CATALYTIC VALORIZATION OF LIGNOCELLULOSIC BIOMASS FOR THE PRODUCTION OF VALUABLE CHEMICALS

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by

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CERTIFICATE

This is to certify that the thesis entitled, **“*Catalytic Valorization of Lignocellulosic Biomass for the Production of Valuable Chemicals*”** being submitted by **Mr. Akshay Raju Mankar** in the fulfilment of requirements for the award of degree of **Doctor of Philosophy** to the Indian Institute of Technology Delhi, (India) is authentic record of work carried out by him. Mr. Akshay Raju Mankar 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 rising fuel prices along with the numerous climatic concerns such as global warming, acid rains, melting of glaciers, etc, severely affect the incessant use of fossil reserves. By the year 2040, it is expected that the exponential rise in energy demands will be enhanced significantly by about 28% of its present value. Lignocellulosic biomass (LCB) is an attractive alternative due to its abundancy and its ability to produce a wide range of fuels and chemicals. Considering the availability of LCB in India (~ 750 million tons), LCB conversion to fuels and feedstocks is significant to tackle the burning clean energy issues. LCB consists of complex networks containing cellulose (30-50%), hemicellulose (20-35%), and lignin (15-30%). A wide range of chemicals e.g., sorbitol, xylitol, ethylene glycol, 5-hydroxymethylfurfural, levulinic acid, guaiacol, vanillin, phenols, etc, can be extracted *via* different reactions viz., dehydration, hydrogenation, oxidation, hydrolysis, hydrodeoxygenation, retro-aldol condensation, etc, in the presence of catalysts.

This thesis is focussed on development of efficient catalysts for valorization of all the three components of LCB which will be beneficial for the commercialization of sustainable future bio-based refineries. Investigation of one-pot hydrolytic hydrogenation of cellulose to ethylene glycol and hexitols by a combination of heteropolyacid/ZrO_2 and Ru/C was done. The heterogeneous system produces 26.5% hexitol and 40% ethylene glycol yield. Mechanistically, it was also proved that initial hydrolysis of cellulose to glucose followed by the formation of glycolaldehyde was also accomplished by heteropolyacid/ZrO_2 support. The intermediate glycolaldehyde and glucose was successively reduced to ethylene glycol and hexitols, respectively, by Ru/C. Moreover, prior treatment of cellulose by ball-milling reduces its crystallinity and thus accounts to high conversion to cellulose. In another study, organicinorganic hybrid metal-free sulfonated porphyrin-based porous organic polymer was synthesized for the production of 5-hydroxymethylfurfurl (HMF) from fructose in water. The research is advantageous and shows high HMF yield of 85% in water, therefore bypassing the use of toxic organic solvents. Incorporation of silica introduces hydrophilicity as well as inter-particle mesopores to enhance interaction and diffusion of bulky substrates like fructose, resulting in high HMF yield. Acid/base bifunctional organocatalyst was developed for direct conversion of glucose to HMF in water giving a HMF yield of 60% under optimum conditions. A thorough kinetic modelling was also done and the values predicted by the developed model were found to give an excellent fit with the experimental data. Environmentally-friendly deep eutectic solvents (DESs) were also synthesized and applied for the synthesis of HMF. HMF yield of 88% was achieved when the reaction was performed under the microwave irradiation at 140 °C for 30 min in the presence of acetone: water and choline chloride (ChCl): lactic acid (LA) DES. The release of H^+ from the DES was favored due to competing hydrogen bonding interactions between OH group of lactic acid and fructose, which promoted the dehydration of fructose to HMF. Furthermore, DESs have also been utilized for the pretreatment of LCB to extract lignin in high purity without much alteration in its native structure. Under optimum conditions (150 °C, 20 min, ChCl: LA DES), lignin yield of 82% was achieved using microwave heating. A study was also done to show the advantages of Ru-single atoms for one-pot hydrogenation of xylose and glucose to xylitol and sorbitol, respectively. The use of Ru-single atom shows significant advantages over Ru-NPs supported catalysts for the hydrogenation of sugar molecules using hydrogen donor solvents and thus avoiding the use of high-pressure external hydrogen. Under such context, Ru-single atom catalyst enables steady production of xylitol with 95% yield. This research deals a mild protocol to utilize biomass-feedstocks for producing commercially important low-calorie sugars.

