at the operational conditions: 50% (w/w) ethanol/water at around 195 °C, and nitrogen pressure around 400 psi. The actual cooking time required for the Alcell pulping process is a function of pH, temperature, alcohol concentration and type of woody biomass feedstock¹².

Organic acids especially acetic acid and formic acid have been applied in lignocellulosic biomass fractionation because of their close Hildebrand's solubility to lignin, which favors the delignification of lignocellulosic biomass⁵³. Xu²⁷ fractionated wheat straw in aqueous alcohol or aqueous organic acid solvents with a liquor/solid ratio of 20:1 (mL/g) at 85 °C for 4 hours. Aqueous organic acids were found to be more effective than the aqueous organic alcohols for delignification of wheat straw.

Acetosolv delignification is an acetic acid based process. Different from the Alcell process, Acetosolv process is generally performed at acetic acid's boiling point of atmospheric condition, and the acetic acid concentration is normally 60-90%, cooking time ranges from 60 min to 180 min, and inorganic acid (e.g., hydrogen chlorite) is generally used as the catalyst (the specific dosage of acid depends on types of acid and the feedstock)^{36, 37, 40}. Hydrolysis of α -aryl ether bonds is the dominant reaction during acetosolv delignification and the feedstock is generally fractionated into pulp, lignin, and hemicellulose (mainly monosaccharides). In a typical Acetosolv process, as much as 95% of the lignin could be recovered through phase separation of the spent liquor by adding water. Generally, increasing pulping time and acetic acid concentration could improve the solubility of acetosolv lignin in some solvents such as dimethyl sulfoxide, pyridine and dioxane. In a study for delignification of *Pinus pinaster* wood in boiling acetic acid solution at atmospheric pressure, acetic acid concentration was found to be the primary factor affecting the delignification degree and that a high concentration

(90%) significantly enhanced delignification. However, when the degree of delignification reached a value around 90%, the selectivity decreased considerably due to lignin condensation⁵⁴.

Another acetic acid based fractionation is the Acetocell process, which was developed by Gottlieb and his co-workers⁵⁵. Acetocell process is generally performed with 80-90% acetic acid at a cooking temperature of 170-190 °C for 2-3 hours under 0.8-1.5 MPa. Combination of formic acid and acetic acid was found to favor lignocellulosic biomass fractionation by promoting the cleavages of the linkages between lignin and carbohydrates^{56,57}. Formacell process is a formic acid based delignification process, which is generally conducted in the mixed solvents of acetic acid and formic acid (containing formic acid of a 5-10%) at 170 °C in autoclaves^{41,42}. Fractionation of rice straw via the Formacell process in 90% formic acid-water solution at 100 °C for 60 min resulted in 85% lignin removal⁵⁸. In the Formacell processes, higher reaction temperatures and prolonged reaction times could lead to a continuous increase in lignin yield. During both Acetosolv and Formacell processes, wood or non-woody biomass feedstocks can be simply fractionated to pulp, lignin and hemicellulose degraded products, making the full utilization of feedstock possible.

Milox process is based on the action of formic acid or the corresponding peroxy acid, which could be accomplished in 80% formic acid or peroxyformic acid. In the Milox system, formic acid shows capability of solubilizing lignin and extractives, and breaking down the hemicellulose chains. Peroxyformic acid causes oxidative depolymerization of lignin, rendering the lignin more hydrophilic and thus enhances its solubility⁵⁹. Typical Milox process could be a one-step process⁶⁰, or a multiple-step process (includes two-step process and three-step process). In a typical two-step Milox process, delignification is first carried out in 80-90% formic acid at the boiling point temperature for 1.5 h, then 2 wt% H₂O₂ with respect to raw material is added for further delignification treatment at 80 °C for 3 hr^{27,61}. Two-step Milox process was found to be more suitable for agricultural residues. In a typical three-step Milox process, the first step involves the feedstock's reaction in a medium containing water, formic acid and

hydrogen peroxide, in which peroxyformic acid is generated *in situ* through an equilibrium reaction between formic acid and hydrogen peroxide. Also during the process, electrophilic H_3O^+ ions are formed and then react with lignin through ring hydroxylation, oxidative ring opening, substitution of side chains, cleavage of beta-aryl ether bonds and epoxidation⁶². In the second stage, the temperature is raised and is kept constant for a given time, when main delignification occurs in this stage due to the hydrolysis of beta-aryl ethers. In the third stage, the delignified solid phase from the first two stages treatments is reacted again with formic acid and hydrogen peroxide, which again results in in-situ generation of peroxyformic acid, which contributes to dissolve the lignin remaining in pulp after the second stage⁶³. Compared with acetosolv lignin, Milox lignin was found to have a higher content of methoxyl and phenolic hydroxyl group, a lower glass transition temperature (T_g)⁶¹.

In addition to above organic solvents, any other organic solvents that are theoretically capable of dissolving lignin or lignin oligomers can be used for lignin isolation. So far, many other co-solvents have been used as lignin isolation reagents, such as methanol/water/NaOH⁶⁴, formic acid/acetone⁴⁴, water/aqueous acetone (accomplished in two steps, where the first step was conducted in hot water, and the second step was accomplished in aqueous acetone)⁶⁵, ethanol/acetone⁶⁶, aqueous butanol⁶⁷, aqueous dioxane^{65,68}, etc. For one specific biomass, delignification degree strongly depends on the solvents used. For delignification of almond (*Prunus amygdalus*) shells, the highest delignification degree could be obtained in aqueous acetone, aqueous ethanol and aqueous 1, 4-dioxane of 75% vol. concentration, respectively, at 210 °C for different delignification durations. For aqueous acetone and aqueous ethanol, the optimal extracting time was reported to be 40 min, while for aqueous 1, 4-dioxane it was 25 min⁶⁸.

1.2.2 Applications of cellulose for sodium carboxymethyl cellulose (CMC)

Sodium carboxymethyl cellulose is a modified polysaccharide that is water-soluble, and anionic⁷⁰. It is an anionic linear polymer in which the original H atom of cellulose hydroxyl group is replaced by carboxymethyl substituent ($-\text{CH}_2-\text{COO}-$)^{71, 72}. Through the conversion of alkali cellulose swollen in aqueous NaOH and a surplus of an organic solvent with monochloroacetic acid or its sodium salt, CMCs with different degree of substitution (generally in the range 0.5 - 1.4 for commercial products) can be obtained⁷³. The degree of substitution (DS) is defined as number of caboxymethyl groups instead of hydroxyl (-OH) group on cellulose polymer which has a maximum value of 3⁷⁴. Hydroxyl groups in cellulose usually replaced by carboxymethyl groups in the order of C6>C2>C3^{75, 76, 77}. Purified CMC, a white- to cream-colored powder, has major contribution in food, pharmaceutical, detergents and coatings. CMC can also be applied for paper or textile improvement⁷⁴.

The molecular structure of sodium carboxymethyl cellulose (DS=1) reaction is shown in Fig. 1.1 for the CMC with the DS < 0.4, it is swelled but insoluble in water, while for DS of more than 0.4, CMC is fully soluble with its hydro-affinity, which increases with the raise of DS⁷⁸.

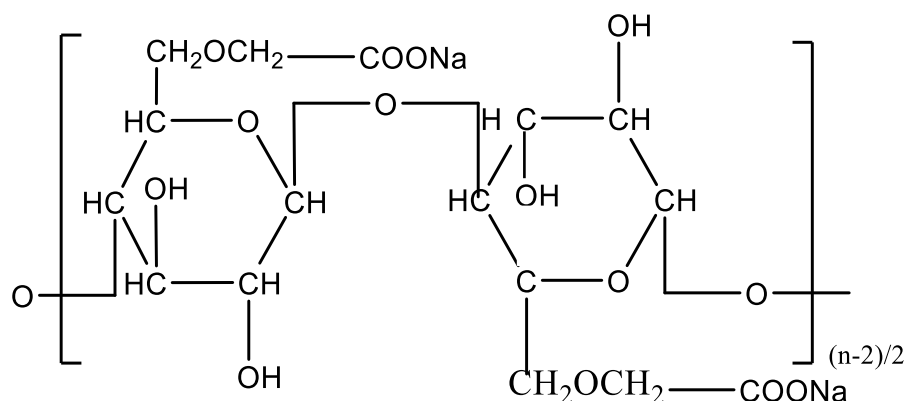


Fig. 1.1: Molecular structure of sodium carboxymethyl cellulose (DS=1)

In the traditional CMC industry, cotton is bleached with sodium chlorite or boiled in an aqueous solution containing sodium hydroxide and nonionic wetting agent before using. Degradation process was then applied on the purified cotton in order to control the substitution degree of final products during the synthesis process. In the study of *Hebeish et al.*⁷⁹, cotton-based carboxymethyl cellulose was synthesized by applying NaOH solution in sequential reactions with monochloroacetate (MCA) at desired condition. The maximum degree of substitution of 0.7 was achieved in 40% MCA and 30% NaOH⁷⁴. However, the high cost of cotton as well as the complex processes conflicts with the increasing demand of CMC. Thus, several other cellulose sources have been tested for the cost-effective CMC production.

In the study of *Mario et al.*⁷⁰, banana pseudo, known as a potential cellulose source, was utilized for CMC synthesis: Banana pseudo was dried, ground, extracted with 8% NaOH and then bleached with 5% NaOCl before synthesis. Optimal degree of substitution (DS), viscosity, purity and crystallinity, i.e. 0.75; 4033 cps; 98.23% and 38.33% respectively, were achieved through alkalization using 15% NaOH and etherification using 1.2 g (w/w) sodium MCA. Sugar beet pulp can be also applied for 0.6670 DS CMC production using isobutyl alcohol as the solvent medium. (30% NaOH, 3.0g sodium MCA for 6.5g mixture)⁸⁰. What's more, high purity cellulose pulp obtained from Milox pulping of *Eucalyptus globulus* wood has been also used for CMC preparation in a heterogeneous medium. The maximum average DS (1.26) was obtained

when a NaOH/cellulose mole ratio of 4.8 and a MCA/cellulose mole ratio of 2.0 were applied⁸¹. As reported by *Asep et al.*⁸², CMC with a DS value as high as 1.76 can be prepared using isobutyl-ethanol mixture (80% ethanol and 20% isobutanol) as the solvent.

As for the cornstalk-based CMCs preparation, various types of pre-treatment were tried by *Han et al* on the fermented cornstalk⁸³, as summarized in Table 1.3. In *Han et al*'s study, bleached fermented cornstalk was found to be the best resource for CMC synthesis, resulting in the best DS (0.71) and viscosity (1320 mPa× s). Steam explosion process led to dramatic degradation of lignin and hemicellulose, which reduced the viscosity of final products. Also, the damage on the inner hydrogen bonds of cellulose caused by high temperature and pressure decreased the polymerization degree of the obtained cellulose, making the cellulose exhibit less useful for CMC preparation. Cornstalk after the alkali soak displayed the highest viscosity, and other shortcomings of the alkali soak pre-treatment such as waste of hemicellulose and lignin should also be taken into the consideration.

Table 1.3: Properties of CMC from different types of cornstalks⁸³

Raw materials	Pre-treatment	Moisture/%	Viscosity (2%, 25°C) /(mPa × s)	DS
Fermentation corncob	Bleaching ¹	5.1	330	0.65
Fermentation cornstalks	Bleaching	4.6	1320	0.71
Fermentation corncob	Alkali wash ² twice	5.5	1000	0.69
Steam explosion cornstalks	Bleaching	4.9	800	0.72

Steam explosion cornstalks	Alkali soak ² +washing twice	6.6	640	0.70
Cornstalks	Alkali soak	3.9	6300	0.73

¹Bleaching: 2%-5% H₂O₂, ²Alkali washing, and alkali soak are all with 3% ~12% NaOH.

1.2.3 Use of lignin for bio-based phenol–formaldehyde resole resin

Lignin is the complex amorphous three-dimensional polymer with aromatic characteristics. Abundant phenolic and alcoholic hydroxyl groups make lignin a promising phenol substitute in the synthesis of bio-based phenol-formaldehyde (BPF) resins. In the general process, formaldehyde reacts mainly with the free ortho position of phenolic units of lignin and very rarely with the side chain of lignin. Taking into account both environmental and economic purposes, Kraft lignin (degraded or chemically modified lignin from sulfate or Kraft pulping), black liquor (a lignin-rich byproduct from the Kraft pulp industry), liginosulfonate (lignin recovered as liginosulfonates from sulfite pulping processes), or organosolv lignin (pulping liquor prepared from woody biomass) have attracted much interest for BPF resin synthesis. For instance, organosolv lignin extracted from sawdust using Alcell process was applied in partially substituting for phenol (25 wt%, 50 wt%, 75 wt%) during PF resin synthesis. It was found that the bonding strengths of these BPF resins-bonded plywood samples could be all above the minimum requirements in accordance to the ASTM standard, although the introduction of sawdust derived Alcell lignin in the resin formula decreased the thermal stability of resulted PF resole ⁸⁴.

Modifications of conventional PF resole resins with lignin have been intensely studied, aiming at reducing either the production costs or formaldehyde use/emission ⁸⁵. The addition of a small amount of lignin (3.4-9.4% of the PF resole) in PF resole synthesis promotes the condensation reaction, which has been evidenced by the increased molar masses and high ratios of methylene bridges to the sum of free ortho and para aromatic

groups with respect to the corresponding reference resin ⁸⁵. Lignin is also reactive if being blended with PF resole resin pre-polymer and can co-polymerize (or cure) with the PF resin pre-polymer for various applications. The use of 20% lignin/80% phenolic resin for auto-motive brake pads contributes to competitive advantages relative to controls with 100% phenolic resin ⁸⁶. However, the use of unmodified lignin to partially replace PF resole is still limited due to its relatively lower reactivity. Lignin methylation through reaction of lignin with formaldehyde under catalysis of a base can enhance the lignin reactivity through the introduction of a methylol group ($-CH_2OH$) on the C5 position of lignin monomer ^{87, 88, 89, 90}. The methylolated lignin can be used as phenol substitute for PF resole synthesis, or can be directly blended with a PF resole pre-polymer for applications.

1.2.4 Summary of the literature

Even though traditional methods applied on lignin extraction for Kraft lignin or Klason lignin, reached a high rate for delignification (92%-99%), the chemical modification on lignin structure like oxidation cannot be avoided, which reduced the reactivity of the lignin. Furthermore, the cellulose component in the crop residues was almost hydrolyzed or decomposed during the process. Meanwhile, in the local pulping industry, lignin was totally decomposed in order to achieve the cellulose with a relatively high purity. Also, some newly released technologies like enzymatic hydrolysis and ionic liquid (\$600-100/kg) were not economical because of the slow process and high cost. Organosolv pulping was recommended for a variety of the advantages, such as mild reaction condition, simple separation process, less hydrolysis for both lignin and cellulose. It was still limited due to the lack of the products purity as well as the considerable solvents dosage. Thus, it is necessary to develop a modified fractionation process on agricultural residues, in order to achieve high quality of both lignin and cellulose simultaneously with considerable yields of the products. Also, for the green and cost-effective purposes, the process should be designed under mild conditions (temperature, residence time, pressure) with a lower

solid/liquid ratio. What's more, the possible applications of the products should be studied to realize high-value utilization of crop residues.

1.3 Objectives

The overall goal of this thesis project was to valorize cornstalk for the production of high value bio-based materials. In order to achieve this overall goal, the following three tasks have been proposed:

Task A: Development of a cost-effective fractionation process for cornstalk;

Task B: Synthesis of sodium carboxymethyl cellulose using bleached crude cellulose derived from cornstalk;

Task C: Production of bio-based phenol formaldehyde resole resins/adhesives using the lignin derived from cornstalk.

Limited by the time, Tasks A and B have been achieved in this thesis work, while Task C will be accomplished in the future work.

Task A (Chapter 2) aimed to investigate organosolv fractionation of cornstalk in formic acid/acetic acid/water mixed solvents at a high solid/solvent ratio, i.e., 1:5 (g/mL), under mild operating conditions. Currently, the solid/solvent ratios tested in literature were mostly in the range of 1:5-1:10 (w/w), due to the relatively lower density of the cornstalk. For the economics consideration, we chose the biomass-to-solvent ratio to be at 1:5 (g/mL) in this work. Effects of fractionation solvents, catalysts, temperatures and residence time on the fractionation efficiency in terms of product yield, purity and chemical composition were investigated.

Task B (Chapter 3) aimed to utilize the cornstalk-derived crude cellulose, after bleaching pretreatment, as a feedstock for the synthesis of CMC. Since the compositions/properties of the purified cotton and the bleached crude cellulose are different, the optimum reaction conditions would be different. This study centered on

determination of best molar ratio of the reaction reagents (alkali reagent/etherifying reagent/cellulose) among the designed conditions for the synthesis of CMC using cornstalk-derived cellulose. The chemical structure, water solubility, average DS as well as other physical properties such as viscosity of the CMC product were measured.

.

