Task-specific ionic liquids for cellulose conversion to 5-hydroxymethyl furfural and fuel additives

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by

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Dedicated to my beloved family & my sister late Sarla Prajapati

CERTIFICATE

This is to certify that the thesis titled **"Task-specific ionic liquids for cellulose conversion to 5-hydroxymethyl furfural and fuel additives"** being submitted by Mr. Komal Kumar 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. Mr. Komal Kumar 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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Komal Kumar

ABSTRACT

Rapid depletion of the non-renewable fossil fuel resources with fast growing energy demand of the teaming population of the world creates an urgent need to develop alternate and renewable energy sources. In this context, the conversion of 2nd generation biomass to liquefied fuel and fuel additives seems to be a promising solution. In this work, the catalytic conversion of this biomass derived microcrystalline cellulose (MCC) into 5-hydroxymethyl furfural (5-HMF) and its subsequent valorization to fuel additives like HMF cyclic acetal has been attempted using functionalized ionic liquid (IL) catalysts alongwith metal salt cocatalysts. Ionic liquids (ILs) having different functional groups (–SO_3H, –COOH, and –OH) and anions were synthesized in the laboratory and characterized by various spectroscopic techniques like ^{1}H, ^{13}C NMR, FT-IR, TGA, and UV-Vis spectroscopy. Among the synthesized IL catalysts, the IL with –SO_3H functionality and CF_3SO_3 anion showed the highest catalytic activity for MCC conversion into 5-HMF. The structure-activity of the catalyst is theoretically Density Functional Theory (DFT) calculations and experimentally were investigated. In addition, conversion of glucose to levulinic acid (LA) was studied using lab synthesized multifunctional IL catalyst and transition metal salts co-catalyst. The kinetics were investigated in batch reactor, rate constant and activation energies were calculated from the best fitting rate model. Further, valorization of biomass derived 5-HMF and LA into HMF-levulinate was also taken-up under solvent free conditions using dual acidic IL catalysts synthesized and characterized in the laboratory. These laboratory synthesized strong dual acidic IL catalyst showed highest catalytic activity with 97.0% 5-HMF conversion and 78.1% yield of HMF-levulinate. The thermodynamic data for the acetal and esters of 5-HMF were also determined using group contribution methods since these are products which lack this data in reported literature. The valorization of 5-HMF into oxygenated fuel additive acetal compound were studied using IL catalyst. Further, the heterogenization of the IL catalysts thus developed, was attempted in the synthesis of HMF-levulinate and HMF-acetal. This heterogeneous catalyst will have the advantage of easy recoverability and recyclability that can be used on industrial scale.

