CATALYTIC CONVERSION OF CELLULOSE TO 5-HYDROXYMETHYL FURFURAL

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by

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Dedicated to my beloved mother

Qaiser Jahan

Without whom, this couldn't have been possible

“Research is creating new knowledge.”

-Neil Armstrong.

CERTIFICATE

This is to certify that the thesis titled **"CATALYTIC CONVERSION OF CELLULOSE TO 5-HYDROXYMETHYL FURFURAL"** being submitted by **Ms**. **Firdaus Parveen** to the Indian Institute of Technology, Delhi, for the award of degree of **Doctor of Philosophy** is a record of bonafide research work carried out by him. **Ms. Firdaus Parveen** has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.

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ABSTRACT

The conversion of renewable lignocellulosic biomass to alternative fuels seems a sustainable approach to the problem of depletion of fossil fuels, global warming, henceforth attracted the immense attention from many researchers around the globe. The hydrolysis of the microcrystalline cellulose in biomass has been attempted using functionalized imidazole based IL with different functional groups, aliphatic/aromatic linkers or direct attachment of $–SO_3H$ groups and various anions were synthesized and characterized with NMR, TGA, FTIR, and UV-Vis spectroscopy. ILs with an aliphatic linker and triflate anion have highest catalytic activity in this hydrolysis yielding 93% of Total Reducing Sugar (TRS) yield at 100 ˚C and 90 min reaction time. Density Functional Theory (DFT) calculations were performed to optimize the IL and their cations and anions at B3LYP 6-311G++ (d, p) level using Gaussian 09 package. Theoretical findings are in agreement with the experimental results. To make the catalyst reusable for the hydrolysis of MCC in water as a solvent the IL immobilized on chloromethyl vinyl benzene (CMVB) with different IL / CMVB ratio. It was found that 40% IL / CMVB catalyst afforded maximum %TRS and glucose yield 58.5 and 47.9% respectively at 160 □C in 6h reaction time. The catalysts synthesized in the laboratory were characterized by FTIR, CHNS and TGA.

One pot conversion of glucose to HMF was carried out using a new class of IL containing halometallate as an anion. The qualitative comparison of the acidities of these ILs were also performed using Density Functional Theory (DFT) and validated with experimental results. The acidity and basicity of these ILs were correlated with theoretically estimated parameters like electrostatic surface potential maxima and minima, average local surface ionization energy, Fukui functions and stabilization energy. Metal atoms showed a significant effect in controlling both the Lewis as well as the Bronsted acidity of these ILs by withdrawing electron density from the cationic counterpart. $ZnCl_3$-containing ILs showed maximum catalytic activity in glucose conversion producing 13.4%, 23.8% and 67.1% yield of HMF, LA, and FA respectively. These ILs possess

environmentally hazardous metal halide that was replaced with environment-friendly organocatalyst having either amino (basic), sulfonic acid (Bronsted acidic) or both the functionalities for the conversion of glucose to 5-hydroxymethyl furfural (HMF). Sulfanilic acid with both the functionalities was found to be a promising multifunctional catalyst yielding 44% HMF. The overall detailed reaction mechanism was studied using density functional theory (DFT). The transformation of open chain glucose to enediol intermediate through Lobry de Bruyn–van Ekenstein rearrangement was found to be the rate-limiting step with the highest energy barrier of 25.2 kcal/mole during glucose isomerization to fructose. The heats of the reactions of two exothermic reactions namely glucose isomerization to fructose and fructose dehydration to HMF are 3.7 kcal/mole and 33.1 kcal/mole respectively.

The thermochemistry of glucose conversion to HMF was studied using a high-level Ab initio method G4. The glucose conversion to HMF followed the reaction sequence as follows (i) Glucose cyclization, (ii) glucose isomerization to fructose, (iii) fructose dehydration to enol intermediate, (iv) tautomerization of enol intermediate to aldol form, (v) dehydration of second water molecule from aldol, (vi) third water molecule elimination to form HMF at different temperatures 298 K to 423 K. The possible pathways for HMF conversion to various fuel component and value-added chemical was also studied.

