CATALYTIC CONVERSION OF LIGNOCELLULOSIC BIOMASS TO VALUE-ADDED CHEMICALS

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April 2018

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by

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Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the

Indian Institute of Technology Delhi
April 2018

Dedicated to

Selam, Milka and Brook

I am grateful to have you in this journey

Certificate

This is to certify that the thesis entitled, **"CATALYTIC CONVERION OF LIGNOCELLUSLOIC BIOMASS TO VALUE-ADDED CHEMCIALS"** submitted by **Mr. Samuel Kassaye** to the **Indian Institute of Technology Delhi** for the award of **Degree of Doctor of Philosophy** is a record of original bonafide research work carried out by him under my guidance and supervision. The thesis has reached the standards of fulfilling the requirements of the regulations of Indian Institute of Technology Delhi for awarding the degree.

The research report and results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

Date: 30/10/2017

New Delhi

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Acknowledgments

I would like to thank, first and foremost my supervisor, Prof. Kamal K. Pant, Department of Chemical Engineering, India Institute of Technology Delhi, for his greatest guidance, patience, support and mentorship towards the accomplishment of this research work. It is truly an honour and great privilege to have the chance of working under his guidance. Despite of busy schedules, he is always there to help, follow research progress, review and edit journal papers. Without his valuable suggestions, insightful guidance and corrections, this work would have not been realized. During this years of study and research work, he helped me a lot and I gained invaluable knowledge and broadened my horizon of wisdom tremendously in many directions.

I would also like to forward my gratitude and appreciation to my co-supervisor Dr. Sapna Jain, Department of Physical Science, Alabama State University, USA. I would not imagine the successful completion of this research work without her constant support and encouragement. I am thankful and appreciate all her kind support and feedbacks which shaped me to be the person I am now.

I would like to thank my research committee members Prof. S. K. Khare, Dr. Sreedevi Upadhyayula and Dr. M. Ali Haider for their valuable suggestions and critics during the course of this research work. I have obtained an enormous insight and valuable comments which improved my research work greatly.

I am very much grateful to be part of an excellent laboratory and working environment which was a profound encouragement to carry out my research work consistently and comfortably. I am thankful for all my lab mates and members. I forward my sincere appreciation to Mr Vishesh Kumar, Mr Krishina Kumar and Mr Suchit Kumar for their valuable help during time of need. I am grateful to senior lab mates; Dr. Pravakar Mohanty, Dr. Snehalkant Parmar, Dr. Tarak Mondal, Dr. Dinesh Kumar and Dr. Sachit Kumar sharing from your experience was a profound help during my stay. I am extremely thankful for my present lab mates; Ms Sonal, Ms Uma, Mr Rohit Kumar, Mr Saurabh Mishra, Mr Ejaz Ahmad, Mr Sonit Balyan, Mr Prashant, Mr Koshal Parmar, Dr. Dinesh Gupta and all the other research scholars with whom I have worked with at Catalytic Reaction Engineering Laboratory (CRE), IIT Delhi. I am very much thankful to the numerous people of Chemical Engineering Department who supported me in my research work both directly and indirectly.

Special thanks to Centre for Rural Development and Technology (CRDT) and Nanoscale Research Facility (NRF) for their support to let me use HPLC equipment. Special thanks to Mr Hari Krishna for his kind support whenever needed. I wish to thank Chemical Engineering Department staff for their constant support specially Prof. Anurag S. Rathore and Dr. Shalini Gupta for helping to me to use their Lab equipment. Special thanks to Mr Rajat Gupta and Sumit Singh helping me with my HPLC analysis.

I am grateful to express the motivation and inspiration I have obtained from my mother, brothers and sister. It would have been very difficult to accomplish this task without your support and advices. Special thanks to my wife Selam, my daughter Milka and son Brook who have been my motivation and I am lucky to have you in my life. I am also thankful to my friends Mr Yohannes, Mr Firew, Mr Solomon, Mr Samuel, Mr Wondalem and all Ethiopian students at IIT-Delhi with whom I spent memorable time.