2 Organosolv fractionation of the cornstalk in to lignin and cellulose

This chapter aimed to investigate organosolv fractionation of cornstalk in formic acid/acetic acid/water mixed solvents at a high solid/solvent ratio, i.e., 1:5 (g/mL), under mild operating conditions. Effects of fractionation solvents, catalysts, temperature and residence time on the fractionation efficiency in terms of product yield, purity and chemical composition were investigated.

2.1 Materials

Cornstalk was supplied by Ontario Federation of Agriculture (OFA). Before use, the cornstalk was air-dried at room temperature, and then ground into particles to pass 20 mesh sieve. Proximate composition and chemical components in cornstalk are listed in Table 2.1. The chemicals used in this study, such as formic acid, acetic acid, ethyl acetate, hydrochloric acid and sulfuric acid were purchased from Caledon laboratory chemicals, and were used as received.

Table 2.1: Proximate composition and chemical components in oven-dried cornstalk feedstock

Proximate composition (wt%)				
C	H	O ¹	N	Ash ²
45.01	5.67	45.38	1.50	2.44
(0.24)	(0.18)	(0.23)	(0.27)	(0.00)
Chemical component (wt%)				
Extractives ³	Lignin ⁴	Cellulose ⁵	Hemi-cellulose ¹	Protein ⁶
1.34	18.57	35.31	32.58	9.76
(0.12)	(1.13)	(0.65)	(2.22)	(1.72)

¹by difference; ²ashed at 575 °C; ³soxhlet extraction in toluene/ethanol (2:1, v/v); ⁴Klason lignin (acid insoluble); ⁵ α -cellulose; ⁶calculated from nitrogen content.

2.2 Methods

2.2.1 Fractionation procedure

Fractionation of cornstalk was carried out in a 100 mL micro bench top reactor (Parr 4590), and the fractionation procedures are as illustrated in Fig. 2.1. In a typical run, 5.0 g air-dried cornstalk, 25 mL mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v) was added into the reactor. The reactor was then sealed under approx. 300 rpm stirring, vacuumed and pressurized to 1.0 MPa with N₂. The reactor was heated at the rate of approx. 10 °C/min to the set temperature, soaking for a specific length of residence time for reaction, and it was cooled down to room temperature. The gas in the reactor was vented and the reactor was opened. Slurry in the reactor was poured into a 250 mL glass beaker, and the reactor was rinsed with ethyl acetate. The spent ethyl acetate was also transferred to the 250 mL glass beaker. After 15 min, mixture in the beaker was filtered, while the filter cake was further rinsed with ethyl acetate till the falling liquor became colorless. The solid residue present in the filtration cake was then rinsed with distilled water, dried at 105 °C in an oven, and designated as crude cellulose. As for the filtrate, it was evaporated under reduced pressure to remove ethyl acetate, organic acid and water for crude lignin recovery. The obtained crude lignin in the flask was then further vacuum dried at 60 °C overnight and weighed for calculating the yield. Yields of crude lignin and crude cellulose were calculated by equations (1) and (2):

$$\text{Lignin yield} = \frac{M_l}{M_c} \times 100\% \quad (1)$$

$$\text{Crude cellulose yield} = \frac{M_{cc}}{M_c} \times 100\% \quad (2)$$

Where M_l is the recovered lignin weight, M_c is the oven-dried cornstalk weight before fractionation (calculated from the air-dried cornstalk feedstock and its moisture content), and M_{cc} is the crude cellulose weight.

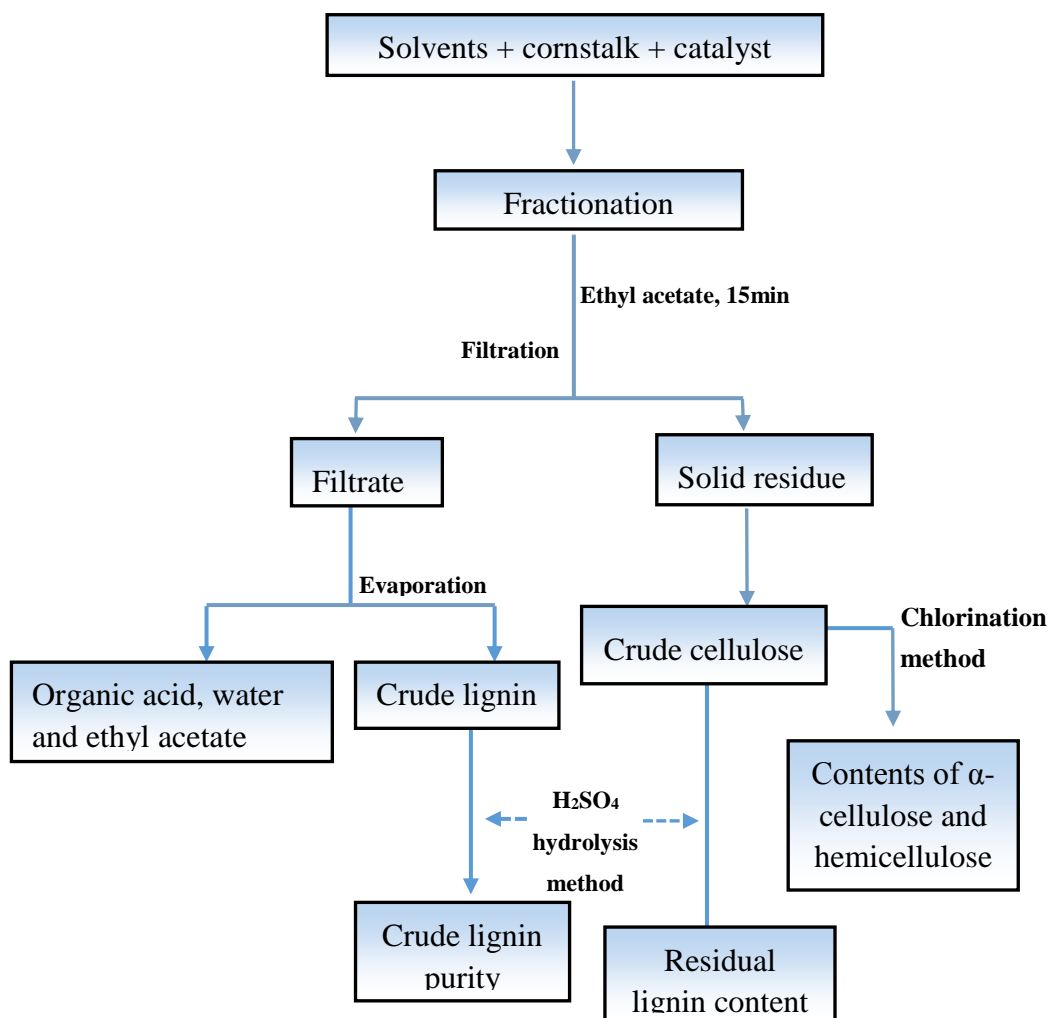


Fig. 2.1: Block diagram of the experimental procedures for organosolv fractionation of Cornstalk

2.2.2 Characterizations of crude cellulose and lignin products

The obtained crude cellulose products were characterized by Fourier transform infrared spectroscopy (FTIR, Perkin Elemer) at the wavelength of $400\text{-}500\text{ cm}^{-1}$ with a resolution of 4 cm^{-1} , to qualitatively determine the chemical components. Residual

lignin content in the crude cellulose and purity of the crude lignin were determined through the sulfuric acid hydrolysis method. Specifically, 0.3 g crude cellulose or lignin was loaded into a glass tube ($\phi 16 \times 100$ mm), then 4.92 g of 72% sulfuric acid was added and the mixture was stirred to thoroughly wet the substrate. The reactor was then sealed and placed in a water shaker at 30 °C. After 120 min, the mixture was transferred into a 100 mL glass pressure reactor and diluted with 84 g water. The mixture was then heated at 121 °C. After 60 min, the reactor was cooled down to room temperature in 20 min, followed by filtration. The solid residue (lignin) was rinsed using distilled water during the filtration, and the obtained residue was then oven dried at 105 °C for 24 hr. Crude lignin purity and residual lignin content in the crude cellulose were calculated by to equations (3) and (4):

$$\text{Crude lignin purity} = \frac{M_{hl}}{M_L} \times 100\% \quad (3)$$

$$\text{Residual lignin content in crude cellulose} = \frac{M_{rl}}{M_c} \times 100\% \quad (4)$$

Where M_{hl} is the lignin weight after hydrolysis in sulfuric acid, M_L is the crude lignin weight before hydrolysis. M_{rl} is the residual lignin weight after the sulfuric acid hydrolysis of the crude cellulose, and M_c is the crude cellulose before hydrolysis.

In addition, purity of crude cellulose (for α -cellulose and holocellulose contents) was tested using a modified Chlorination method. Briefly, 2.5 g crude cellulose, 80 mL hot distilled water (50 °C), 0.5 mL acetic acid and 1.0 g sodium chlorite were added into a 250 mL Erlenmeyer flask. The mixture was then heated in a water bath at 70 °C for 60 min, then 0.5 mL acetic acid and 1.0 g sodium chlorite were added. After each succeeding 60 min, a fresh portion of 0.5 mL acetic acid and 1.0 g sodium chlorite were added over 8 hr for chloriting. Then the mixture was left in the 70 °C water bath for 24 hr. The reactor was then cooled down and filtered, solid residue was further rinsed with acetone during filtration. Then the obtained holocellulose (residue after filtration) was vacuum dried at 65 °C for 24 hr and weighed. Crude cellulose purity was determined by equation (5):

$$\text{Crude cellulose purity} = \frac{M_{ho}}{M_{co}} \times 100\% \quad (5)$$

Where M_{ho} is the dried holocellulose weight, and M_{co} is the weight of used crude cellulose.

Furthermore, the contents of α -cellulose and hemicellulose in the crude cellulose were also tested. Specifically, 2.0 g dried holocellulose obtained previously was fed into a 100 mL three neck glass reactor, followed by the addition of 10 mL 17.5% NaOH solution. The mixture was stirred for 5 min at room temperature, extra 5 mL of 17.5% NaOH was added and the mixture was further stirred for 40 min. 33 mL distilled water was added and the mixture was left at room temperature for 60 min. The mixture was then filtered, and the filtration residue was transferred into a 250 mL beaker, stirred and washed with 100 mL 8.3% NaOH solution at room temperature. The filtration residue was further washed and transferred with distilled water into a 250 mL beaker. Mixture in the 250 mL beaker was filtered again and filtration residue was further rinsed using distilled water. The filtration and rinsing was repeated for three times. In the last filtration run, 15 mL 10% acetic acid was added into the residue and the acid was removed using vacuum filtration. Residual acetic acid in the solid residue was removed through water rinsing/vacuum filtration cycles. The rinse and filtration were repeated till the acetic acid was completely removed (determined with PH measurement). The solid residue was finally rinsed with 250 mL distilled water, then dried at 105 °C for 24 hours, weighed and designated as α -cellulose. Contents of cellulose and hemicellulose in crude cellulose were calculated by equations (6) and (7), respectively.

$$\alpha - \text{cellulose content} = \text{Crude cellulose purity} \times \frac{M_{\alpha}}{M_{ho}} \times 100\% \quad (6)$$

$$\text{Hemicellulose content} = M_h \times \frac{\text{crude cellulose purity}}{M_{ho}} \times 100\% \quad (7)$$

Where M_{α} is the weight of α -cellulose in holocellulose, M_h is the weight of hemicellulose in holocellulose, M_{ho} is the weight of holocellulose.

2.3 Results and discussions

2.3.1 FTIR spectra of cornstalk and crude cellulose derived from the cornstalk

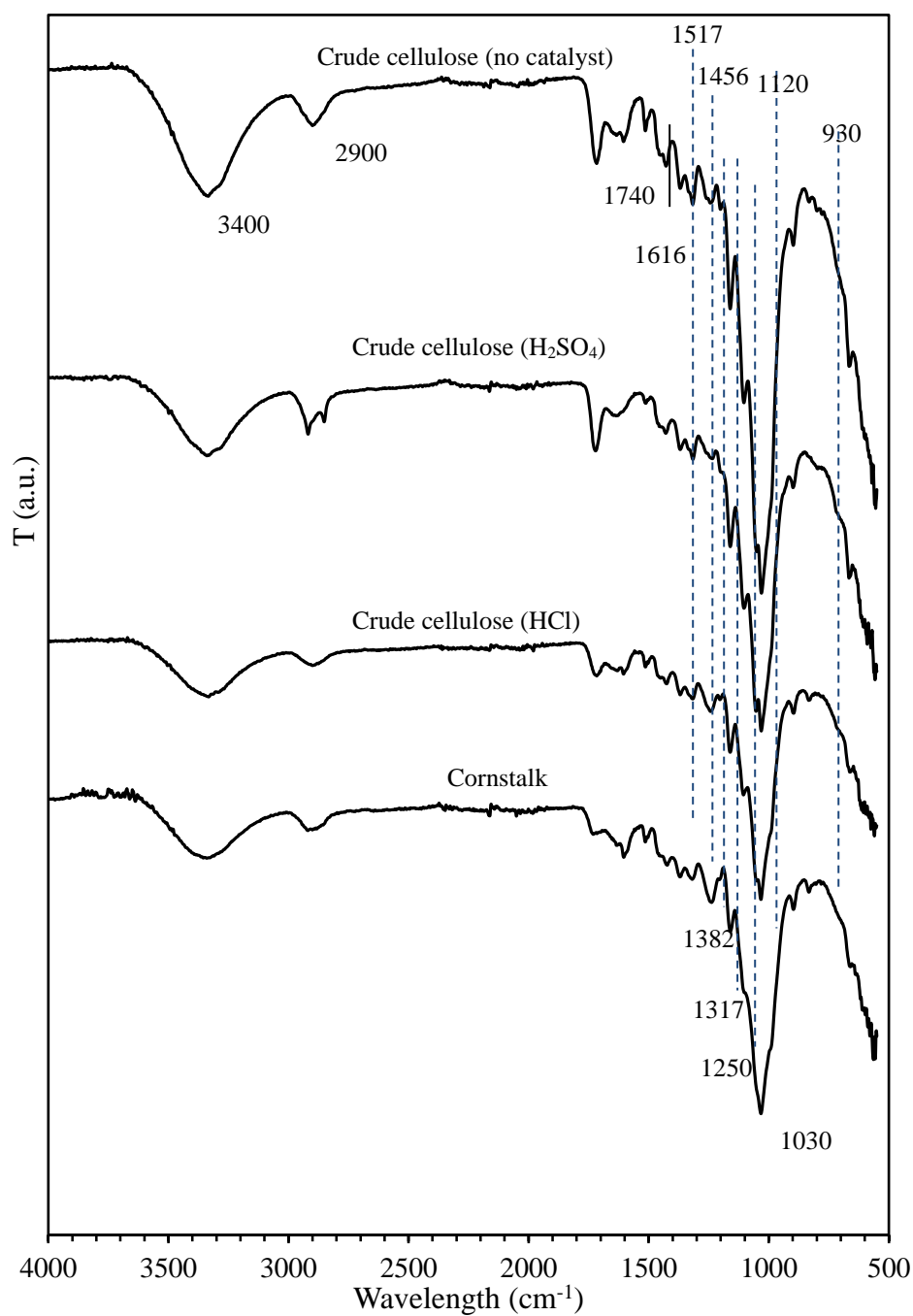


Fig. 2.2: FTIR spectra of cornstalk and various crude cellulose products

Cornstalk and typical crude celluloses obtained from fractionation of the cornstalk at 90 °C for 180 min with a catalyst (HCl) were characterized by FTIR, and the resulted FTIR spectra are displayed in Fig. 2.2. As clearly shown in the figure, spectra of various crude cellulose samples from fractionation with catalyst display very similar transmittance characteristics with that of the cornstalk, all showing characteristic cellulose peaks at 3400 cm^{-1} (-OH), 2900 cm^{-1} (-CH), 1382 cm^{-1} (-CH), 1317 cm^{-1} (C-O-C), 1120 cm^{-1} (C-O-C), 1030 cm^{-1} (C-OH), and lignin functional groups: -OH bond stretch (3600-3200 cm^{-1}), -CH (2960-2850 cm^{-1}), the stretching of aromatic C=C groups (1616 cm^{-1} , 1517 cm^{-1}), aromatic CH bends (1456 cm^{-1}), phenolic OH (1317 cm^{-1}), C-O-C ether or ester (1250 cm^{-1}), methoxy (1120 cm^{-1}), aromatic -CH bend at 930 cm^{-1} and 830 cm^{-1} . Meanwhile, absorbance at 1740 cm^{-1} can be also observed, indicating the existence of hemicellulose in both cornstalk and crude celluloses. The results thus suggest that the obtained crude cellulose samples still contains residual lignin and maybe hemicellulose. Hence, the contents of cellulose, hemicellulose and residual lignin in the crude cellulose products need to be analyzed so as to understand the fractionation efficiency under different conditions. In the following sections, effects of fractionation solvents, catalysts, temperature, and residence time on the yields and purity of crude cellulose and crude lignin, and their chemical composition will be discussed.