सार

अक्षय लिग्नॉसेल्यूलस बायोमास को वैकल्पिक ईंधन में परिवर्तित करने से जीवाश्म ईंधन, ग्लोबल वार्मिंग की कमी की समस्या के लिए एक स्थायी दृष्टिकोण लगता है, अब से दुनिया भर के कई शोधकर्ताओं से अत्यधिक ध्यान आकर्षित किया गया है। बायोमास में माइक्रोक्रिस्टेलिन सेल्युलोज के हाइड्रोलिसिस को कार्यात्मककृत इमिजाजोल आधारित आईएल का उपयोग करने के लिए विभिन्न कार्यात्मक समूहों, एलीफाइट / सुगंधित लिंकर्स या सल्फोनिक समूहों के प्रत्यक्ष लगाव और विभिन्न आयनों को संश्लेषित और एनएमआर, टीजीए, एफटीआईआर, और यूवी-विज़ स्पेक्ट्रोस्कोपी के साथ लगाया गया है। एलीफाइट लिंकर और ट्राइफ्लेट आयनों के साथ आईएलएस में इस हाइड्रोलिसिस में कुल उत्प्रेरक गतिविधि होती है, जो कुल घटते चीनी (टीआरएस) की पैदावार 90 मिनट प्रतिक्रिया समय पर 93% उपज देती है। घनत्व कार्यात्मक सिद्धांत (डीएफटी) गणना आईएसएल और उनके संबंधों और एयनियों को बी3एलईपी 6-311 जी ++ (डी, पी) स्तर पर गाऊसीयन 09 पैकेज का उपयोग करने के लिए किया गया था। सैद्धांतिक निष्कर्ष प्रायोगिक परिणामों के साथ समझौते में हैं। एमएलसी के पानी में एक विलायक के रूप में हाइड्रोलिसिस के लिए उत्प्रेरक पुन: प्रयोज्य बनाने के लिए आईएल ने विभिन्न आईएल / सीएमवीबी अनुपात के साथ क्लोरोमिथाइल विनील बेंजीन (सीएमवीबी) पर स्थिर किया। यह पाया गया कि 40% आईएल / सीएमवीबी उत्प्रेरक ने अधिकतम टीआरएस और ग्लूकोज की पैदावार क्रमश: 58.5 और 47.9% की दर से 160 ° सी 6h प्रतिक्रिया समय में उठाया। प्रयोगशाला में संश्लेषित उत्प्रेरक, एफटीआईआर, सीएनएनएस और टीजीए की विशेषता थे।

एचएमएफ को ग्लूकोज के एक बर्तन के रूपांतरण को आयनों के रूप में एचएएल युक्त एक नए वर्ग का इस्तेमाल किया गया था। इन आईएलएस की अम्लीयतियों की गुणात्मक तुलना भी घनत्व कार्यात्मक सिद्धांत (डीएफटी) का प्रयोग करके और प्रायोगिक परिणामों के साथ मान्य की गई थी। इन आईएलओ की अम्लता और मूलभूतता, सैद्धांतिक रूप से अनुमानित पैरामीटर जैसे कि इलेक्ट्रोस्टैटिक सफ़ल संभावित अधिकतममा और मिनिमा, औसत स्थानीय सतह आयनीकरण ऊर्जा, फुकुई फ़ंक्शंस और स्थिरीकरण ऊर्जा से संबंधित थे। धातु परमाणुओं ने लेविस के साथ-साथ इन आईएलएस के ब्रॉन्स्टेड अम्लता को कैथिक समकक्ष से इलेक्ट्रॉन घनत्व निकालने में एक महत्वपूर्ण प्रभाव दिखाया। जेएनसीएल 3 युक्त आईएलएस ने ग्लूकोज रूपांतरण में अधिकतम उत्प्रेरक गतिविधि को 13.4%, 23.8% और 67.1% उत्पादित एचएमएफ, एलए, और एफए क्रमशः दिखाया है। इन आईएलएस के पास पर्यावरणीय रूप से खतरनाक धातु के हलाइड होते हैं जो कि पर्यावरण के अनुकूल ऑर्गेनैटैटिस्ट से प्रतिस्थापित किया गया था, जो कि एमिनो (मूल), सल्फोनिक एसिड (ब्रॉन्स्टेड अम्लीय) या ग्लूकोज के 5-हाइड्रोक्सीमाइथाइल फुरफ्यूरल (एचएमएफ) के रूपांतरण के लिए दोनों क्रियात्मकताएं थीं। दोनों कार्यात्मकताओं के साथ सल्फाइलिलिक एसिड 44% एचएमएफ उपज देने वाला एक बहुआयामी उत्प्रेरक साबित हुआ। समग्र विस्तृत प्रतिक्रिया तंत्र