New Delhi (**SAMUEL KASSAYE**)

April 2018

Abstract

Non-renewability of fossil fuels and the challenges associated with its utilization such as price fluctuation due to political instability of oil rich regions, environmental concerns, imbalance between energy supply and population growth and uneven distribution of these resources in the globe are some of the compelling factors to research for sustainable and renewable energy resources. Biomass is one of the most promising candidate along with solar, wind and hydrothermal energies for sustainable and renewable energy demand. Being the most abundant and bio-renewable resource, lignocellulosic biomass has the potential to serve as feed stock for the production of second generation bioethanol and platform chemicals without computing with food supply. Lignocellulosic biomass is composed of three bio-polymeric components: cellulose (35–50%), hemicellulose (20–35%) and lignin (5–30%). Valorisation of lignocellulosic biomass provides a wide range of valuable renewable chemicals such as glucose, 5-hydroxymethyfurfural (5-HMF) and levulinic acid which can be used for the production of bioenergy and industrially valuable bio-chemicals. 5-HMF has been considered as one of the most important biomass derived chemical due to its applicability for the production of biofuel and industrially important intermediate chemicals.

In this work, hydrolysis of microcrystalline cellulose (MCC) and cellulosic bamboo biomass (CBB) were investigate for sugar production using the most commonly known hydrophilic ionic liquid, 1-butyl3-methyl imidazolium chloride ([BMIM] Cl), in the presence of catalyst. Hydrolysis of model microcrystalline cellulose (MCC) and cellulosic bamboo biomass using catalysts such as dilute sulphuric acid, chromium impregnated zeolite (Cr/H-ZSM-5) and sulfate ion promoted zirconia (SZ) catalyst in synergy with 1-butyl-3-methylimidazolium chloride ([BMIM] Cl) ionic liquid were studied in a batch reactor. [BMIM] Cl was synthesized by nucleophilic substitution

reaction and characterized using Fourier transforms infrared spectroscopy (FTIR), proton-nuclear magnetic resonance (H-NMR) spectroscopy and Thermogravimetric analysis (TGA). The solid biomass samples and catalysts were also characterized using BET-surface area analyser, Elemental analysis, FTIR, XDR, SEM, H-NMR, Ammonia-TPD and TGA. The effect of depolymerization temperature, time, catalyst loading, substrate type and solvent type studied in detail.

Hydrolysis of MCC using dilute sulphuric acid in [BMIM] Cl ionic liquid was studied vigorously. MCC was dissolved in [BMIM] Cl and subsequently hydrolysed by catalytic amount of dilute sulphuric acid. It was observed that prior dissolution of MCC with [BMIM] Cl resulted with high yield of total reducing sugars (TRS) (92%) compared with the direct mixing of MCC, [BMIM] Cl and sulphuric acid catalyst which resulted in lower yield of TRS (25%). Similarly, cellulosic bamboo biomass was hydrolysed in dilute sulphuric acid in the presence of [BMIM] Cl and the investigation revealed that the TRS yield increased to 64% after alkaline solution pre-treatment in comparison to untreated bamboo biomass (BB) which yielded 30% TRS. However incorporation of [BMIM] Cl treatment after alkaline solution pre-treatment steps, improved the yield of TRS to 80%.

Furthermore, depolymerization of MCC was further studied using solid acid catalyst to overcome the challenges associated with homogeneous acid catalyst. In this regard, sulfated zirconia catalyst was effective in depolymerizing MCC yielding a maximum of TRS of 57% (38% glucose and 14% fructose), 9.5% LA and 5.1 of 5-HMF at a temperature of 180 ^{o}C and 3 h of depolymerization time. In addition, sulfated zirconia was tested for dehydration of glucose and fructose and a yield of 26% and 62% of 5-HMF were obtained, respectively. In addition, protonated zeolite (H-ZSM-5, SAR number 55) and chromium impregnated H-ZSM-5 catalysts (Cr/H-ZSM-5) were investigated for transformation of MCC and hexoses (fructose and glucose) to value added