2.3.2 Effects of fractionation solvent composition

Fig. 2.3 exhibits the yields of crude cellulose and crude lignin obtained from cornstalk fractionation in various fractionation solvent systems without catalyst at 90 °C for 180 min. Fractionation in sole acetic acid led to a relatively high crude cellulose yield but low crude lignin yield: approximate 72.5% and 18.6%, respectively, associated with 66.9% and 43.9% purity, respectively as displayed in Fig. 2.4. The crude cellulose 44.1% contains cellulose, 22.8% hemicellulose and 11.1% residual lignin.

While for the fractionation in sole formic acid, yields of crude cellulose and crude lignin are 59.1% and 17.9%, respectively, both lower than that obtained from the

fractionation in sole acetic acid. It may thus be concluded by higher amount of the lignin extraction (13.5%) in acetic acid that fractionation of cornstalk in acetic acid is more efficient than that in formic acid (10.4%) under the tested conditions, which is consistent with the results in a previous work by *Villaverde* in 2010⁸⁵. In contrast, the fractionation in acetic acid resulted in increased purity for the crude cellulose product (71.7%), but reduced crude lignin purity (33.4%), compared with those in acetic acid (66.9% and 43.9% purity, respectively). The increased purity of crude cellulose accompanied by reduced crude lignin purity was likely due to better catalytic effects of formic acid over acetic acid on hydrolysis of the hemicelluloses, probably caused by the higher acidity of formic acid, resulting in a higher cellulose content but lower, resulting in a higher cellulose content but lower hemicellulose content in the crude cellulose product³¹.

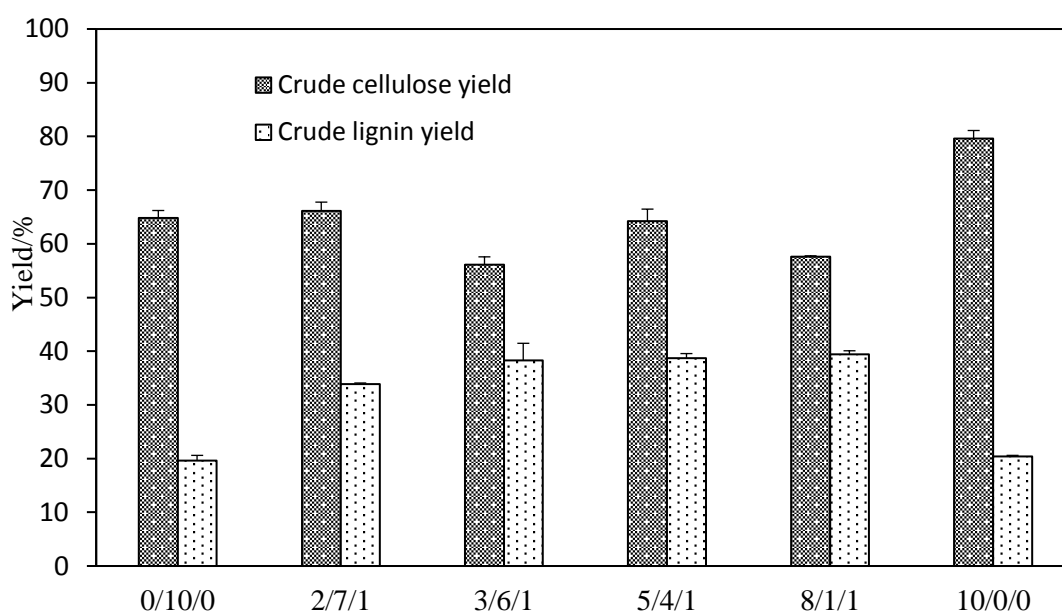


Fig. 2.3: Effects of fractionation solvent composition on the yields of crude cellulose and crude lignin products from the operations without catalyst at 90 °C for 180 min (The ratio as shown on the horizontal axis is the volumetric ratio of acetic acid/formic acid/water)

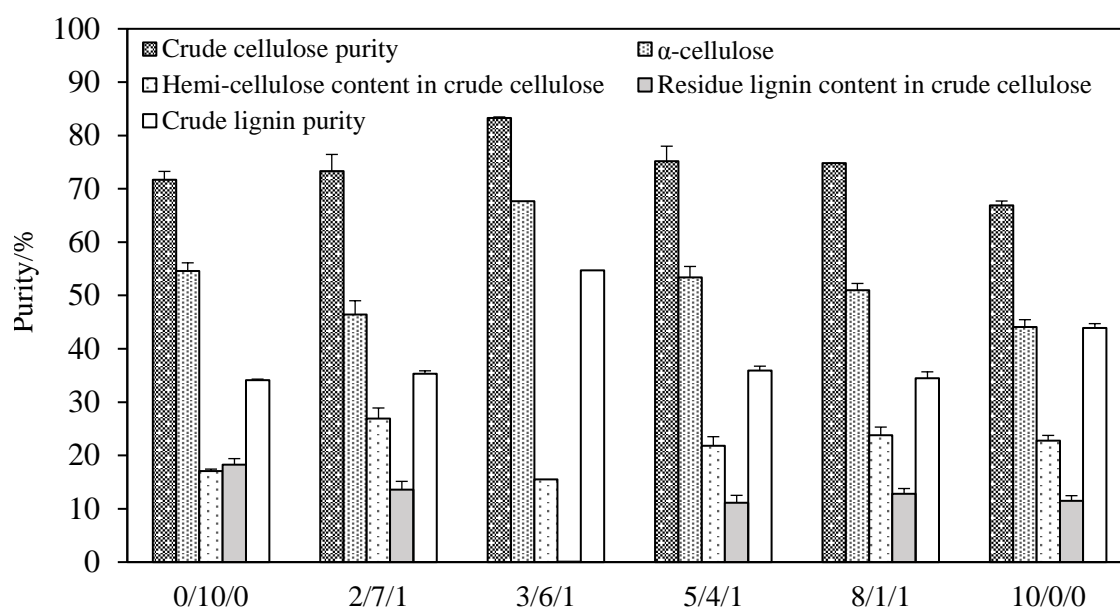


Fig. 2.4: Effects of fractionation solvent composition on the purities of crude cellulose and crude lignin products, as well as contents of α -cellulose, hemicellulose and residual lignin in the crude cellulose products from the operations without catalyst at 90 °C for 180 min (ratio on the horizontal axis is the volumetric ratio of acetic acid/formic acid/water)

Use of a mixture of acetic acid and formic acid with 10 vol% water resulted in a significantly reduced yield of crude cellulose (51.1-60.2%), but a drastically increased crude lignin yield (30.9-35.9%), when compared with those obtained with a mono-solvent of either acetic or formic acid. Generally, the fractionation with a mixed solvent led to an increased purity for the crude cellulose (73.3-83.3%) and a decreased crude lignin purity (~35%) except for the mixed solvent of acetic acid/formic acid/water at the volumetric ratio of 3:6:1, where the purity of crude cellulose and crude lignin purity is as high as 83.3% and 54.7%, respectively. Moreover, α -cellulose content in the crude cellulose obtained from cornstalk fractionation in mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v) is 67.7%, much higher than that in any other solvent systems (44.1-51.6%). Meanwhile, the contents of hemicellulose and lignin in the crude cellulose product is very low (15.5%, and 0.1%, respectively). As a result, in our subsequent tests, the solvent system was fixed as the mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v). These excellent data may be explained by

quantities of radicals generated by cavitation bubbles, which possibly indirectly assist hydrolysis of cellulose and hemicellulose by cleavage of lignin carbohydrate matrix components, thus inducing the delignification reaction. However, the contribution of this effect was expected to be relatively small as most of the hydrolysis occurs through H^+ ions ⁸⁶.

2.3.3 Effects of catalysts

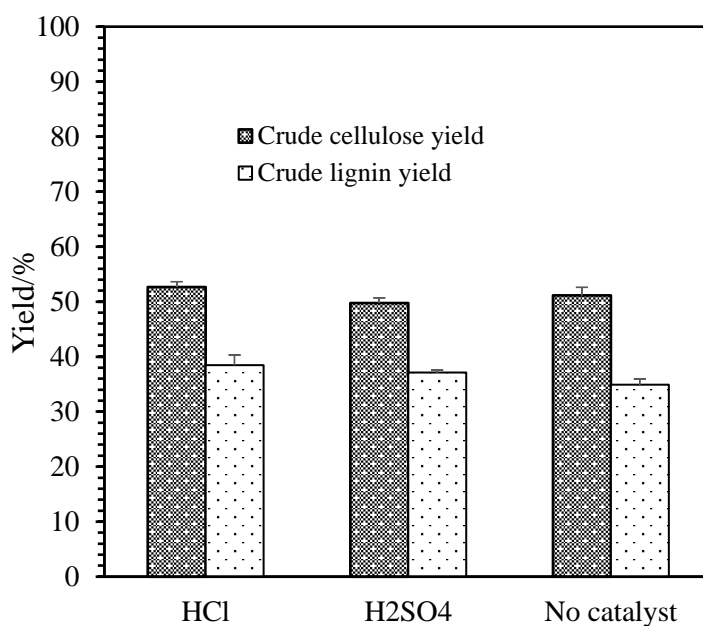


Fig. 2.5: Effects of catalysts on the yields of crude cellulose and lignin products from the fractionation operations at 90 °C for 180 min in mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v)

Fig. 2.5 displays effects of catalysts on yields of crude cellulose and crude lignin obtained from cornstalk fractionation in mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v) at 90 °C for 180 min. The yields of crude cellulose and crude lignin products from cornstalk fractionation without catalyst was approx. 51% and 35%, respectively. With the catalysis of HCl, the crude cellulose and lignin yields increased to 52.7% and 38.3%, respectively. However, effects of H₂SO₄ on the product yields are minimal, as shown in the figure. Moreover, the use of H₂SO₄ led to reduced crude cellulose purity likely due to the hydrolysis of cellulose catalyzed by

the strong acid of H_2SO_4 . As for the contents of α -cellulose, hemicellulose and residual lignin in the crude cellulose products the presence of an acid catalyst (either HCl or H_2SO_4) had insignificant effects on the purity and composition of the resulted crude cellulose products, as illustrated in Fig. 2.6. Nevertheless, the residual lignin in the crude cellulose obtained from the HCl catalyzed operations was slightly higher than that obtained from the H_2SO_4 catalyzed or the non-catalyzed operations, which could be due to formation of pseudo-lignin by HCl catalyzed reactions of lignin and carbohydrate products in the fractionation process⁸⁷. Residual lignin content in the crude cellulose is a very important index indicating the delignification degree for the lignocellulosic biomass. The very low content of residual lignin (<4%) in all crude cellulose products suggests high delignification efficiency for cornstalk in the selected mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v). Furthermore, the use of a mineral acid catalyst led to a much lower hemicellulose content in the resulted crude cellulose products, due to the fact that amorphous structure of hemicellulose can be more easily hydrolyzed than cellulose in the presence of a mineral acid as the hydrolysis catalyst. It is worthy to mention that, the total contents of α -cellulose, hemicellulose and residual lignin in crude cellulose ranges from approximate 84% to 86%, less than 100%, which is most likely due to the existence of some other components such as extractives, protein retained in the crude cellulose products. Lignin yield from cornstalk fractionation without catalyst is 35.0%, with a purity of 55.0%. Under the catalysis of HCl and H_2SO_4 , the crude lignin yield increased slightly to 38.3% and 37.0%, but the purity of the crude lignin decreased to 44% and 52%, correspondingly.

From the above results, it is evident that the use of HCl as the catalyst could produce crude cellulose and crude lignin at a higher yield without sacrificing the product purity too much. Accordingly, HCl was used as the catalyst in the subsequent experiments to investigate on effects of temperature and residence time.

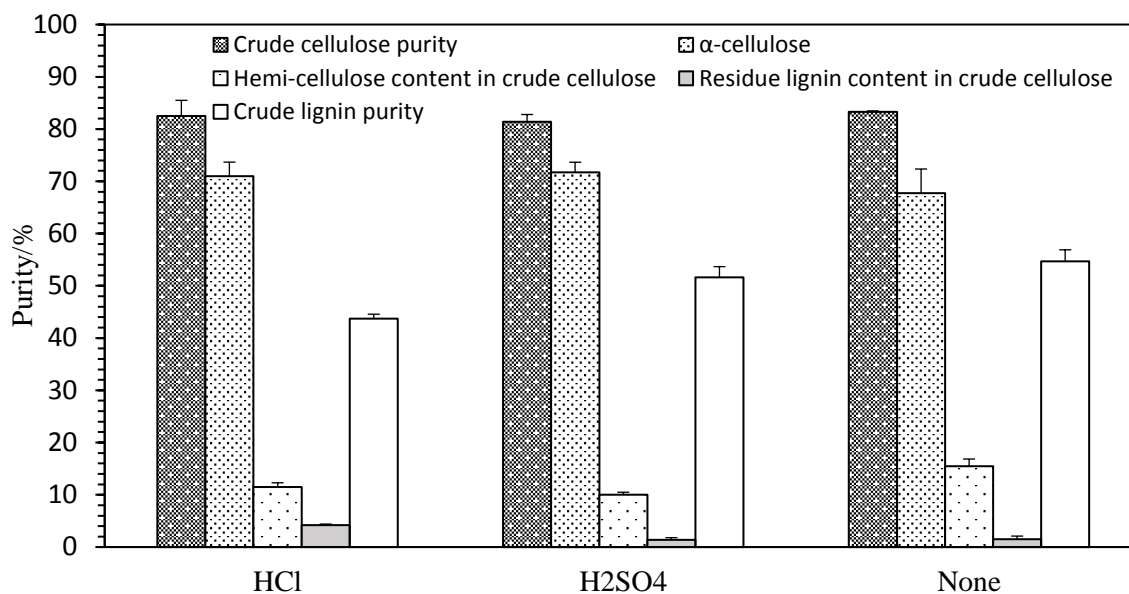


Fig. 2.6: Effects of catalysts on the purity of crude cellulose and lignin, contents of α - cellulose, hemicellulose and residual lignin in the crude cellulose products from the fractionation operations at 90 °C for 180 min in mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v)

2.3.4 Effects of temperature

Fig. 2.7 displays the yields of crude cellulose and crude lignin obtained from HCl catalyzed fractionation of cornstalk at various temperatures for 180 min in mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v). As shown in the figure, the yields of crude cellulose and crude lignin strongly depend on the fractionation temperature. The crude cellulose yield in cornstalk fractionation at 80 °C, 90 °C and 100 °C was 63.3%, 52.7% and 62.7%, respectively, while the associated crude lignin yield was 28.2%, 38.3% and 28.3%, respectively. It is thus clear that the dependency of crude cellulose yield on temperature shows opposite trend to that of the dependency of crude lignin yield on temperature. For instance in the range of 80-100 °C, the fractionation at 90 °C led to the lowest crude cellulose yield (52.7%) but the highest crude lignin yield (38.3%).