सार

दुनिया की टीमिंग आबादी की तेजी से बढ़ती ऊर्जा मांग के साथ गैर-नवीकरणीय जीवाश्म ईंधन संसाधनों की तेजी से कमी वैकल्पिक और अक्षय ऊर्जा स्रोतों को विकसित करने की तत्काल आवश्यकता पैदा करती है। इस संदर्भ में, तरलीकृत ईंधन और ईंधन योजकों के लिए दूसरी पीढ़ी के बायोमास का रूपांतरण एक आशाजनक समाधान प्रतीत होता है। इस काम में, इस बायोमास व्युत्पन्न माइक्रोक्रिस्टलाइन सेलुलोज (MCC) के उत्प्रेरक रूपांतरण को 5-हाइड्रॉक्सिमेथाइल फूर्फूरल (5-HMF) में और इसके बाद के ईंधन को योजक में HMF चक्रीय असेटल जैसे ईंधन के साथ कार्यात्मक आयनिक तरल (IL) उत्प्रेरक, धातु नमक सह-उत्प्रेरक के साथ का उपयोग करने का प्रयास किया गया है। आयनिक तरल पदार्थ (ILs) में अलग-अलग कार्यात्मक समूह ($-SO_3H$, $-COOH$, और $-OH$) और आयनों को प्रयोगशाला में संश्लेषित किया गया और ^{1}H, ^{13}C NMR, FT-IR, TGA, और UV-Vis स्पेक्ट्रोस्कोपी जैसी विभिन्न स्पेक्ट्रोस्कोपिक तकनीकों से चिन्हित किया। संश्लेषित IL उत्प्रेरक के बीच, IL-SO_3H कार्यक्षमता और CF_3SO_3 आयन के साथ IL ने MCC-रूपांतरण के लिए उच्चतम उत्प्रेरक गतिविधि को 5-HMF में दिखाया। उत्प्रेरक की संरचना-गतिविधि सैद्धांतिक रूप से घनत्व कार्यात्मक सिद्धांत (DFT) गणना है और प्रयोगात्मक रूप से जांच की गई थी। इसके अलावा, लेवुलिनिक अम्ल (LA) में ग्लूकोज के रूपांतरण का अध्ययन लैब संश्लेषित बहुआयामी IL उत्प्रेरक और संक्रमण धातु लवण सह-उत्प्रेरक का उपयोग करके किया गया था। बलगति की जांच बैच रिएक्टर में की गई, दर स्थिर और सक्रियता ऊर्जा की गणना सर्वश्रेष्ठ फिटिंग दर मॉडल से की गई। इसके अलावा, बायोमास प्राप्त 5-HMF और LA को एचएमएफ-लेवुलिनेट में मान्यता देने से भी विलायक मुक्त परिस्थितियों में दोहरी अम्लीय आईएल उत्प्रेरक का उपयोग करके संश्लेषित और प्रयोगशाला में विशेषता के तहत लिया गया। इन प्रयोगशाला ने मजबूत दोहरी अम्लीय आईएल उत्प्रेरक को संश्लेषित किया, जिसमें 97.0% 5-HMF रूपांतरण और एचएमएफ-लेवुलिनेट की 78.1% उपज के साथ उच्चतम उत्प्रेरक गतिविधि दिखाई दी। 5-HMF के एसिटल और एस्टर के लिए थर्मोडायनेमिक डेटा भी समूह योगदान विधियों का उपयोग करके निर्धारित किए गए थे क्योंकि ये उत्पाद हैं जो रिपोर्ट किए गए साहित्य में इस डेटा की कमी है। 5-HMF के ऑक्सीजन युक्त ईंधन एडिटिव एसिटल कंपाउंड के वैलोराइजेशन का अध्ययन आईएल उत्प्रेरक का उपयोग करके किया गया था। इसके अलावा, इस प्रकार विकसित IL उत्प्रेरकों का विषमकरण, एचएमएफ-लेवुलिनेट और एचएमएफ-एसिटल के संश्लेषण में किया गया था। इस विषम उत्प्रेरक को आसान पुनर्प्राप्ति और पुनर्चक्रण का लाभ होगा जिसका उपयोग औद्योगिक पैमाने पर किया जा सकता है।

Table of Contents

List of Tables

List of Figures

LIST OF ABBREVIATIONS AND ACRONYMS

Microcrystalline cellulose	**MCC**
5-hydroxymethyl furfural	**5-HMF**
Levulinic acid	**LA**
Formic acid	**FA**
Ionic Liquid	**IL**
Butyl methyl imidazolium chloride	**[Bmim]Cl**
1-ethyl-3-methylimidazolium chloride	**[Emim]Cl**
1-(4-sulfonic acid) butyl-3-methylimidazolium chloride	**IL-SO_3H**
1-(5-Carboxypentyl)-3-methylimidazolium Chloride	**IL-COOH**
1-(4-Hydroxybutyl)-3-methylimidazolium Chloride	**IL-OH**
1-butyl-3-methylimidazolium tetrachloroferrate	**[Bmim][$FeCl_4$]**
1-butylsulfonic-3-methylimidazolium tetrachloroferrate	**[BSO_3Hmim][$FeCl_4$]**
1-sulfonic acid-3-methylimidazolium chloride	**[Smim][Cl]**
1-sulfonic acid-3-methylimidazolium tetrachloroferrate	**[Smim][$FeCl_4$]**
1-ethyl-3-methylimidazo-lium acetate	**[Emim]Ac**
1-(4-Hydroxybutyl)-3-methylimidazolium Chloride	**IL-OH**
Electrostatic surface potential	**ESP**
Methyl isobutyl ketone	**MIBK**
Dichloromethane	**DCM**
Natural bond orbital	**NBO**
Divinylbenzene	**DVB**
Dimethylfuran	**DMF**
5-ethoxymethylfurfural	**EMF**
Dimethyl sulfoxide	**DMSO**
Tetrahydrofuran	**THF**
γ-valerolactone	**GVL**
Dihydroxymethylfuran	**DHMF**

2,5-diformylfuran	**DFF**
5-hydroxymethyl-2-furancarboxylic acid	**HMFCA**
2,5-dimethyltetrahydrofuran	**DMTHF**
2,5-bis-(hydroxymethyl)furan	**BHMF**
Furandicarboxylic acid	**FDCA**
Hammett function	$\mathbf{H_0}$
Temperature, °C	**T**

LIST OF APPINDICES