सारांश

वैश्विक तापमान वृद्धि, अम्ल वर्षा, ग्लेशियरों के पिघलने आदि जैसी कई जलवायु संबंधी चिंताओं के साथ बढ़ती ईंधन की कीमतें जीवाश्म भंडार के निरंतर उपयोग को गंभीर रूप से प्रभावित करती हैं। वर्ष 2040 तक, यह उम्मीद की जाती है कि ऊर्जा मांगों में घातीय वृद्धि इसके वर्तमान मूल्य के लगभग 28% तक बढ़ जाएगी। लिग्नोसेल्यूलोसिक बायोमास (एलसीबी) इसकी प्रचुरता और ईंधन और रसायनों की एक विस्तृत श्रृंखला का उत्पादन करने की क्षमता के कारण एक आकर्षक विकल्प है। भारत में एलसीबी की उपलब्धता (~ 750 मिलियन टन) को ध्यान में रखते हुए, जलती हुई स्वच्छ ऊर्जा के मुद्दों से निपटने के लिए ईंधन और फीडस्टॉक्स में एलसीबी रूपांतरण महत्वपूर्ण है। एलसीबी में जटिल नेटवर्क होते हैं जिनमें सेल्युलोज (30-50%), हेमिकेलुलोज (20-35%), और लिग्निन (15-30%) होते हैं। रसायनों की एक विस्तृत श्रृंखला जैसे, सोर्बिटोल, ज़ाइलिटोल, एथिलीन ग्लाइकॉल, 5-हाइड्रॉक्सीमिथाइलफ्यूरफ्यूरल, लेवुलिनिक एसिड, गुआयाकोल, वैनिलिन, फिनोल, आदि को विभिन्न प्रतिक्रियाओं जैसे निर्जलीकरण, हाइड्रोजनीकरण, ऑक्सीकरण, हाइड्रोलिसिस, हाइड्रोडीऑक्सीजनेशन, उत्प्रेरकों की उपस्थिति में एल्डोल संघनन आदि माध्यम से निकाला जा सकता है।

यह शोध कार्य एलसीबी के सभी तीन घटकों के मूल्यांकन के लिए कुशल उत्प्रेरक के विकास पर केंद्रित है जो भविष्य की जैव-आधारित रिफाइनरियों के व्यावसायीकरण के लिए फायदेमंद होगा। हेटेरोपॉलीएसिड/ZrO_2 और Ru/C के संयोजन द्वारा एथिलीन ग्लाइकॉल और हेक्सिटोल में सेल्युलोज

के एकक हाइड्रोलाइटिक हाइड्रोजनीकरण की जांच की गई। विषम प्रणाली 26.5% हेक्सिटोल और 40% एथिलीन ग्लाइकॉल का उत्पादन करती है। यंत्रवत् रूप से, यह भी साबित हो गया था कि ग्लाइकोलाडिहाइड के गठन के बाद सेल्युलोज के ग्लूकोज के प्रारंभिक हाइड्रोलिसिस को भी हेटरोपॉलीएसिड / ZrO_2 समर्थन द्वारा पूरा किया गया था। मध्यवर्ती ग्लाइकोलडिहाइड और ग्लूकोज क्रमशः Ru/C द्वारा एथिलीन ग्लाइकॉल और हेक्सिटोल में क्रमशः कम हो गए थे। इसके अलावा, बॉल-मिलिंग द्वारा सेल्युलोज के पूर्व उपचार से इसकी क्रिस्टलीयता कम हो जाती है और इस प्रकार सेलूलोज़ में उच्च रूपांतरण होता है। एक अन्य अध्ययन में, पानी में फ्रुक्टोज से 5-हाइड्रॉक्सीमिथाइलफुरफुरल (HMF) के उत्पादन के लिए कार्बनिक-अकार्बनिक संकर धातु-मुक्त सल्फोनेटेड पोर्फिरिन-आधारित कार्बनिक बहुलक को संश्लेषित किया गया था। अनुसंधान फायदेमंद है और पानी में 85% की उच्च एचएमएफ उपज दिखाता है, इसलिए जहरीले कार्बनिक विलायक के उपयोग को दरकिनार कर देता है। सिलिका को शामिल करने से हाइड्रोफिलिसिटी के साथ-साथ अंतर-कण सतह छिद्रों का परिचय होता है, जिससे फ्रुक्टोज जैसे भारी सबस्ट्रेट्स के संपर्क और प्रसार में वृद्धि होती है, जिसके परिणामस्वरूप उच्च एचएमएफ की प्राप्ति होती है।

अम्ल/क्षार बाइफंक्शनल ऑर्गेनोकैटेलिस्ट को पानी में ग्लूकोज के एचएमएफ में सीधे रूपांतरण के लिए विकसित किया गया था, जिससे इष्टतम परिस्थितियों में 60% एचएमएफ उपज मिलती है। एक संपूर्ण काइनेटिक मॉडलिंग भी किया गया था और विकसित मॉडल, अनुमानित मूल्य प्रयोगात्मक डेटा के साथ एक उत्कृष्ट फिट देने के लिए पाए गए थे। एचएमएफ के संश्लेषण के लिए पर्यावरण के अनुकूल गहरे