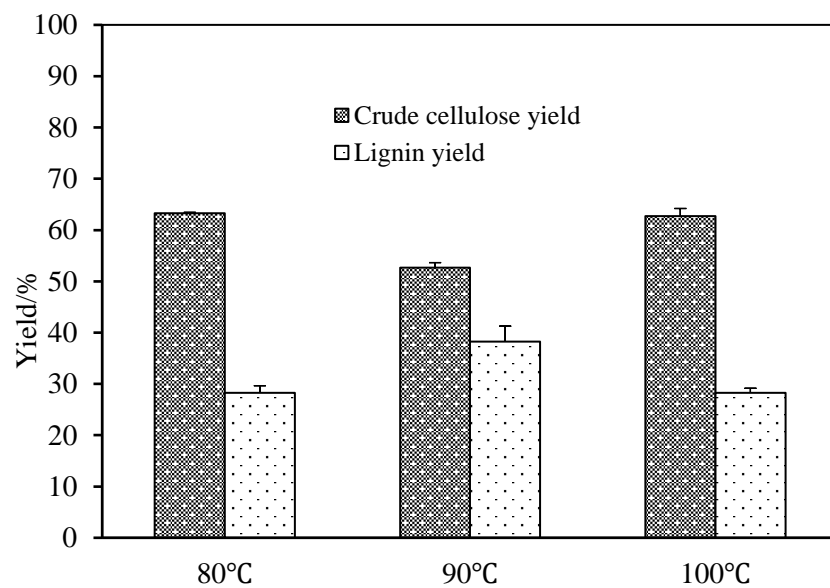


Fig. 2.7: Effects of temperature on yield and purity of the crude cellulose products obtained the fractionation operations in mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v) for 180 min with HCl catalyst

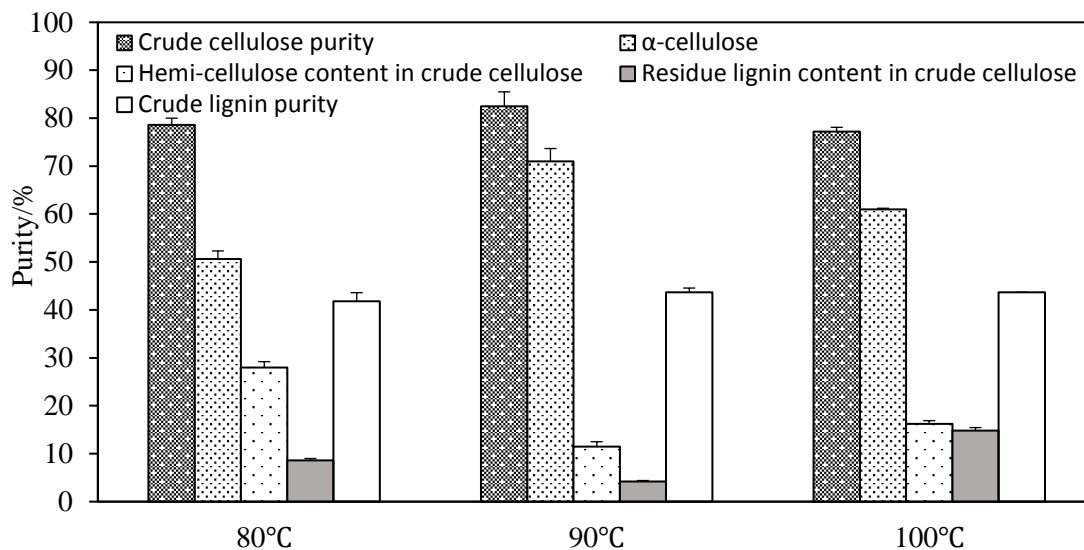


Fig. 2.8: Effects of temperature on the purity of the crude cellulose and crude lignin products, contents of α -cellulose, hemicellulose and residual lignin in the crude cellulose products obtained the fractionation operations in mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v) for 180 min with HCl catalyst

The opposite trend between the yields of crude cellulose and crude lignin is actually expected by mass conservation (Feedstock = crude lignin + crude cellulose + weight loss), which indicates the efficiency of the fractionation. The increasing crude lignin yield at the temperature from 80 °C to 90 °C mainly related to the extent of hemicellulose hydrolysis. A greater extent of hemicellulose hydrolysis would result in a decreased crude cellulose yield and hence an increased crude lignin yield, which can be evidenced by the drastically increased purity of the obtained crude cellulose (82.5%), a high content of α -cellulose content (71.0%), and the significantly reduced hemicellulose content (~10%) in the crude cellulose at 90 °C (Fig. 2.8). Not surprising, fractionation at 80 °C led to the highest crude cellulose yield, but lowest lignin yield. The highest crude cellulose yield obtained at 80 °C can be attributed to the relatively high content of hemicellulose (26.0%) and residue lignin (8.2%) in the crude cellulose, as evidenced in Fig. 2.8. While fractionation of cornstalk even at 100 °C produced crude cellulose containing 14.8.1% residual lignin. In a fractionation process with formic/acetic acids, cleavages of weaker β -O-4 (as compared with the

aromatic C–C linkages) takes place, so the observed high residual lignin content in the crude cellulose at 100 °C could partially be due to re-polymerization of the unstable degradation intermediates from the original lignin in the feedstock^{56, 88}. Thus it is reasonable to set the temperature at the range of 80-100 °C.

It is interesting that lignin purity varies at a very narrow range of 41.8%-43.7%, indicating temperatures at the range of 80-100°C do not affect purity of the lignin products. It can be explained by the co-effect of partial hydrolysis of hemicellulose (80 °C) and cellulose (100 °C) as well as the efficiency of the fractionation.

2.3.5 Effects of residence time

Effects of residence time ranging from 120 to 240 min on cornstalk fractionation were also investigated. Based on previous results, the fractionations were carried out at 90 °C with the catalysis of HCl in mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v) for various lengths of residence time (120 - 240 min). As illustrated in Fig. 2.9, fractionation of cornstalk for 120 -210 min produced crude cellulose at a similar yield of 52.6-58.6%. Interestingly, when the residence time was extended to 240 min, the crude cellulose yield sharply dropped to 37.4%. The possible reason could be that at a long enough residence time, the organic acids formed from degradation of cellulose would accumulate to a certain level that could catalyze the hydrolysis of cellulose and thus result in a low crude cellulose yield⁸⁹, which is in a good agreement with the results shown in Fig. 2.10, where the α -cellulose content in the crude cellulose product from the 240-min runs is 57.0%, much lower than that from the 150-210 min runs (61.4-72.6%). From the Figs. 2.9 and 2.10, the best reaction time appears to be 180-210 min where the highest crude cellulose yield (58.6% for 210 min, compared with 53.0% for 180 min) and the highest crude lignin yield (38.5% for 180 min, compared with 32.0% for 210 min), while the 180 min runs resulted in the lowest residual lignin content in crude cellulose. Taking into account both the yields of crude cellulose and crude lignin as well as the residual lignin in the crude cellulose product and the process economy, it is more beneficial to perform the fractionation process for

180 min.

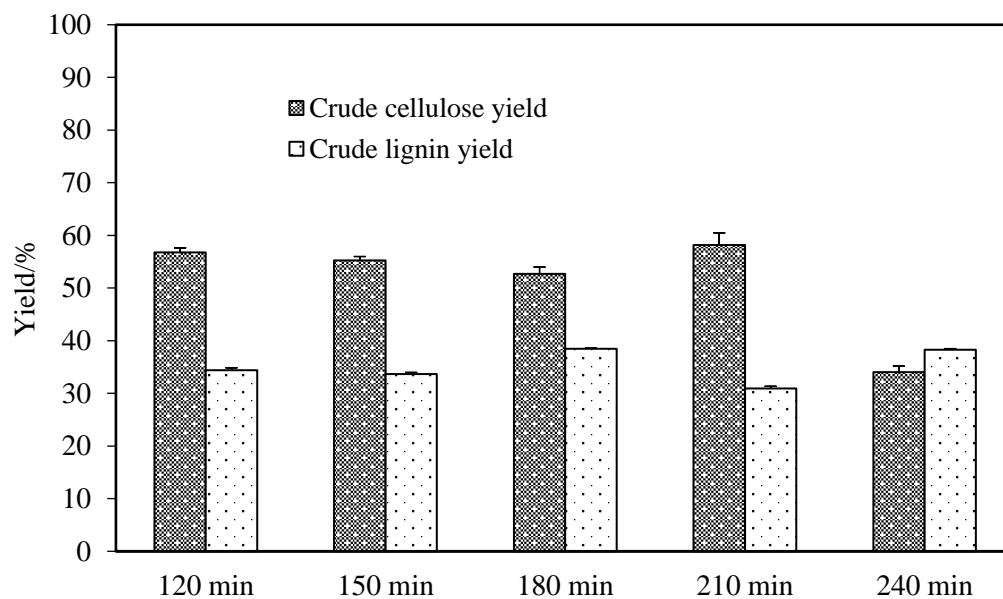


Fig. 2.9: Effects of residence time on the yields of crude cellulose and crude lignin products obtained the fractionation operations in mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v) at 90°C with HCl catalyst

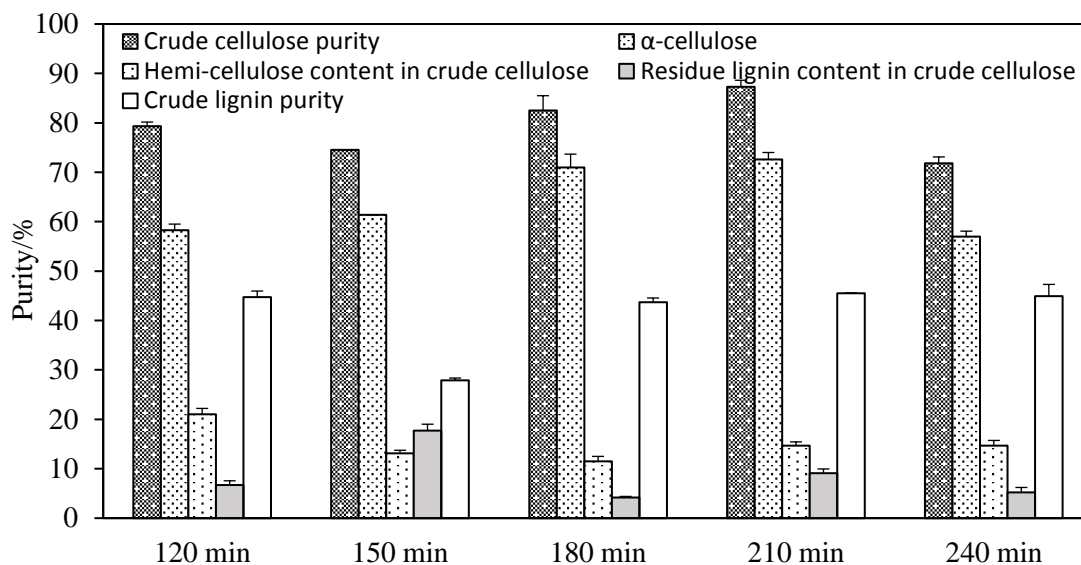


Fig. 2.10: Effects of residence time on purity of the crude cellulose and crude lignin products, and the contents of α -cellulose, hemicellulose and residual lignin in the crude cellulose products obtained the fractionation operations in mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v) at 90°C with HCl catalyst

2.4 Project summary

Cornstalk was efficiently fractionated into crude cellulose and crude lignin in mixed solvents of acetic acid, formic acid and water at a solid/agent ratio of 1:5 (g/mL) at 80-100 °C for 120-240 min. Effects of fractionation agents, catalysts, temperature and residence time on the product yields, purity and composition of the final products were investigated. The following conclusions can be drawn based on the results:

- Fractionation of cornstalk in mixed solvent of acetic acid, formic acid and water at the volumetric ratio of 3:6:1 resulted in high yield and purity of crude cellulose and lignin products.
- The use of HCl as the catalyst led to high crude cellulose yield, while H₂SO₄ resulted in a decreased crude cellulose yield. The use of both catalysts contributed to much lower hemicellulose contents in the resulted crude cellulose products,

while did not alter the α -cellulose contents in the resulted crude cellulose products.

- Fractionation operations at 90 °C for 180 min in mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v) with a catalyst, produced crude cellulose products with very low residual lignin contents (<4%).
- The best conditions during the test for organosolv fractionation of cornstalk appeared to be as follows: mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v), HCl as the catalyst, 90 °C and 180 min residence time, where the yield (and purity) of crude cellulose and lignin products were approximate 53% (85%) and 38% (44%), respectively, on the basis of mass of oven-dried cornstalk.

Table 2.2: Comparison the invented process and the existing organosolv fractionation process employing organic acid(s) as the reaction medium

Feedstock	Process conditions	Biomass/solvent (g/ml)	Cellulose yield (and purity) and delignification ratio
Banana stem ⁵⁷	70-90 vol % formic acid in water, 80°C, 60-120 min	1:10	52.9-62.1%, 75-83%
Beech ⁹¹	80% formic acid in water, 110-130°C, 180 min	1:10	45-50%, 80-90%
Rice straw ⁵⁸	70-98 vol % formic acid in water, 90-115°C, 30-120 min	1:20	32.1-69.8%, 85-90%
Wheat straw ²⁸	Formic acid/acetic acid/water=3/6/1 (v/v/v), 85°C, 240 min	1:20	47.2%, 94.1%
Wheat straw ⁹²	Formic acid/acetic acid/water=3/5.5/1.5 (v/v/v), 105°C, 180 min	1:10	48% (63%), 98%

Table 2.2 gives comparison of the invented process and the existing organosolv fractionation process employing similar solvents containing organic acid (s) ^{57, 91, 58, 28, 92}. Compared with the previous work on biomass fractionation using water solution of formic acid containing 70-98 vol% formic acid operating at 80-130°C for 30-180 min, our cost-effective process employs mixture of formic acid/acetic acid/ water at 90 °C for 180 min, which is similar to the processes reported by *Xu* et al in 2006 and *Snelders* et al in 2014 ^{28, 92}. However our process differs from the literature processes in that:

- (1) Different solvent composition: formic acid/acetic acid/ water = 6/3/1 (v/v/v) (this invention) vs. 3/6/1 (v/v/v) or 3/5.5/1.5 (v/v/v);
- (2) Different substrate concentration: Biomass/ solvent (g/ml) = 1:5 vs. 1:20 and 1:10;
- (3) Different cellulose yield (and purity) and delignification ratio: 57% (67%) and 99%, respectively (this study) vs. 48% (63%) and 98%, although the feedstock used was also different (cornstalk in this study vs. wheat straw in the literature work).

3 Synthesis of the sodium carboxymethyl cellulose by using bleached cellulose

In our previous work, cornstalk was effectively fractionated into cellulose-rich (crude cellulose) and lignin-rich (crude lignin) fractions through organic solvent. After the bleaching process, the treated crude cellulose was used as feedstock to replace expensive purified cotton for synthesis of CMC. This chapter centered on determination of best molar ratio of the reaction reagents (alkali reagent/etherifying reagent/cellulose) among the test conditions for the synthesis of CMC using cornstalk-derived cellulose. The chemical structure, water solubility, average DS as well as other physical properties such as viscosity of the CMC product were measured.

3.1 Materials and Methods

3.1.1 Materials

Cornstalk used in this work was supplied by Ontario Federation of Agriculture (OFA). The cornstalk was air-dried at room temperature to a moisture content of < 10 wt%, and then ground into particles to pass 20 mesh sieve. The chemicals used in this study, such as sodium hydroxide (50 wt% solution), chloroacetic acid (solid, 99 wt%), ethanol (95 wt%), hydrochloric acid (36.5-38 wt%), etc. were all purchased from Caledon Laboratory Chemicals, and were used as received.

3.2 Methods

3.2.1 Cornstalk fractionation

Fractionation of cornstalk process has been reported in Chapter 2. The solid residue collected in the filtration cake was rinsed with distilled water, dried at 105 °C in an oven, and designated as crude cellulose.

3.2.2 Crude cellulose bleaching

Sodium chlorite was used for crude cellulose bleaching. Briefly, 2.5 g crude cellulose, 80 mL hot distilled water (50 °C), 0.5 mL acetic acid and 1.0 g sodium chlorite were added into a 250 mL Erlenmeyer flask. The mixture was then heated under stirring in a water bath at 70 °C for 60 min, then additional 0.5 mL acetic acid and 1.0 g sodium chlorite were added. After each succeeding 60 min, a fresh portion of 0.5 mL acetic acid and 1.0 g sodium chlorite were added. After 7-8 hours of bleaching under stirring, the mixture was left in the water bath for 24 hr. The mixture was then cooled to room temperature and filtered, and the collected residue was further rinsed with distilled water during filtration. Then the obtained bleached cellulose (residue after filtration) was vacuum dried at 65 °C for 24 h, weighed (for bleached crude cellulose yield calculation), and then ground into particles to pass 20 mesh sieve, subject to CMC synthesis.

3.2.3 CMC synthesis

Taking into account the < 100% purity for the bleached cornstalk-derived cellulose and its poorer reactivity than pure cellulose, molar ratio of the etherification agent to CMC was set at 2.0-3.0, higher than the conventional ratio (0.5-1.5) while pure cellulose is used. The CMC synthesis procedure can be described by a block flow diagram, as shown in Fig. 3.1. Taking the CMC synthesis at the 4:2:1 molar ratio of sodium/chloroacetic acid/cellulose for an example, briefly 1.00 g bleached cellulose was weighed in a 50 ml glass beaker, treated with 0.99g 50 wt% NaOH solution and 10 mL distilled water for alkalization. The beaker was then covered with aluminum foil and left in the 35°C water bath for 1 hour. After that, another isometric of 0.99g 50 wt% NaOH solution was pre-mixed with 1.17g chloroacetic acid. The mixture was diluted with 35 mL 95% ethanol and added into the beaker. The reactor was then heated in 75°C water bath for 1.5 h. After cooling down to room temperature, all the mixture was neutralized with hydrochloric acid and filtered, rinsed with 95% ethanol

3 times. The residues were then dried in an oven at 105 °C for 3 h, and the dried residues were collected as the CMC products.