घनत्व कार्यात्मक सिद्धांत (डीएफटी) के माध्यम से अध्ययन किया गया था। लॉबरी डी ब्रुइन-वैन एकेनस्टीन पुनर्व्यवस्था के जरिए खुले चेन ग्लूकोज को एन्डिओल इंटरमीडिएट के परिवर्तन को फ्रूटोस के ग्लूकोज आइसोमराइज़ेशन के दौरान 25.2 किलो कैलोरी / मोल की उच्च ऊर्जा बाधा के साथ दर-सीमित कदम पाया गया। दो एक्ज़ोथिर्मिक प्रतिक्रियाओं की प्रतिक्रियाओं के हीट जैसे कि फ्रुकोस के लिए ग्लूकोज आइसोमराइज़ेशन और एचएमएफ को फ्रुक्टोज निर्जलीकरण क्रमशः 3.7 किलो कैलोरी / तिल और 33.1 किलो कैलोरी / तिल है।

एचएमएफ में ग्लूकोज रूपांतरण के थर्माकोमेस्ट्री को उच्च-स्तरीय एब इनिटियो विधि जी 4 का उपयोग करके अध्ययन किया गया था। एचएमएफ में ग्लूकोज रूपांतरण निम्नानुसार अनुक्रमित किया गया है: (i) ग्लूकोज सार्ककरण, (ii) फ्रुकोटोस के लिए ग्लूकोज आइसोमराइज़ेशन, (iii) ईील इंटरमीडिएट के लिए फ्रोकोस डिहायड्रेशन, (iv) एनाल इंटरमीडिएट के अल्टोल फॉर्म को टॉटोमायराइजेशन, (v) निर्जलीकरण अलडोल से दूसरे पानी के अणु, (vi) तीसरे पानी के अणु का उन्मूलन अलग तापमान पर एचएमएफ बनाने के लिए 298 केल्विन से 423 केल्विन। विभिन्न ईंधन घटक और मूल्यवर्धित रासायनिक में एचएमएफ रूपांतरण के लिए संभव मार्ग भी अध्ययन किया गया था।

PERMISSIONS

The permission from the respective journals has been taken for the publications which are included in this thesis.

List of publications related to the thesis till the date of submission.

PEER-REVIEWED JOURNAL PUBLICATIONS

1 **F. Parveen**, T. Patra, S. Upadhyayula, Hydrolysis of microcrystalline cellulose using functionalized Bronsted acidic ILs-a comparative study, Carbohydrate Polymers. 135 (2015) 280–284.

2 **F. Parveen**, K. Gupta, S. Upadhyayula, Synergistic effect of chloro and sulphonic acid groups on the hydrolysis of microcrystalline cellulose under benign conditions, Carbohydrate Polymers. 159 (2017) 146–151.

3 **F. Parveen**, S. Upadhyayula Efficient conversion of glucose to HMF using organocatalysts with dual acidic and basic functionalities- A mechanistic and experimental study, Fuel Processing Technology, 162 (2017) 32–36

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LIST OF ABBREVIATIONS AND ACRONYMS

MCC	Microcrystalline cellulose
IL	Ionic liquid
HMF	5-hydroxymethyl furfural
TRS	Total Reducing Sugar
FA	Formic acid
DMF	Dimethyl Furan
[BMIM] Cl	Butyl methyl imidazolium chloride
IL-SO_3H	1-(4-sulfonic acid) butyl-3-methylimidazolium chloride
IL-COOH	1-propionic acid-3-methylimidazolium chloride
IL-OH	1-(2-hydroxyethyl)-3-methylimidazolium chloride
IL-N-SO_3H	3-sulfonic acid methylimidazolium chloride
IL-Benz-SO_3H	1-(4- sulphonic acid) benzyl-3- methylimidazolium chloride
IL-HSO_4	1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate
IL-CF_3SO_3	1-(4-sulfonic acid) butyl-3-methylimidazolium trifluoromethane sulfonate
IL-CH_3SO_3	1-(4-sulfonic acid) butyl-3-methylimidazolium methane sulfonate
DNS	3, 5-Dinitrosalicylic acid
CVMB	Chloromethyl vinyl benzene
LA	Levulinic acid
MIBK	Methyl isobutyl ketone
DFF	Diformyl furan
FDCA	Furan dicarboxylic acid
HMFA	Hydroxymethyl furoic acid
FFCA	5-formylfuran -2- carboxylic acid
H_o	Hammett function