ईयूटेक्टिक सॉल्वैंट्स (डीईएस) को भी संश्लेषित किया गया था। एसीटोन: पानी और कोलीन क्लोराइड (ChCl): लैक्टिक एसिड (LA) DES की उपस्थिति में 30 मिनट के लिए 140 ° C पर माइक्रोवेव विकिरण के तहत प्रतिक्रिया करने पर 88% की HMF उपज प्राप्त हुई। डीईएस से एच + की रिहाई को लैक्टिक एसिड और फ्रुक्टोज के ओएच समूह के बीच प्रतिस्पर्धात्मक हाइड्रोजन बॉन्डिंग इंटरैक्शन के कारण पसंद किया गया, जिसने एचएमएफ को फ्रुक्टोज के निर्जलीकरण को बढ़ावा दिया। इसके अलावा, डीईएस का उपयोग एलसीबी के प्रीट्रीटमेंट के लिए भी किया गया है ताकि उच्च शुद्धता में लिग्निन निकालने के लिए इसकी मूल संरचना में बहुत बदलाव किए बिना। इष्टतम स्थितियों (150 डिग्री सेल्सियस, 20 मिनट, ChCl: LA DES) के तहत, माइक्रोवेव हीटिंग का उपयोग करके 82% की लिग्निन उपज प्राप्त की गई। ज़ाइलोज़ के एक-पॉट हाइड्रोजनीकरण और ज़ाइलिटोल और सोर्बिटोल के ग्लूकोज के क्रमशः आरयू-एकल परमाणुओं के लाभों को दिखाने के लिए एक अध्ययन भी किया गया था। हाइड्रोजन डोनर सॉल्वैंट्स का उपयोग करके चीनी अणुओं के हाइड्रोजनीकरण के लिए आरयू-एनपी समर्थित उत्प्रेरकों पर आरयू-सिंगल परमाणु का उपयोग महत्वपूर्ण लाभ दिखाता है और इस प्रकार उच्च दबाव वाले बाहरी हाइड्रोजन के उपयोग से बचा जाता है। ऐसे संदर्भ में, आरयू-एकल परमाणु उत्प्रेरक 95% उपज के साथ xylitol के स्थिर उत्पादन को सक्षम बनाता है। यह शोध व्यावसायिक रूप से महत्वपूर्ण कम कैलोरी शर्करा के उत्पादन के लिए बायोमास-फीडस्टॉक्स का उपयोग करने के लिए एक हल्के प्रोटोकॉल से संबंधित है।

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LIST OF ABBREVIATIONS

1,2-dichloroethane	DCE
1-akyl-3-methylimidazolium chloride	[EMIM]Cl
1-butyl-3-methylimidazolium hexafluorophosphonate	$[BMIM]PF_6$
1-butyl-3-methyl-imidazolium tetrafluoroborate	$[BMIM^+BF_4^-]$
2,5- dimethylfuran	DMF
2,5-bis(hydroxymethyl)furan	BHMF
2,5-diformylfuran	DFF
2,5-dimethyltetrahydrofuran	DMTF
2,5-furandicarboxylic acid	FDCA
3-(aminopropyl) triethoxysilane	APTES
4-nitroaniline	NA
5-hydroxymethylfurfural	5-HMF
acid/base bifunctional organocatalyst	Si-AB
activation energy	E_a
ammonia fiber explosion	AFEX
bond dissociation energy	BDE
carbon black	CB
carbon nanotubes	CNTs
catalytic transfer hydrogenation	CTH
catechol	Cat
cellulase secreting bacterial pretreatment	CBP
choline chloride	ChCl
co-solvent enhanced lignocellulosic fractionation	CELF
Deep eutectic solvents	DESs
difructose anhydride	DFA
dimethoxymethane	DMM
Dimethyl sulfoxide	DMSO

dry ball milling method	DBM
Heteropolyacids	HPAs
hydrodeoxygenation	HDO
hydrogen bond acceptor	HBA
hydrogen bond donor	HBD
hydrothermal upgrading	HyThUp
Ionic liquids	ILs
lactic acid	LA
levoglucosan	LGA
lignin carbohydrate complex	LCC
lignocellulosic biomass	LCB
liquid ammonia pretreatment	LAT
liquid-to-solid ratio	LSR
metal-organic frameworks	MOFs
methyl ethyl ketone	MEK
microcrystalline cellulose	MCC
Microwave	MW
minimum ethanol selling price	MESP
Mobil composition of matter	MCM
N, N-diethyl-4- nitroaniline	DENA
nanoparticles	NPs
oil palm empty fruit bunch	OPEFB
para-toluene sulfonic acid	PTSA
p-coumaric acid	PCA
phosphomolybdic acid	PMA
phosphotungstic acid	PTA
polycyclic aromatic hydrocarbons	PAHs
polyoxometallates	POM
sulfonated porphyrin-based porous organic polymer	PorPOPS
prairie cord grass	PCG

pre-exponential factor	A
ruthenium-based triphenylamine containing porous ligand	Ru-AmPh
ruthenium-catechol-based porous ligand	Ru-Cat
silicoalumoniphosphate	SAPO
silicotungstic acid	STA
soyabean hulls	SH
spent coffee waste	SCW
sugarcane bagasse	SB
tetraethylammonium chloride	TEAC
Tetraethylorthosilicate	TEOS
Tetrahydrofuran	THF
triphenylamine	A
triphenylphosphine	PPh
wet disk milling	WDM