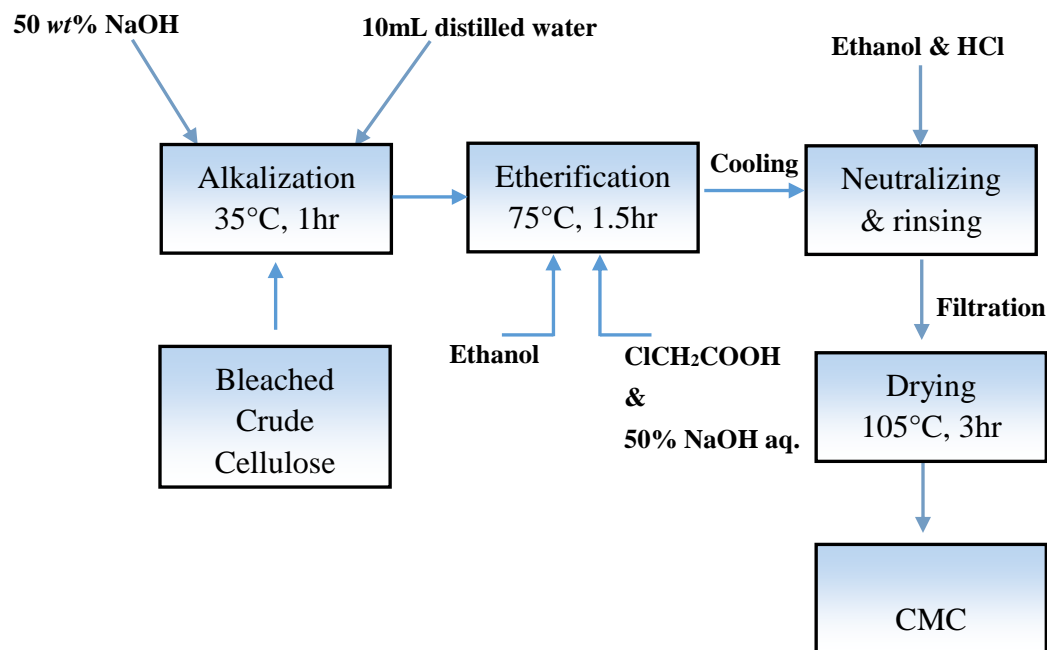
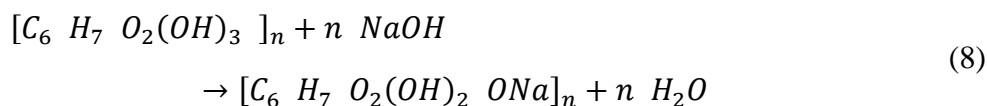
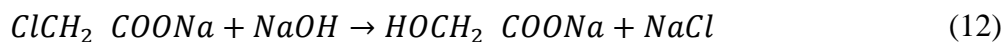
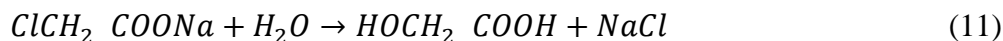
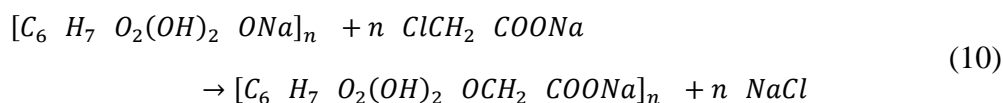


Fig. 3.1: Block diagrams of the experimental procedure for synthesis of CMC with bleached cornstalk-derived cellulose

In the process of CMC synthesis, there are two main chemical reactions: Alkalization and Etherification. In alkalization, cellulose is modified by sodium hydroxide to produce sodium cellulose, as shown in Eq. (8) below. In etherification, firstly, chloroacetic acid dissolve in the sodium hydroxide to form sodium chloroacetate, as shown in Eq. (9). Then, the chlorine in sodium chloroacetate reacted with the sodium cellulose to generate CMC, as given below in equation (10). Since this system is under alkaline condition, there are some by-products generated, such as glycolic acid, sodium glycolate, water, and sodium chloride, as shown in equations. (11) and (12) ⁸³. It shall be noted, during the process, hemicellulose can also be etherified.





3.3 Characterizations

3.3.1 Characterizations of crude cellulose

Bleached crude cellulose were characterized by Fourier transform infrared spectroscopy (FT-IR, Perkin Elmer) at the wavelength of 4000-500 cm^{-1} with a resolution of 4 cm^{-1} , to qualitatively determine the functional structure.

In addition, the contents of α -cellulose and hemicellulose in the bleached crude cellulose were measured. Briefly, 2.0 g dried bleached crude cellulose (also called hollocellulose) obtained previously was fed into a 100 mL three-neck flask, followed by the addition of 10 mL 17.5 wt% NaOH solution. The mixture was stirred for 5 min at room temperature, extra 5 mL of 17.5 wt% NaOH was then added and the mixture was further stirred for 40 min. 33 mL distilled water was added and the mixture was left at room temperature for 60 min. The mixture was filtered, and the filtration residue was transferred to a 250 mL beaker, stirred and rinsed with 100 mL 8.3 wt% NaOH solution at room temperature. The mixture was filtered. The filtration residue was rinsed with distilled water followed by filtration. Such rinsing and filtration operations were repeated for 3 times. 15 mL 10% acetic acid was added into the filtration residue. After 5 minutes, the acid was removed through vacuum filtration. Residual acetic acid in the solid residue was removed by water rinsing followed by vacuum filtration. The water rinsing-filtering operations were repeated till the acetic acid was completely removed from the sample (determined with PH measurement).

The residue was finally rinsed with approx. 250 mL distilled water, then dried at 105 °C for 24 h, weighed and designated as α -cellulose. The α -cellulose content was then calculated based on the *wt%* mass of the α -cellulose in the bleached crude cellulose. The content of hemicellulose in the bleached crude cellulose was calculated simply by difference.

3.3.2 Characterizations of CMC products

The functional structure of the CMC products obtained from the synthesis at different reactant ratios were characterized by FT-IR (Perkin Elmer) at the wavelength of 4000-500 cm^{-1} with a resolution of 4 cm^{-1} . Furthermore, the CMC products dissolved in D_2O were characterized by proton nuclear magnetic resonance ($^1\text{H-NMR}$). The $^1\text{H-NMR}$ spectra for the CMC products were acquired at 25 °C using a Varian Inova 600 NMR spectrometer equipped with a Varian 5 mm triple-resonance indirect-detection HCX probe. A total of 16-32 scans were accumulated using a 2 s recycle delay and 3.6 s acquisition time. Furthermore, the micro-structure of the CMC products were observed by Scanning Electron Microscope (SEM) on a Hitachi's Tabletop Electron Microscope TM3030Plus.

3.3.3 Water solubility of the CMC products

Water solubility of the CMC products was measured by quantifying residual solids in 1 *wt%* CMC-water solution. Specifically, 0.50 g CMC sample was weighed to mix with 50.0 g water at room temperature (25 °C) in a 100 ml glass beaker. The beaker was then left in the ultrasonic oscillator for 5 min followed by shaking at 180 rpm for 24hr. The residue was collected by vacuum filtration. The residue was dried at 105°C for 3 hr and weighed. The dry weight of the residue was then used for calculation of water solubility of the CMC product.

3.3.4 Structure, viscosity and molecular weight of the CMC products

The functional structure of the CMC products were qualitatively analyzed by FT-IR (Perkin Elmer) at the wavelength of 4000-500 cm^{-1} with a resolution of 4 cm^{-1} .

The viscosity of the CMC-water solution and the viscosity-based average molecular weight (M_v) were measured on a Rheometer AR-G2 and an Ubbelohde Viscometer, respectively, at 25 °C and 101 kPa, using distilled water as a reference ($\mu_{water} = 0.8937 \text{ mPa} \cdot \text{s}$ at 25 °C). The time (t) taken by a solution with the certain concentration to flow from the start point to the end set in the Ubbelohde Viscometer, was recorded. The intrinsic viscosity ($[\eta]$) was calculated by two linear regression of y - x intercepts at $C_i \rightarrow 0$, where x is the concentration% of the solution, while y can be calculated by Eqs. (13) and (14)

$$y_1 = \left(\frac{t_i}{t_6} - 1\right) / c_i, i = 1, 2, 3, 4, 5 ; \quad (13)$$

$$y_2 = \ln\left(\frac{t_i}{t_6}\right) / c_i, i = 1, 2, 3, 4, 5. \quad (14)$$

The t_6 in the equations above is the time cost by reference solution during the measurement. Theoretically, the two intercepts should be the same value and must > 0 . $[\eta]$ can be then calculated by multiply one of the intercepts by 1000. Viscosity-based average molecular weight (M_v) can be estimated by Eq. (15):

$$[\eta] = (6.3 \times 10^{-3})M_v^{0.8} \quad (15)$$

3.3.5 Average degree of substitution for the CMC products

The average DS for the CMC products was determined by standard method of ASTM D 139⁹⁰, as briefly described below: 4 g CMC was weighed, stirred with 75 ml 95% ethanol and 5 ml HNO_3 to convert the water soluble CMC to solid particles. The

slurry was then heated and boiled for 5 min and then agitated by stirring for 15 min. The slurry was precipitated with 80% ethanol until all of the acid has been removed (using diphenylamine). The residue was washed with a small amount of the anhydrous methanol and dried. 1-1.5 g solid sample was weighed, mixed with 100 ml water and 25 ml 0.3-0.5 N NaOH, stirred and heated to boiling for 15-30 min. While the solution is hot, excess NaOH was titrated with 0.3-0.5 N HCl to a phenolphthalein end point. The DS of the CMC product was then determined by the amount of NaOH consumed determined by titration. In this work, CMC products with a DS up to 0.85 were obtained with the bleached crude cellulose (derived from cornstalk).

3.4 Results and discussion

3.4.1 Characterizations of bleached crude cellulose

The yield and composition of oven-dried bleached crude cellulose are shown in Table 3.1.

Table 3.1: Yield and composition of oven-dried bleached crude cellulose

Yield ¹ %	Components/ wt%	
	Cellulose ²	Hemicellulose
42.56 (±1.64)	81.3 (±4.65)	18.6 (±4.82)

¹Yield based on the weight of the air-dried cornstalk; ² α -cellulose

On one hand, bleached crude cellulose with 81.3 wt% α -cellulose content was used the cellulosic material for CMC synthesis. On the other hand, after alkalization and etherification process, 18.6% hemicellulose is expected to be modified into short chain molecule containing carboxymethyl groups which has lower viscosity as well as good water solubility compared with the commercial CMC products. Thus the viscosity of CMC-water solution would be decreased. However, abundant xylan generated by the hydrolysis of hemicellulose would adhere to and mask the

molecules of cellulose tightly. A part of the cellulose molecules masked by xylan have limited access to the alkalization or etherification reactants, which would result in a lower reaction efficiency and DS⁸³. Taking into consideration the poor reactivity of the bleached crude cellulose due to the masking effects of xylan, a high molar ratio (2-3:1) of the etherification agent-to- the bleached crude cellulose was employed in this study.

3.4.2 Effects of the reactants molar ratio on water solubility of the CMC products

Water solubility of the CMC products, depending on their degree of substitution (DS), is a key property for many applications. Thus, effects of the reaction conditions, in particular the reactants molar ratio, on water solubility of the CMC products (measured by the residues content in water) were examined in this work. To this end, two series of the tests were performed to explore (1) effects of the alkali agent (NaOH), (2) effects of the etherification agent (ClCH₂COOH) and the best molar ratio of NaOH:ClCH₂COOH:Cellulose under the test conditions.

In series (1) tests, the molar ratios of NaOH/ClCH₂COOH/cellulose were in the range of 4~5:2:1 (mol/mol/mol), where the ClCH₂COOH: cellulose ratio was fixed at 2:1 (mol/mol) in all tests for this series. The variations of water solubility of the CMC products (represented by their residue contents in water) with varying the amount of NaOH in the reaction feed are shown in Fig. 3.2.

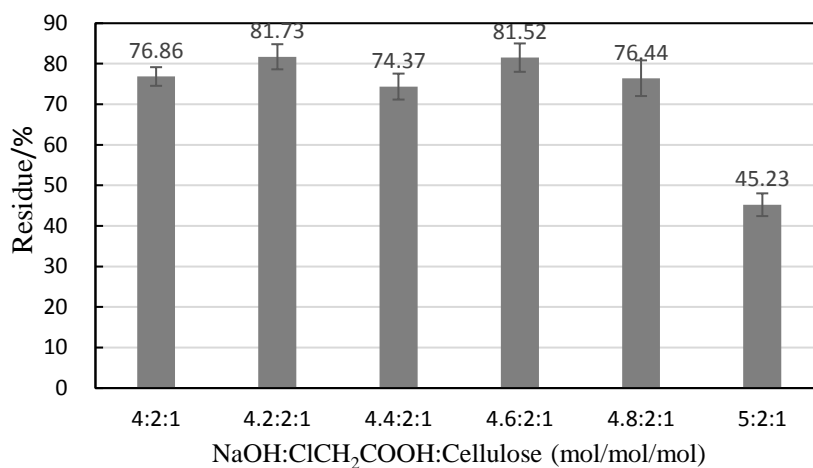


Fig. 3.2: Effects of the alkali agent (NaOH) on water solubility of the CMC products obtained at various molar ratios of NaOH/ClCH₂COOH/cellulose in the range of (4~5): 2: 1.

From Fig 3.2 a, it can be observed that effects of the alkali agent (NaOH) on water solubility of the CMC products are minimal. While increasing the molar ratio of NaOH/ClCH₂COOH/cellulose from 4:2:1 to 4.8:2:1, there was almost no significant change in the water solubility of the CMC products, with over 70% residue content in water suggesting relatively poor etherification efficiency. Although the water solubility of the sample obtained at the molar ratio of 5:2:1 greatly improved, the obtained CMC products at such high alkali dosage shows yellow caking appearance, suggesting serious degradation at an excessive dosage of NaOH. Thus a too high dosage of alkali agent is not recommended.

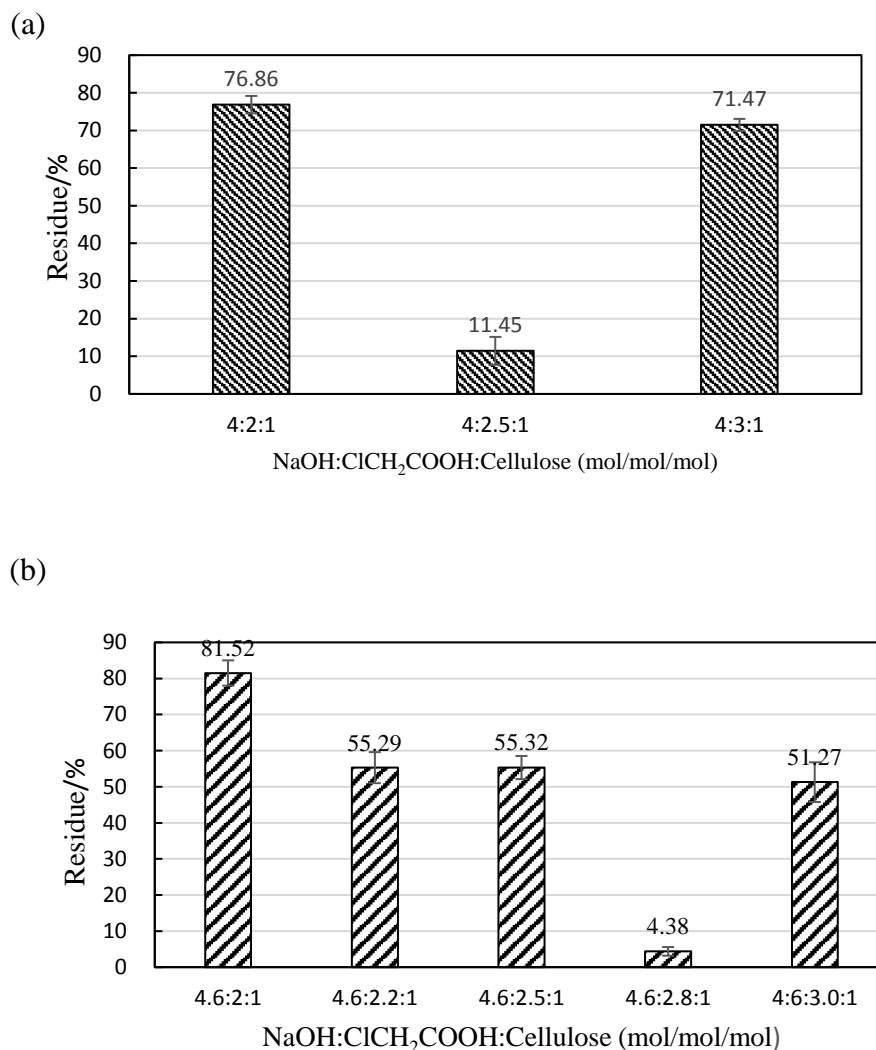


Fig. 3.3: Effects of etherifying agent (ClCH₂COOH) on water solubility of the CMC products obtained at various molar ratios of NaOH/ClCH₂COOH/cellulose in the range of 4: (2.0~3.0): 1 (a) or 4.6: (2.0~2.8): 1 (b).