chemicals. H-ZSM-5 depolymerized MCC to give a TRS of 70% (34% glucose, 8% fructose) and 3.4% 5-HMF while Cr/H-ZSM-5 catalyst was found to dehydrate fructose and glucose yielding 55% and 24% of 5-HMF, respectively. The strong Bronsted acidity in H-ZSM-5 catalyst played a crucial role for cellulose hydrolysis while improved Lewis acidity due to the incorporation of chromium metal in Cr/H-ZSM-5 enhanced fructose dehydration. Further, the reaction kinetics of cellulose depolymerization was studied using H-ZSM-5 catalyst. The results revealed that activation energy of for both formation and degradation of sugar was found to be 85.83 kJ mol^{-1} and 42.5kJmol^{-1}, respectively. The use of [BMIM] Cl ionic liquid significant decreased the activation energy of both steps due to the ionic effect of [BMIM] Cl ionic liquid compared with aqueous solution media.

सार

लिग्नाकोलेलोसिक बायोमास में भोजन की आपूर्ति के साथ कंप्यूटिंग किए बिना दूसरी पीढ़ी के बायोएथेनॉल के उत्पादन के लिए फ़ीड स्टॉक के रूप में काम करने की क्षमता है। यह तीन जैव-पोलीमरिक घटकों से बना है: सेलूलोज़ (35-50%), हेमिसेल्यूलोज़ (20-35%) और लिग्निन (5-30%)। लिगोनोक्लुलोजिक बायोमास के मूल्य निर्धारण में ग्लूकोस, 5-हाइड्रोक्साइमेथफ़ूरफ्यूरल (5-एचएमएफ) और लेव्लिनिक एसिड जैसे मूल्यवान अक्षय रसायनों की एक विस्तृत श्रृंखला उपलब्ध है जो जैव-ऊर्जा और औद्योगिक रूप से मूल्यवान जैव रसायन के उत्पादन के लिए इस्तेमाल किया जा सकता है। जैव ईंधन और औद्योगिक रूप से महत्वपूर्ण मध्यवर्ती रसायनों के उत्पादन के लिए 5-एचएमएफ को इसकी प्राप्यता के कारण सबसे महत्वपूर्ण बायोमास व्युत्पन्न रासायनिक के रूप में माना गया है। इस शोध कार्य में, ईओण तरल का विशेष रूप से इमिडाज़ोलियम आधारित विघटन, हाइड्रोजन बॉन्डिंग नेटवर्क को तोड़कर, क्रिस्टलिटी को कम करने और पॉलिमराइजेशन की डिग्री को कम करके, लिगोनोसेल्यूलस बायोमास के अवशेष प्रकृति को भंग करने और दूर करने के लिए सबसे अधिक कुशल सॉल्वेंट माना जाता है, जो सभी को बढ़ाते हैं सेलूलोज़ का हाइड्रोलिसिस पतला सल्फ्यूरिक एसिड, क्रोमियम गर्भवती जियोलाइट (सीआर / एच-जेएसएम -5) और सल्फेटेड आयन जैसे उत्प्रेरक का उपयोग करके मॉडल माइक्रोक्रिस्टलाइन सेल्युलोज (एमसीसी) और सेल्यूलोसिक बांस बायोमास का हाइड्रोलिसिस 1-ब्युटिले -3 के साथ तालमेल में ज़िरकोनिया