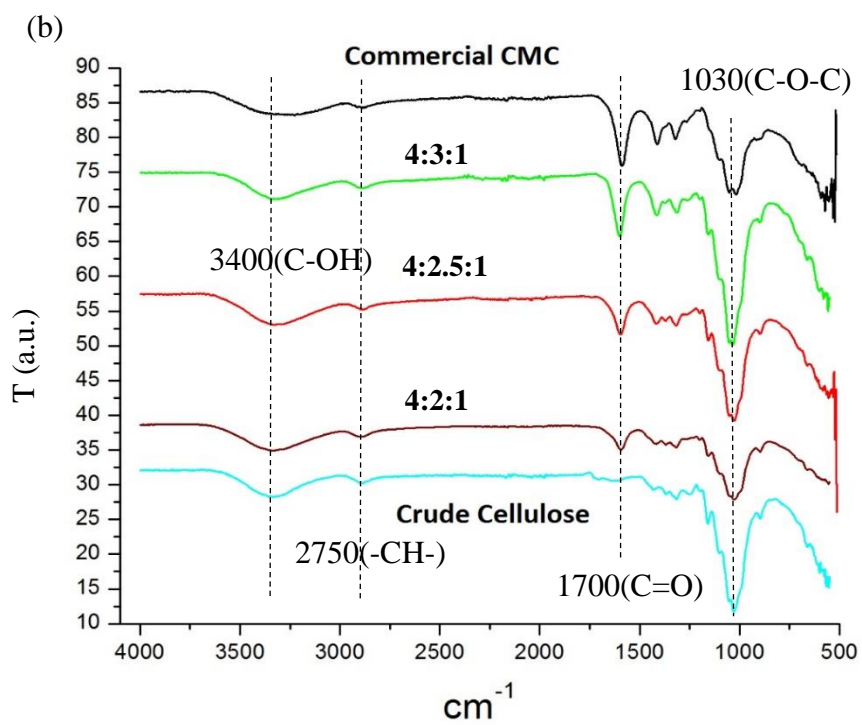
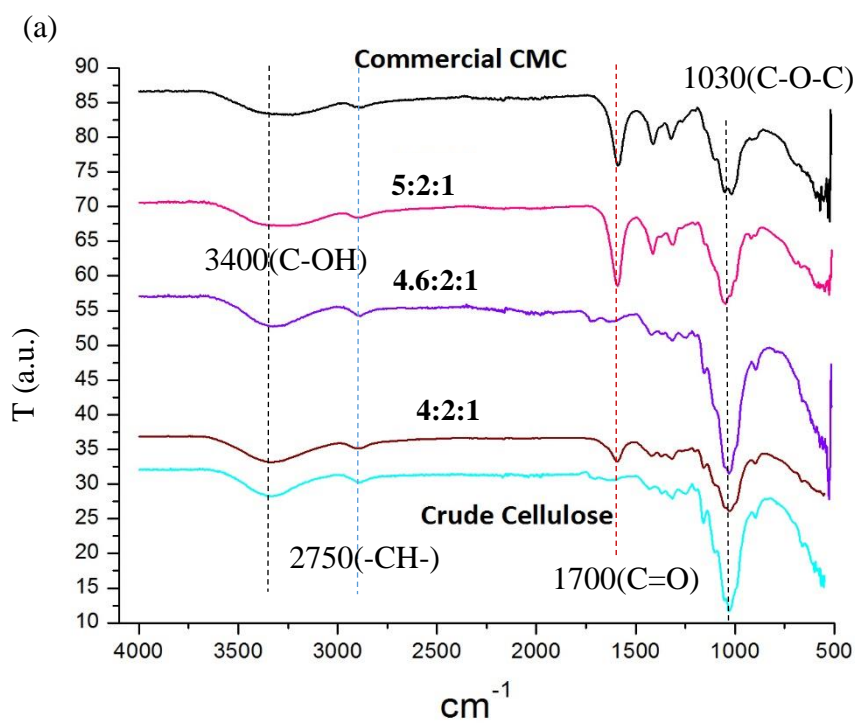
In series (2) tests, two alkali dosages, NaOH/cellulose = 4:1 and 4.6:1, i.e., a lower and medium high molar ratios, were selected, while the molar ratio of ClCH₂COOH-to-cellulose was increased from 2:1 to 3:1. The variations of water solubility of the CMC products (represented by their residue contents in water) with varying the amount of ClCH₂COOH in the reaction feed are shown in Fig. 3.3. Generally an increased dosage of the etherification agent in the reaction feed enhanced the water solubility of the resulted CMC products, as expected due to the increased extent of etherification reactions. However, there appears to be an excellent dosages for the

etherification agent, at which the product solubility attains maximum values. As shown in Fig. 3.3 a, a too high dosage of ClCH_2COOH led to reduced solubility of the CMC product, likely because the presence of excessive acid would neutralize OH^- of alkali compound, reducing the alkalization of cellulose and thus reducing the nucleophilic replacement of the chlorine in chloroacetic acid, leading to a lower etherification efficiency. From Figs. 3.3 a and 3.3 b, it is clearly shown that the molar ratios of 4:2.5:1 and 4.6:2.8:1 seem to be best feed compositions, resulting in very low residue contents in water (both $< 5\%$), that is $> 95\%$ water solubility. Coincidentally, the two outstanding molar ratios of 4:2.5:1 and 4.6:2.8:1 give the similar ratio of $\text{NaOH}/\text{ClCH}_2\text{COOH}$, being 1.6-1.64.

3.4.3 FT-IR analysis of the CMC products

Functional compositions of the obtained CMC products were analyzed by FT-IR, and the spectra of some typical samples are shown in Fig. 3.4, where all spectra were normalized with respect to the peak intensity of $-\text{CH}-$ group at around 2750 cm^{-1} that was believed to be unchanged in CMC and cellulose. Normalization of the FTIR spectra makes it easy for the comparison of other characteristic peaks.

The peak detected at 1030 cm^{-1} refers to the C-O bond of ether (C-O-C) and alcohol in glucose units in both cellulose and CMC. The characteristic peak at 1700 cm^{-1} refers to the C=O in the substituent group of the CMC products or some C=O group containing by-products. Due to the negligible mass of by-products, the C=O peak can be employed as a characteristic IR absorption peak for the ester group of the CMC products. The intensity of this C=O peak can thus be used to evaluate the etherification extent for the cellulose sample. Meanwhile, the peak observed at around 3400 cm^{-1} attributed to the hydroxyl group ($-\text{OH}$) that is substituted during the etherification reaction. Thus, from the comparisons of C=O and $-\text{OH}$ peaks intensities, the extent of substitution can be estimated.



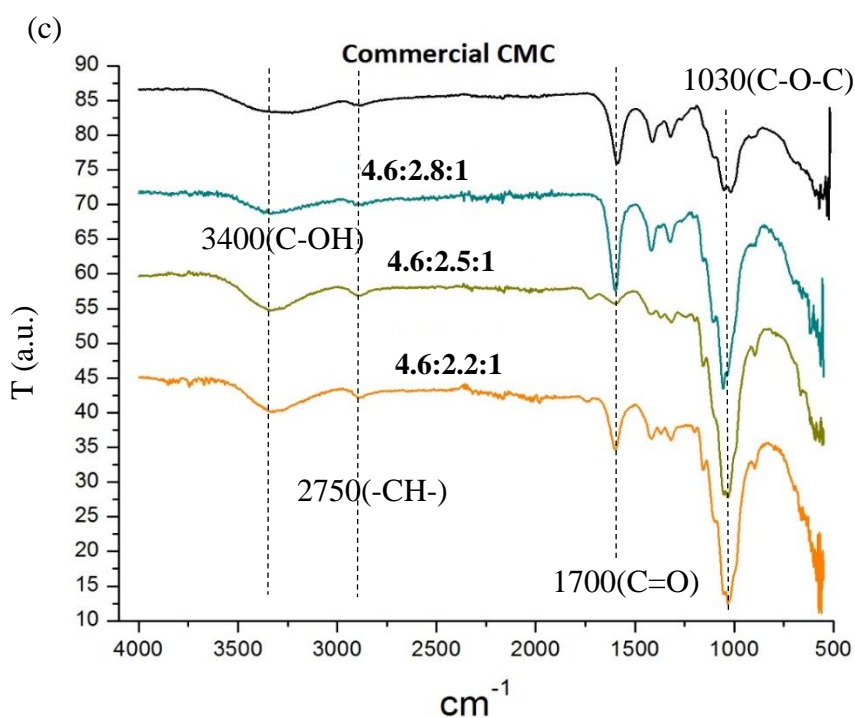


Fig. 3.4: FTIR spectra of the CMC products obtained at various molar ratios of NaOH/CICH₂COOH/cellulose in the range of (4~5): 2: 1 (a), 4: (2.0~3.0): 1 (b) and 4.6: (2.0~2.8): 1 (c).

From Fig. 3.4 a, the characteristic C=O peak at 1700 cm⁻¹ is present in all CMC products obtained at various molar ratios of NaOH/CICH₂COOH/cellulose in the range of (4~5): 2: 1. The strong C=O peak for the CMC product at 5:2:1 (mol/mol/mol) implies a large extent of etherification at such a high dosage of NaOH in the CMC synthesis. However, as mentioned previously, the obtained CMC product at 5:2:1 (mol/mol/mol) shows a yellow caking appearance, suggesting serious degradation at an excessive dosage of NaOH. Figs. 3.4 b and 3.4 c present the effects of the etherification agent, i.e., chloroacetic acid, on the functional compositions of CMC products. Commonly, with an increase in the dosage of chloroacetic acid, the C=O peak in the resulting CMC product becomes stronger, indicating a greater etherification extent for the cellulose sample at a larger excess dosage of the etherification agent. However, for the CMC product obtained at 4:3:1 (mol/mol/mol), although it exhibits a strong C=O peak, there is an obvious increase in the C-O peak probably due to

production of a mass of glucose produced by hydrolysis of the un-reacted cellulose and CMC. As such, an extremely large excess of chloracetic acid should be for CMC production.

From Figs. 3.4 b and 3.4 c, CMC products obtained at molar ratios of 4:2.5:1 and 4.6:2.8:1 exhibit prominent strength of C=O peak and lower -OH peak, suggesting a relatively high content of the carboxymethyl groups in the CMC products. Thus, the best NaOH/ClCH₂COOH/cellulose molar ratios for CMC synthesis from the cornstalk-derived bleached cellulose appears to be at 4:2.5:1 or 4.6:2.8:1, i.e., NaOH/ClCH₂COOH \approx 1.6-1.64 (mol/mol) during the process. The greater etherification extent for the cellulose in the CMC products at the best molar ratio explains their better water solubility as discussed in the previous section (Fig. 3.3).

3.4.4 SEM micrographs of the CMC products

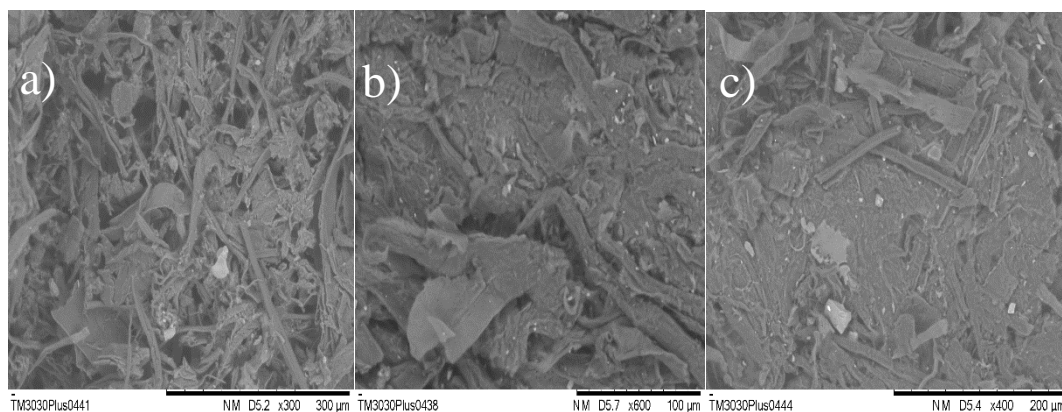
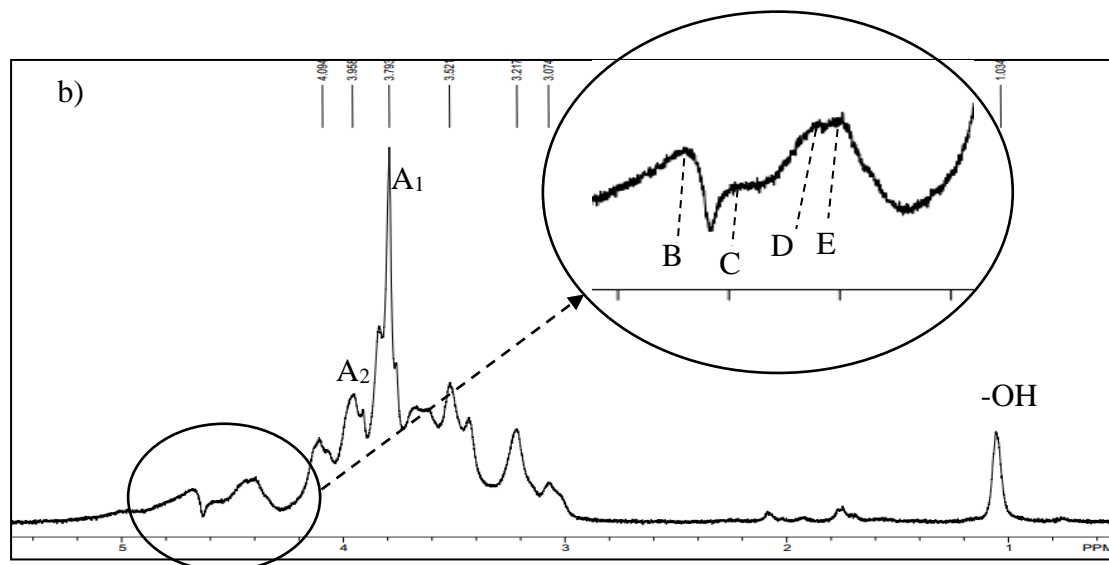
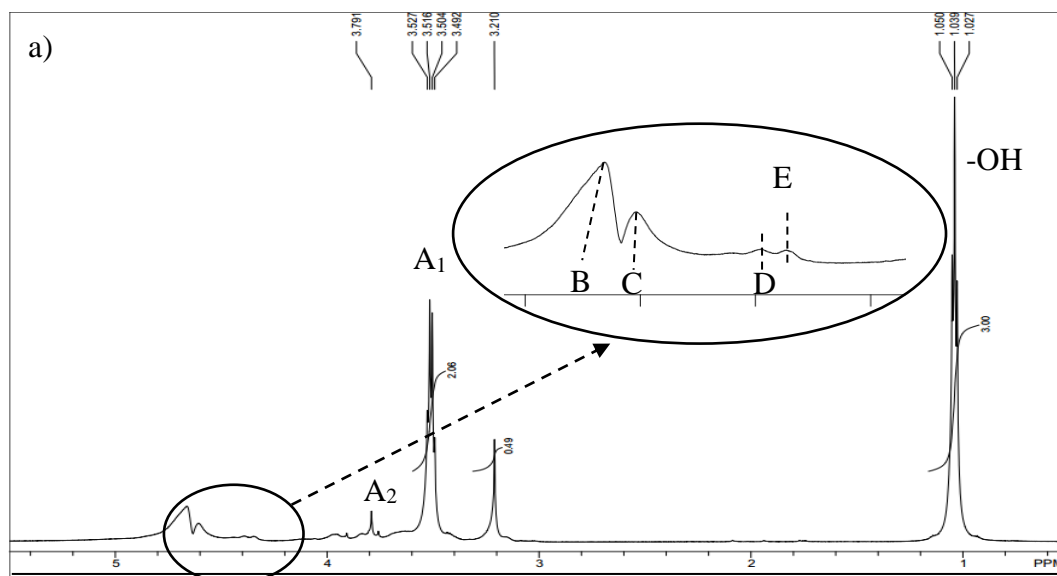


Fig. 3.5: SEM micrographs of powders: (a) CMC products at the feedstock molar ratio of 4.0:2.5:1; (b) CMC products at the feedstock molar ratio of 4.6:2.8:1; (c) bleached crude cellulose

Fig. 3.5 illustrates SEM micrographs of the CMC products obtained at two outstanding molar ratios, i.e., 4.0:2.5:1 (b) and 4.6:2.8:1 (a), compared with that of the bleached crude cellulose. The micrographs of all samples are similar, containing

fibrous particles structure. Thus, it is clear that etherification of cellulose does not change the fibrous particles structure of cellulose.

3.4.5 $^1\text{H-NMR}$ spectra of the CMC products



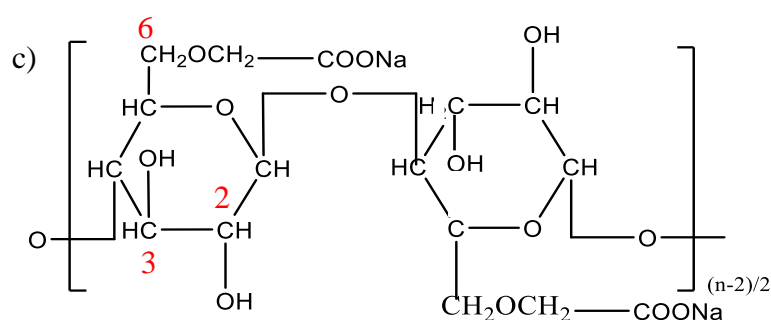


Fig. 3.6: $^1\text{H-NMR}$ spectra the CMC products in D_2O obtained at molar ratios of 4.0:2.5:1 (a) and 4.6:2.8:1 (b) and the molecular structure of sodium CMC at $\text{DS}=1$ (c).

Fig. 3.6 illustrates $^1\text{H-NMR}$ spectra the CMC products in D_2O obtained at molar ratios of 4.0:2.5:1 and 4.6:2.8:1 as well as the molecular structure of sodium CMC at $\text{DS}=1$. Characteristic ^1H chemical shifts of the protons substitution at the position of C6, C2 (α), C2 (β) and C3 (given in Fig. 3.6 c), respectively are in the range of 4.2-4.7 ppm⁹³, also shown in zoomed pictures, where the 4 characteristic peaks are designated as B, C, D and E. Unsubstituted hydroxyl groups are shown at around 1ppm. The double peaks of strong intensity at 3.4-3.8 ppm (peak A) can be attributed to the methylene groups (A_1 is the $-\text{CH}_2$ on C6 without any substitution, A_2 is the $-\text{CH}_2$ within the carboxymethyl groups) on the branch chain of the glucose rings. Therefore, the $^1\text{HNMR}$ spectra also confirm the successful etherification of the cornstalk-derived cellulose. Comparing the area integration of B, C, D, E with that of the unsubstituted hydroxyl group peaks in Fig. 3.6, the relative values of DS may be obtained. Comparing Figs. 3.6 a and b, one may conclude that the CMC product obtained at the molar ratio of 4.6:2.8:1 appears to have a relatively higher DS than that of the CMC product obtained at the molar ratio of 4:2.5:1.

3.4.6 Physical and chemical properties of the CMC products

As displayed in Table 3.2, both CMC products obtained at molar ratios of 4.0:2.5:1 and 4.6:2.8:1, or at the best molar ratio of $\text{NaOH}/\text{ClCH}_2\text{COOH} \approx 1.6-1.64$ (mol/mol)

among the test conditions, are collected as white powders, and their water solutions (2 wt%) have reasonably high viscosity, i.e., 9-16 mPa.s (or cP) likely due to the excellent water solubility of these two CMC products.

As shown in Table 3.3, the viscosity-average molecular weight M_v of these two CMC products obtained at molar ratios of 4.0:2.5:1 and 4.6:2.8:1 is in the range of 1.19×10^5 – 1.49×10^5 g/mol, and the average DS of the two products are 0.57 and 0.85, respectively. The measured DS values are smaller than the targeted DS (DS = 2), which was likely resulted from the formation of by-products during the synthesis, e.g., $\text{HOCH}_2\text{COONa}$, xylan, NaCl and modified hemi-cellulose present in the cellulose feedstock (bleached crude cellulose from cornstalk). These impurities in the final CMC products would hence decrease the average DS and viscosity dramatically, while show less effects on the appearance and water solubility of the CMC products. It shall be noted that these CMC products can be purified in the industrial operations by removing impurities by some work-up processes such as methanol rinse and H_2SO_4 acidification.

Table 3.2: Appearance and viscosity of the CMC products

Molar ratio of the reactant (Alkali/ether/feedstock) / (mol/mol/mol)	Molar ratio of alkali/etherifying agent / (mol/mol)	Appearance	Viscosity of CMC- water solution (2 wt%, 25 °C) / (mPa·s)
4.0 : 2.5 : 1	1.60	White powders	8.65
4.6 : 2.8 : 1	1.64	White powders	16.24

Table 3.3: Molecular weight and DS of the bio-based CMC

Molar ratio of the reactant (Alkali/ether/feedstock) / (mol/mol/mol)	Viscosity-average molecular weight $M_v / (\text{g}\cdot\text{mol}^{-1})$	Inherent viscosity $[\eta]/$ ($\text{dL}\cdot\text{g}^{-1}$)	Water solubility	DS
4.0 : 2.5 : 1	1.19×10^5	72.43	88.6 %	0.57
4.6 : 2.8 : 1	1.49×10^5	86.63	95.6 %	0.85

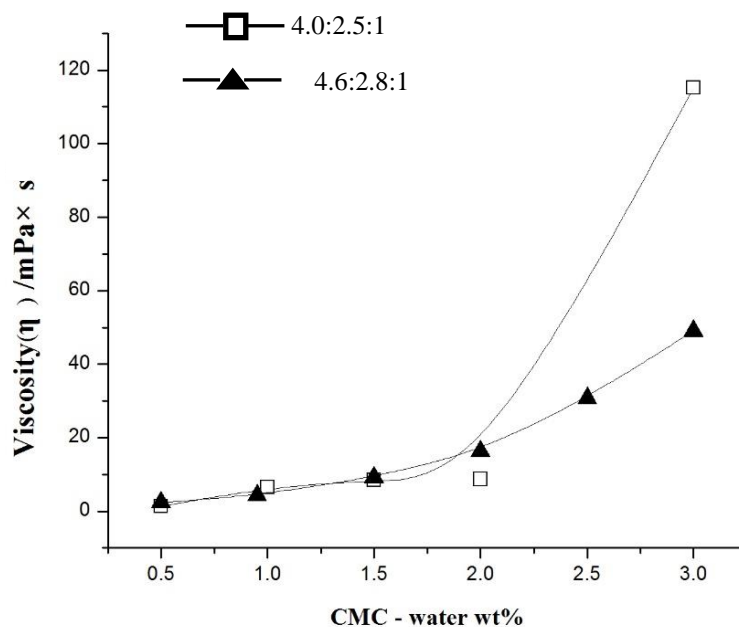


Fig. 3.7: Dependency of viscosity of the CMC-water solution on the CMC concentration (wt%) measured at 25 °C, 101.3 kPa and 100 s⁻¹ shear rate

Fig. 3.7 shows variations of viscosity of the CMC-water solution with the CMC concentration (wt%). With both CMC products (obtained at molar ratios of 4.0:2.5:1 and 4.6:2.8:1), commonly while increasing the CMC concentration in the solution, the viscosity of CMC – water solution increases slightly and linearly until the CMC concentration is 2 wt%. Such viscosity-substrate concentration relationship, i.e., the viscosity of the solution increases linearly with the concentration of solute, is typical

of Newton fluids. As also in Fig. 3.7, when the solute concentration is above 2 wt%, the viscosity of the CMC-water solution exhibits nonlinear (exponential) increasing with increasing of the solute concentration (typical of non-Newton fluids), caused mainly by the inter-enwinding of CMC molecular chains⁸³. Furthermore, the viscosity of the water solution of CMC product obtained at the molar ratio of 4.0:2.5:1 exhibited a faster increase, more dramatically than and surpassing that of the water solution of the other CMC product (4.6:2.8:1, mol/mol/mol) at the solute concentration above 2 wt%. This is possibly caused by outstanding swelling behavior of the CMC molecule with a lower DS⁹⁴.

3.5 Project Summary

Sodium carboxymethyl cellulose (CMC) materials were successfully synthesized using bleached crude cellulose derived from cornstalk after alkalization and etherification processes:

- The CMC products synthesized at molar ratio (NaOH/CICH₂COOH/cellulose) of 4.0:2.5:1 and 4.6:2.8:1, or at the best molar ratio of NaOH/CICH₂COOH \approx 1.6-1.64 (mol/mol) among the test conditions, are white powders, and their water solutions (2 wt%) have reasonably high viscosity, i.e., 9-16 mPa.s (or cP) likely due to the excellent water solubility of these two CMC products.
- The viscosity-average molecular weight M_v of these two CMC products obtained at molar ratios of 4.0:2.5:1 and 4.6:2.8:1 is in the range of 1.19×10^5 – 1.49×10^5 g/mol, and the average DS of the two products are 0.57 and 0.85, respectively.
- As the solute concentration is above 2 wt%, the viscosity of the CMC-water solution exhibits nonlinear (exponential) increasing with increasing of the solute concentration (typical of non-Newton fluids). Hence the obtained CMC products can be utilized as surfactants or thickeners in coatings and detergents or other industrial applications.

4 Conclusions and Recommendation for future works

4.1 Conclusions

Cornstalk was efficiently fractionated into crude cellulose and crude lignin in mixed solvents of acetic acid, formic acid and water at a solid/agent ratio of 1:5 (g/mL) at 80-100 °C for 120-240 min. Effects of fractionation agents, catalysts, temperature and residence time on the product yields, purity and composition of the final products were investigated. The best conditions designed for organosolv fractionation of cornstalk were as follows: mixed solvent of acetic acid/formic acid/water (3:6:1, v/v/v), HCl as the catalyst, 90 °C and 180 min residence time, where the yield (and purity) of crude cellulose and lignin products were approximate 53% (85%) and 38% (44%), respectively, on the basis of mass of oven-dried cornstalk, and the obtained crude cellulose products have very low residual lignin contents (<4%).

This newly invented organosolv fractionation process for cornstalk fractionation has several major advantages over the existing technologies:

- (1) Feedstock with a high water content can be used directly, avoiding the costly drying process;
- (2) 1:5 g/ml solid/liquid ratio is recommended which is relatively lower than all of the current published technologies;
- (3) The process operates at mild conditions (90 °C, 0.1-2.5 MPa) in a completely different mixture of solvents;
- (4) Solvents (water and organic acids) used for the process can be recycled and reused, reducing the production cost and making the process more cost-effective and greener;

(5) The process produces crude cellulose and lignin at high yields and good purity. The resulted cellulose and lignin can be further applied in CMC sodium synthesis and the preparation of bio-based phenol formaldehyde resins, respectively

Thus, a green and efficient process could be built for both cellulose and lignin products with a relatively lower cost for supplies and energy.

What's more, crude cellulose derived from cornstalk was used as feedstock for the synthesis of sodium carboxymethyl cellulose (CMC). It was revealed that the reactants alkali reagent/chloroacetic acid/cellulose at the molar ratio of 4.6:2.8:1 and 4:2.5:1, or at the molar ratio of NaOH/ClCH₂COOH \approx 1.6-1.64 (mol/mol), resulted in CMC products of relatively high water solubility and reasonably high viscosity and molecular weights. The viscosity-average molecular weight M_v of these two CMC products obtained at molar ratios of 4.0:2.5:1 and 4.6:2.8:1 is in the range of 1.19×10^5 – 1.49×10^5 g/mol, and the average DS of the two products are 0.57 and 0.85, respectively.

The successful synthesis of sodium CMC using the bleached crude cellulose from cornstalk confirms the great potential of replacing expensive purified cotton with inexpensive crop-residue-derived cellulose in CMC industry. Decreased production cost by using crop residue as cellulose feedstock for the synthesis of CMC and other bio-based materials could lead to vast opportunities for adding additional revenues to the agricultural sector.

4.2 Recommendation for Future works

In the future plan, the cornstalk-derived organosolv lignin will be pre-treated with sodium hydroxide solution or by methylation with formaldehyde, and then blended with commercial phenol-formaldehyde (PF) resole resins to prepare lignin-containing bio-based PF (BPF) resole resins for wood adhesives applications. Our target bio-substitution ratio for the BPF adhesives is up to 50 wt% (i.e., replacing up to 50 wt% of the PF resole with lignin). Curing behaviors lignin-containing BPF resole blends

will be investigated using differential scanning calorimetry (DSC), and Fourier transform infrared spectroscopy (FTIR) as well as Nuclear magnetic resonance (NMR) will be employed to analyze the chemical structure of the BPF resoles. The BPF resoles will be further applied as adhesives for making 3-ply plywood samples whose dry and wet bond strengths will be measured.

References

1. http://www.omafra.gov.on.ca/english/stats/crops/estimate_new.htm.
Kumuduni Kulasekera. Ministry of agriculture, food and rural affairs, Ontario. 2015.
2. *Saha, B., C. Hemicellulose bioconversion. J. Ind. Microbiol. Biotechnol. 2003; 30: 279-291.*
3. *Mahmood, N., Yuan, Z., Schmidt, J., Xu, C. Depolymerization of Lignins and their Applications for the Preparation of Polyols and Rigid Polyurethane Foams: A review. Renew. Sust. Energ. Rev. 2006; 60: 317-329.*
4. *Wang, M., Leitch, M., Xu, C. Synthesis of phenol-formaldehyde resol resins using organosolv pine lignins. European Polymer Journal. 2009; 45: 3380–3388.*
5. *Hebeish, A., Higazy, A., El-Shafei, A., Sharaf, S. Synthesis of carboxymethyl cellulose (CMC) and starch-based hybrids and their applications in flocculation and sizing. Carbohydrate Polymers. 2010; 79(1): 60–69.*
6. *Amine, M., Antonio, P., Ahmed, A., Fatima, C., Bertrand, C. Cornstarch and tannin in phenol–formaldehyde resins for plywood production. Industrial Crops and Products. 2009; 30:199-193.*
7. *Nihat, S., Cetin, Nilgul, O. Use of organosolv lignin in phenol–formaldehyde resins for particleboard production I. Organosolv lignin modified resins. International Journal of Adhesion & Adhesives. 2002; 22: 477–480.*

8. Yu, J., Zhang, J., B., He, J., Liu, Z., D., Yu, Z., N. *Combinations of mild physical or chemical pretreatment with biological pretreatment for enzymatic hydrolysis of rice hull. Bioresour Technol.* 2009; 100: 903.
9. Hu, Z., J., Yeh, T., F., Chang, H., M., Matsumoto, Y., Kadla, J., F. *Elucidation of the structure of cellulolytic enzyme lignin. Holzforschung.* 2006; 60: 389-397.
10. Ikead, T., Holtman, K., Kadla, J., F., Chang, H., M., Jameel, H. *Studies on the effects of ball milling on lignin structure using a modified DFRC method. Journal of Agricultural and Food Chemistry.* 2002; 50: 129-135.
11. Wegener, G., Fengl, D. *Studies on milled wood lignins from spruce part 1. Composition and molecular properties. Wood Science and Technology.* 1977; 11: 133-145.
12. El hage, R., Brosse, N., Chrusciel, L., Sanchez, C., Sannigrahi, P., Ragauskas, A. *Characterization of milled wood lignin and ethanol organosolv lignin from miscanthus. Polymer Degradation and Stability.* 2009; 94: 1632-1638
13. Villaverde, J., J., Li, J., B., Ek, M., Ligerio, P., Vega, D., A. *Native lignin structure of Miscanthus× giganteus and its changes during acetic and formic acid fractionation. J. Agric. Food Chem.* 2009; 57: 6262-6270.
14. Guerra, A., Filpponen, I., Lucia, A., L., Saquing, C., Baumberger, S., Argyropoulos, S., D. *Towards a better understanding of the lignin isolation process from wood. Journal of Agricultural and Food Chemistry.* 2006; 54: 5939-5947.
15. Polcin, J., Bezuch, B. *Enzymic isolation of lignin from wood and pulps. Wood Science and Technology.* 1978; 12: 149-158.

16. Guerra, A., Filpponen, I., Lucia, A., L., Argyropoulos, S., D. *Comparative evaluation of three lignin isolation protocols for various wood species. J. Agric. Food Chem.* 2006; 54: 9696-9705.
17. Lin, S., Y., Dence, C., W. *Methods in lignin chemistry.* Springer, Berlin. 1992.
18. Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., Crocker, D. *Determination of structural carbohydrates and lignin in biomass. NREL/TP-510-42618.* 2010.
19. Schwanninger, M., Hinterstoisser, B. *Klason lignin: modification to improve the precision of the standardized determination. Holzforschung.* 2002; 56: 161-166.
20. Maekawa, E., Ichizawa, T., Koshijima, T. *An evaluation of the acid soluble lignin determination in analysis of lignin by the sulfuric acid method. Journal of Wood Chemistry and Technology.* 1989; 9(4): 549-567.
21. Yasuda, S., Fukushima, K., Kakehi, A. *Formation and chemical structures and acid-soluble lignin I: sulfuric acid treatment time and acid-soluble lignin content of hardwood. J. Wood Sci.* 2001; 47:69-72.
22. Avellar, B., K., Glasser, W., G. *Steam-assisted biomass fractionation. I. Process considerations and economic evaluation. Biomass and Bioenergy.* 1998; 14(3): 205-218.
23. Lloyd, T., A., Wyman, C., E. *Combined sugar yields for dilute sulfuric acid pretreatment of corn stover followed by enzymatic hydrolysis of the remaining solids. Bioresour Technol.* 2005; 96: 1967.
24. Kim, T., H., Lee, Y., Y. *Pretreatment of corn stover by soaking in aqueous ammonia. Appl Biochem Biotechnol.* 2005; 121: 1119.