(एसजेड) उत्प्रेरक को बढ़ावा देता है। मेथिलिमिडाजोलियम क्लोराइड ([बीएमआईएम] सीएल) एक बैच रिएक्टर में ईओणिक तरल का अध्ययन किया गया। [बीएमआईएम] सीएल न्यूक्लियोफ़िलिक प्रतिस्थापन प्रतिक्रिया द्वारा संश्लेषित किया गया था और फूरियर का उपयोग अवरक्त स्पेक्ट्रोस्कोपी (एफटीआईआर), प्रोटॉन-परमाणु चुंबकीय अनुनाद स्पेक्ट्रोस्कोपी (एचएनएमआर) और थेर्मोग्राविमेट्रिक विश्लेषण (टीजीए) को बदलकर किया गया था। ठोस बायोमास नमूनों और उत्प्रेरक भी बीईटी सतह क्षेत्र विश्लेषक, एलिमेंटल विश्लेषण, एफटीआईआर, एक्सडीआर, एसईएम, एच-एनएमआर, अमोनिया-टीपीडी और टीजीए का उपयोग कर रहे थे। डिपोलीराइजेशन तापमान, समय, उत्प्रेरक लोडिंग और विलायक प्रकार का प्रभाव विस्तार से अध्ययन किया। एसएजेड उत्प्रेरक एमसीसी द्वारा प्रतिदिन कम करने वाली चीनी (टीआरएस) की अधिकतम क्षमता को 57% (38% ग्लूकोज और 14% फ्रक्टोज़), 9.5% एलए और 5-एचएमएफ का 5.1 डिग्री सेल्सियस पर 180 डिग्री सेल्सियस और 3 एच उपज देने से प्रभावी साबित हुआ। एसजेड क्रमशः 26% और 62% 5-एचएमएफ उपज देने वाले शर्करा (फ्रुक्टोज और ग्लूकोस) को फैलाने में भी प्रभावी था। इसके अलावा, एसएजेड उत्प्रेरक और आयनिक तरल के synergistic प्रभाव में सेलूलोज़ डिपोमिराइज़ेशन के एक बैच गतिज मॉडल अध्ययन शामिल हैं।

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Abbreviation	**Explanation**
MCC	Microcrystalline cellulose
BB	Bamboo biomass
RBI	Recovered bamboo biomass I, alkaline treated biomass
RBII	Recovered bamboo biomass II, ionic liquid treated bamboo
HPLC	High performance liquid chromatography
TGA-DTA	Thermogravimetric and Differential thermogravimetric analysis
XRD	X-ray diffraction
FTIR	Fourier transform infrared
ATR-FTIR	Attenuated Total Reflectance-Fourier transform spectroscopy
BET	Brunauer-Emmett-Teller
CHNS	Carbon-hydrogen-nitrogen-sulphur
SEM	Scanning Electron Microscope
NH_3-TPD	Temperature programmed desorption of ammonia
SZ	Sulfated Zirconia
[BMIM] Cl	1-butyl-3-methylimidazoliumchrloride
PS-BIM-Cl	Polystyrene supported butyl imidazolium chloride
IL	Ionic Liquid
LCB	Lignocellulosic Biomass
CPP	Clean Power Plan
5-HMF	5-hydroxymethylfurfural
LA	Levulinic acid

2,5-DMF	2,5-dimethylfuran
2,5-DFF	2,5-diformylfuran
2,5-BHF	2,5-bis(hydroxylmethyl)-furan
2,5-FDCA	2,5-furandicarboxylic acid
H-ZSM-5	Protonated Zeolite Socony Mobil–*5*
AFEX	Ammonia fiber explosion pre-treatment
H-NMR	Proton Nuclear Magnetic Resonance
DMSO	Dimethylsulfoxide
DMF	Dimethylformamide
DMA	Dimethylacetamide
CrI	Crystallinity index
NREL	National Renewable Energy Laboratory procedure
T.C.D	Thermal conductivity detector
RID	Refractive index detector
DNS	3, 5-dinitrisalcylic acid method
UV-vis	UV–Visible spectroscopy
TRS	Total reducing sugar
T	Tetragonal phase
M	Monoclinic phase

Greek letters

λ	X-ray wavelength
κ	constant in XRD

θ	Radiation angle
β	Peak width at half height

NOMENCLATURE

E_i	Activation energy for rate constant of reaction, kJ mol^{-1}
$\mathbf{k}_i$	Rate constant for reaction, mol^{-1}