25. Holladay, J., E., Bozell, J., J., White, J., F., Johnson, D. *Top value-added chemicals from biomass. Volume II-Results of screening for potential candidates from biorefinery lignin. Pacific Northwest National Laboratory. 2007.*
26. Koo, B., Kim, H., Park, N., Lee, S., Yeo, H., Choi, I. *Organosolv pretreatment of Liriodendron tulipifera and simultaneous saccharification and fermentation for bioethanol production. Biomass. bioenerg. 2011; 35 (5): 1833–1840.*
27. Zhao, X., B., Dai, L., M., Liu, D., H. *Characterization and comparison of acetosolv and milox lignin isolated from croton weed stem. Journal of Applied Polymer Science. 2009; 114: 1295-1302.*
28. Xu, F., Liu, C., F., Geng, Z., C., Sun, J., X., Sun, R., C., Hei, B., H. *Characterisation of degraded organosolv hemicelluloses from wheat straw. Polym Degrad Stab. 2006; 91: 1880*
29. Liu, J., Takada, R., Karita, S., Watanabe, T., Honda, Y., Watanabe, T. *Microwave-assisted pretreatment of recalcitrant softwood in aqueous glycerol. Bioresour. Technol. 2010; 101: 9355-9360.*
30. Huijgen, W., J., J., Van, der, Laan, R., R., Reith, J., H. *Modified organosolv as a fractionation process of lignocellulosic biomass for co-production of fuels and chemicals. 16th European Biomass Conference & Exhibition, Valencia, Spain. 2008; 2-6.*
31. Villaverde, J., J., Ligeró, P., de, Vega, A. *Fractionation of Miscanthus × giganteus via modification of the formacell process. Ind. Crop. Prod. 2015; 77: 275-281.*
32. Viell, J., Harwardt, A., Seiler, J., Marquardt, W. *Is biomass fractionation by Organosolv-like processes economically viable? A conceptual design study. Bioresour. Technol. 2013; 150: 89–97.*

33. Zhang, K., Pei, Z., Wang, D. *Organic solvent pretreatment of lignocellulosic biomass for biofuels and biochemical: A review. Bioresour. Technol.* 2016; 199: 21-33.
34. Tian, X., Rehmann, L., Xu, C., Fang, Z. *Pretreatment of eastern white pine (Pinus strobes L.) for enzymatic hydrolysis and ethanol production by organic electrolyte solutions. ACS Sustainable Chem. Eng.* 2016; 4 (5): 2822–2829.
35. Sarkanen, K., V. *Acid-catalyzed delignification of lignocelluloses in organic solvents, in Progress in Biomass Conversion, K V Sarkanen and D A Tillman, Editors, Academic Press.* 1980; pp: 127-144.
36. Pan, X., J., Xie, D., Yu, R., W., Lam, D., Saddler, J., N. *Pretreatment of lodgepole pine killed by mountain pine beetle using the ethanol organosolv process: Fractionation and process optimization. Ind. Eng. Chem. Res.* 2007; 46(8): 2609-2617.
37. Ligeró, P., Vega, A., Bao, M. *Acetosolv delignification of Miscanthus sinensis bark influence of process variables. Industrial crops and products.* 2005; 21: 235-240.
38. Ligeró, P., Villaverde, J., J, Vega, A., Bao, M. *Acetosolv delignification of depithed cardoon (Cynara cardunculus) stalks. Industrial crops and products.* 2007; 25: 294-300.
39. Abad, S., Santos, V., Parajo, J., C. *Simulation of acetosolv pulping of eucalyptus wood. J. Wood Chem. Technol.* 1999; 19: 225-246.
40. Pan, X., J., Sano, Y. *Acetic acid pulping of wheat straw under atmospheric pressure. J. Wood Sci.* 1999; 45: 319-325.
41. Lehnen, R., Saake, B., Nimz, H., H. *Impact of pulping conditions on Formacell aspen lignin: investigation of methoxyl and ester groups, carbohydrates, molar mass and glass transition temperatures. Holzforschung.* 2002; 56: 498-506.

42. Sixta, H., Harms, H., Dapia, S., Parajo, J., C., Puls, J., Saake, B., Fink, H., P. *Evaluation of new organosolv dissolving pulps. Part I: Preparation, analytical characterization and viscose processability. Cellulose. 2004; 11: 73-83.*
43. Benar, P, Gonclaves, R., A, Mandelli, D, Schuchardt, U. *Eucalyptus organosolv lignins: study of the hydroxymethylation and use in resoles. Bioresource Technology. 1999; 68: 11-16.*
44. Ferraz, A., Rodriguez, J., Freer, J., Baeza, J. *Formic acid/acetone organosolv pulping of white –rotted pinus radiata softwood. J. Chem. Technol. Biotechnology. 2000; 75(12): 1190-1196.*
45. Jimenez, L., Torre, M., J., de la, Bonilla, J., L., Ferrer, J., L. *Organosolv pulping of wheat straw by use of acetone-water mixture. Process Biochemistry, 1998; 33(4): 401-408.*
46. Gilarranz, M., A., Oliet, M., Rodriguez, F., Tijero, J. *Methanol-based pulping of Eucalyptus Globulus. The Canadian journal of chemical engineering. 1999; 77: 515-521.*
47. Buranov, U., A., Ross, A., K., Mazza, G. *Isolation and characterization of lignins extracted from flax shives using pressurized aqueous ethanol. Bioresource Technology. 2010; 101: 7446-7455.*
48. Ni, Y., Hu, Q. *Alcell lignin solubility in ethanol-water mixtures. Journal of Applied Polymer Science. 1995; 57: 1441-1446.*
49. Bendzala, J., Kokta, B., V. *Optimization and fundamentals of high-yield pulping with ethanol. Wood Science and Technology. 1995; 29: 467-47.*
50. Bryan, L., Tomas, R., Kaye, F., Graeme, B. *A preliminary assessment of aqueous ethanol pulping of bagasse:the ecopulp process. International sugar journal. 2005; 107(1283): 611-615.*

51. Pan, X., J., Sano, Y. *Fractionation of wheat straw by atmospheric acetic acid process. Bioresource Technology.* 2005; 96: 1256-1263.
52. Pasquini, D., Pimenta, T., B., M., Ferreira L., H., Curvelo, A., P., S. *Extraction of lignin from sugar cane bagasse and Pinus taeda wood chips using ethanol-water mixtures and carbon dioxide at high pressures. Journal of Supercritical Fluids.* 2005; 36: 31-39.
53. Zhao, X., B., Dai, L., M., Liu, D., H. *Characterization and comparison of acetosolv and milox lignin isolated from croton weed stem. Journal of Applied Polymer Science.* 2009; 114: 1295-1302.
54. Vazquez, G., Antorrena, G., Gonzalez, J., Freire, S., Lopez, S. *Acetosolv pulping of pine wood. Kinetic modeling of lignin solubilization and condensation. Bioresource Technology.* 1997; 59: 121-127.
55. Gottlieb, K., Preuss, A., W., Meckel, J. B. *Proc. Solvent Pulping Symp. Boston. Tappi, Atlanta.* 35 Neumann N, Balser K. 1993; *Das Papier.* V16.
56. Vanderghem, C., Richel, A., Jacquet, N., Blecker, C., Paquot, M. *Impact of formic/acetic acid and ammonia pre-treatments on chemical structure and physico-chemical properties of Miscanthus × giganteus lignin. Polym. Degrad. Stab.* 2011; 96: 1761–1770.
57. Jahan, M., S., Chowdhury, D., A., N., Islam, M., K. *Atmospheric formic acid pulping and TCF bleaching of dhaincha (Sesbania aculeata), kash (Saccharum spontaneum) and banana stem (Musa Cavendish). Ind Crops Prod.* 2007; 26: 324.
58. Lam, Q., H., Delmas, M., B., Avignon, G. *Formic acid pulping of rice straw. Ind. Crop. Prod.* 2001; 14: 65-71
59. Abad, S., Santos, V., Parajo, J., C. *Formic acid-peroxyformic acid pulping of aspen wood:an optimization study. Holzforschung.* 2000; 54: 544-552.

60. Ligeró, P., Villaverde, J., J., Vega, A., Bao, M. *Pulping cardoon (Cynara cardunculus) with peroxyformic acid (MILOX) in one single stage. Bioresource Technology. 2008; 99: 5687-5693.*
61. Zhao, X., B., Liu, D., H. *Chemical and thermal characteristics of lignins isolated from Siam weed stem by acetic acid and formic acid delignification. Industrial Crops and Products. 2010; 32: 284-291.*
62. Gierer, J. *The chemistry of delignification. A general concept. Part II. Holzforschung. 1982; 36: 55-64.*
63. Hortling, B., Poppius, K., Sundquist, J. *Formic acid/ peroxyformic acid pulping. IV. Lignins isolated from spent liquors of three-stage peroxyformic acid pulping. Holzforschung. 1991; 45: 109-120.*
64. Goncalves, R., A., Benar, P. *Hydroxymethylation and oxidation of organosolv lignins and utilization of the products. Bioresource Technology. 2001; 79: 103-111.*
65. Hasegawa, I., Tabata, K., Okuma, O., Mae, K. *New pretreatment methods combining a hot water treatment and water/acetone extraction for thermochemical conversion of biomass. Energy & Fuels. 2004; 18: 755-760.*
66. Jimenez, L., Perez, I., Lopez, F., Ariza, J., Rodriguez, A. *Ethanol/acetone pulping of wheat straw influence of the cooking and the beating of the pulps on the properties of the resulting paper sheets. Bioresource Technology. 2002; 83: 139-143.*
67. Jimenez, L., Maestre, F., Perez, I. *Use of butanol-water for making wheat straw pulp. Wood Sci. Technol. 1999b; 33(2): 97-109.*
68. Quesada-Medina, J., López-Cremades, F., J., Olivares-Carrillo, P. *Organosolv extraction of lignin from hydrolyzed almond shells and*

- application of the δ -value theory. Bioresource Technology. 2010; 101(21): 8252-8260.*
69. Pan, X., J., Xie, D., Yu, R., W., Lam, D., Saddler, J., N. *Pretreatment of lodgepole pine killed by mountain pine beetle using the ethanol organosolv process: Fractionation and process optimization. Ind. Eng. Chem. Res. 2007; 46(8): 2609-2617.*
70. Mario, P., Adinugraha, Djagal, W., Marseno, H. *Synthesis and characterization of sodium carboxymethylcellulose from cavendish banana pseudo stem (Musa cavendishii LAMBERT). Carbohydrate Polymers. 2005; 62: 164–169.*
71. Baar, A., Kulicke, W., M., Szablikowski, K., Kiesewetter, R. *Nuclear magnetic resonance spectroscopic characterization of carboxymethylcellulose. Macromolecular Chemistry and Physics. 1994; 195: 1483.*
72. Heinze, T. *New ionic polymers by cellulose functionalization. Macromolecular Chemistry and Physics 1998; 199: 2341–2364.*
73. Heinze, T., Pfeiffer, K. *Studies on the synthesis and characterization of carboxymethylcellulose. Die Angewandte Makromolekulare Chemie. 1999; 266: 37–45.*
74. Heydarzadeh, H., D., Najafpour, G., D, Nazari-Moghaddam, A., A. *Catalyst-free conversion of alkali cellulose to fine carboxymethyl cellulose at mild conditions. World Applied Sciences Journal. 2009; 6(4): 564-569.*
75. Ho, F., F., L., Klosiewicz, D., W. *Proton nuclear magnetic resonance spectrometry for determination of substituents and their distribution in carboxymethylcellulose. Analytical Chemistry. 1980; 52(6): 913–916.*
76. Reuben, J., Conner, H., T. *Analysis of the ^{13}C NMR spectrum of hydrolyzed O-(carboxymethyl) cellulose: Monomer composition and substitution patterns. Carbohydrate Research. 1983; 115(1): 1–13.*

77. Tezuka, Y., Tsuchiya, Y., Shiomi, T. *¹³C NMR determination of substituent distribution in carboxymethylcellulose by use of its peresterified derivatives. Carbohydrate Research. 1996; 291: 99–108.*
78. Waring, M., Parsons, J. *Physico-Chemical characterization of carboxymethylated spun cellulose fibres. Biomaterials. 2001; 22: 903-912.*
79. Hebeish, A., A., El-Rafie, M., H., Abdel-Mohdy, F., A., Abdel-Halim E., S., Emam, H., E. *Carboxymethyl cellulose for green synthesis and stabilization of silver nanoparticles. Carbohydrate Polymers. 2010; 82: 933-941.*
80. Hasan, T., Nurhan, A. *Production of carboxymethyl cellulose from sugar beet pulp cellulose and rheological behaviour of carboxymethyl cellulose. Carbohydrate Polymers. 2003; 54: 73–82.*
81. Dapia, S., Santos, V., Parajo, J., C. *Carboxymethylcellulose from totally chlorine free-bleached milox pulps. Bioresource Technology. 2003; 89: 289-296.*
82. Asep, H., S., Linnisa, Q., Alia, B. P. *Synthesis and characterization of carboxymethylcellulose (CMC) from water hyacinth using ethanol-isobutyl alcohol mixture as the solvents. International Journal of Chemical Engineering and Application. 2014; 5(1): 36-40.*
83. Han, C., Wang, C., Jin, T., Chu, F. *Preparation of carboxymethyl cellulose by using bio-butanol by-product as raw material. Biomass Chemical Engineering. 2010; 6(4): 40-45.*
84. Wang, M., Leitch, M., Xu, C. *Synthesis of phenol–formaldehyde resol resins using organosolv pine lignins. European Polymer Journal. 2009; 45: 3380-3388.*
85. Villaverde, J., J., Ligeró, P., de, Vega, A. *Formic and acetic acid as agents for a cleaner fractionation of Miscanthus × giganteus. J. Clean. Prod. 2010; 18: 395-401.*

86. Kelothu, S., Amrita, R., Shuchi, S., Vijayanand, S., M. *Mechanistic investigations in sono-hybrid techniques for rice straw pretreatment. Ultrasonics Sonochemistry. 2014; 21: 200–207.*
87. Sannigrahi, P., Kim, D., H., Jung, S., Ragauskas, A. *Pseudo-lignin and pretreatment chemistry. Energy. Environ. 2011; Sci. 4: 1306–1310.*
88. Jahan, M., S., Rumeen, N., J., Rahman, M., M., Quaiyyum, A. *Formic acid/acetic acid/water pulping of agricultural wastes. Cellulose. Chem. Technol. 2014; 48(1-2): 111-118.*
89. Shuchi, S., Swati, K., Vijayanand S., M., Arun, G. *Screening and optimization of pretreatments for Parthenium hysterophorus as feedstock for alcoholic biofuels. Applied Science. 2014; 129: 195-206.*
90. ASTM (American Society for Testing and Materials). *Standard Test Methods for Carboxymethylcellulose. ASTM D. 2003; 1439-2003.*
91. Dapia, S., Santos, V., Parajo, J., C. *Study of formic acid as an agent for biomass fractionation. Biomass Bioenergy. 2002; 22: 213.*
92. Snelders, J., Dornez, E., Benjelloun-Mlayah, B., Huijgen, W., J., J., de, Wild, P., J., Gosselink, R., J., A., Gerritsma, J., Courtin, C., M. *Biorefining of wheat straw using an acetic and formic acid based organosolv fractionation process. Bioresource Technology. 2014; 156: 275-282.*
93. Yang, Y., Chen, H. *Preparation of carboxymethylcellulose from steam exploded crop straw. CIESC Journal. 2009; 60(7): 1843-1849.*
94. Navard, P., Cuissinat, C. *Cellulose swelling and dissolution as a tool to study the fiber structure. 7th International Symposium “Alternative Cellulose: Manufacturing, Forming, Properties”. 2006; 7.*

Curriculum Vitae

Name: Tao Shui

Post-secondary Education and Degrees:

1. East China University of Science and Technology
Shanghai, China
2010-2014 B.A. in Polymer Materials
2. The University of Western Ontario
London, Ontario, Canada
2014-2016 M.A. in Chemical and Biochemical Engineering

Honours and Awards:

1. Academic scholarship, Grade III
2011-2012, 2012-2013
2. Academic scholarship, Grade II
2013-2014
3. Distinguished Contribution Award in 3rd Dow-ECUST
Architectural Coatings Innovation Competition
2013
4. Department funding for master's research
2014-2016
5. Winner of the first-place grand prize in the poster contest at the
OMAFRA Conference
2016

Related Work Experience:

1. Tutor
Anhui University of Technology
2012-2013
2. Trainee researcher
Changzhou Branch of Akzo Nobel in China
2013
3. Research Assistant
University of Western Ontario
2014-2016

Publications:

1. Hengfu Shui, Lei Yang, Tao Shui, Chunxiu Pan, Haiping Li, Zhicai Wang, Zhiping Lei, Shibiao Ren, Shigang Kang (2014). Hydro-liquefaction of thermal dissolution soluble fraction of Shenfu subbituminous coal and reusability of catalyst on the hydro-liquefaction. (Fuel 115 (2014), 227 -231)
2. Hengfu Shui, Wenjuan Zhao, Chunjun Shan, Tao Shui, Chunxiu Pan, Zhicai Wang, Zhiping Lei, Shibiao Ren, Shigang Kang (2014). Caking and coking properties of the thermal dissolution soluble fraction of a fat coal. (Fuel 118 (2014), 64-68)
3. Tao Shui, Shanghuan Feng, Zhongshun Yuan, Takashi Kuboki, Chunbao (Charles) Xu (2016). Highly efficient organosolv fractionation of cornstalk into cellulose and lignin in organic acids. (Bioresource Technology 218 (2016), 953-961)