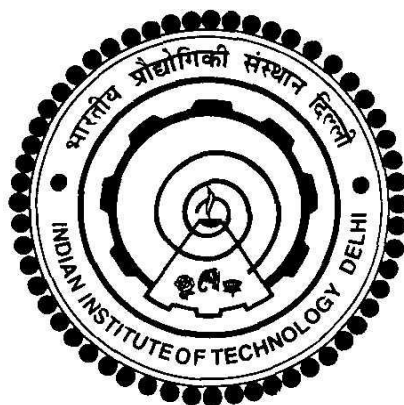


**EXPERIMENTAL AND THEORETICAL INVESTIGATIONS
INTO VALORIZATION OF BIOMASS-DERIVED PHENOLS
BY C-C COUPLING WITH LIGHT OXYGENATE**

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**DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI**

OCTOBER 2020

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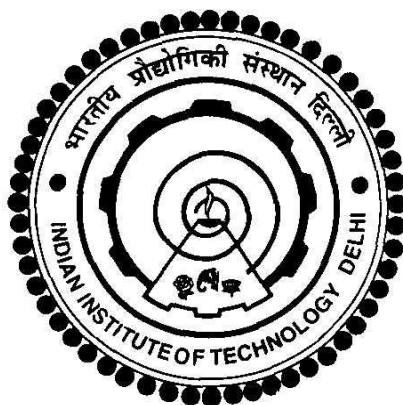
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Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

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Dedicated to my Grandmother, Uma Habiba
for her endless love, support, and encouragement

CERTIFICATE

This is to certify that the thesis titled “**Experimental and theoretical investigations into valorization of biomass-derived phenols by C-C coupling with light oxygenate**” being submitted by **Ms. Gul Afreen** 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 her. Ms. Gul Afreen 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 global concern for fossil fuel depletion and emission of greenhouse gases has led to increased research on the production of transportation fuels, alternate fuels, and value-added chemicals from the renewable 2nd generation lignocellulosic biomass. Among the different routes, fast pyrolysis is an eco-friendly, efficient, and cost-effective technology for biomass conversion, which produces liquid bio-oil (~80% yield), solid biochar, and pyrolytic gases. However, immediate commercial implementation of the condensed bio-oil formed by pyrolysis is impossible due to the presence of a high percentage of oxygen functionalities (~30-40%). The existing upgrading process includes the catalytic hydrodeoxygenation (HDO) of bio-oil (to remove oxygenates); however, it operates under harsh reaction conditions, which results in the loss of C₁–C₄ light oxygenate fractions (5-15%) in the form of non-condensable gases that could have otherwise contributed in increasing the heating value of the biofuel and chemicals. This loss can be suppressed by valorization of lignin-derived phenolic compounds via C–C coupling by an alkylation reaction with such light oxygenates to produce C₁₀–C₁₃ fuel range alkylphenols prior to HDO. The present work is focused on the alkylation of *m*-cresol, an abundant species in pyrolysis bio-oil, with *iso*-propanol (as light oxygenate) over metal loaded zeolites to form stable C₁₀ fuel precursor and important value-added chemical, thymol.

A thermodynamic analysis is performed to understand the thermodynamic limits of the *m*-cresol alkylation reaction with *iso*-propanol alongwith all the possible side-reactions to assess the thermodynamically controlled and kinetically controlled reactions. After identifying the thermodynamic boundaries of this reaction, the zeolites HZSM5, HMCM22, HBEA, and HY having different medium and large pore architecture and varied acidity are screened as catalysts for maximizing the desired mono-C-alkylated product, thymol, in a continuous flow atmospheric packed bed reactor. The structure-activity relationship is found

to be highly significant for this reaction. Therefore, the tuning of Bronsted and Lewis acidity and pore dimensions of the zeolite catalysts by ion exchanging with different metals are performed and the amount of metal is optimized, which enhances the conversion of *m*-cresol to near equilibrium conversion and with the selective formation of thymol. The disruption in structure and stability of the zeolite framework and its degraded catalytic performance is also observed at a very high amount of metal loading. After choosing the promising catalyst, statistical design of experiments is used to investigate the effect of important process parameters like reaction temperature, weight hourly space velocity, *iso*-propanol to *m*-cresol mole ratio, and their individual and interactive effects on the conversion of *m*-cresol and thymol selectivity in alkylation reaction for optimization of process parameters over the most promising catalyst.

Mechanistic insights into this reaction mechanism over metal loaded zeolite are investigated using Density Functional Theory (DFT) calculations and the effect of acidity on the reaction mechanism is elucidated by comparing the results with the parent zeolite. The rate of reaction and thermodynamic stability of thymol is found to be higher in case of metal loaded large pore protonated zeolite, resulting from higher acidity of this catalyst. Finally, the kinetics of this reaction is investigated over the most promising catalyst in an external and intraparticle mass diffusion-free regime. The time-on-stream behavior shows that the catalyst deactivates, especially at high temperatures (~300 °C) due to active site loss and pore plugging by coke. However, the rate of deactivation of this modified catalyst is significantly lower than the rate of deactivation of the parent zeolite. Based on the product distribution, a reaction network is elucidated and a kinetic model is developed. The kinetic parameters are estimated in the temperature range of 200 °C to 300 °C. The catalyst deactivation is also included in the model to check the temperature dependence of the catalyst deactivation parameters.

सार

जीवाश्म ईंधन की कमी और ग्रीनहाउस गैसों के उत्सर्जन के लिए वैश्विक चिंता ने अक्षय द्वितीय पीढ़ी के लिग्नोसेलुलॉसिक बायोमास से परिवहन ईंधन, वैकल्पिक ईंधन, और मूल्य वर्धित रसायनों के उत्पादन पर अनुसंधान को बढ़ा दिया है। विभिन्न मार्गों में, तेजी से पायरोलिसिस बायोमास रूपांतरण के लिए एक पर्यावरण-अनुकूल, कुशल और लागत प्रभावी तकनीक है, जो तरल जैव-तेल (~ 80% उपज), ठोस बायोचार और पाइरोलाइटिक गैसों का उत्पादन करती है। हालांकि, पायरोलिसिस द्वारा गठित संघनित जैव-तेल का तत्काल वाणिज्यिक कार्यान्वयन ऑक्सीजन फंक्शंसिटीज़ (~ 30-40%) के उच्च प्रतिशत की उपस्थिति के कारण असंभव है। मौजूदा अपग्रेडिंग प्रक्रिया में बायो-ऑइल के उत्प्रेरक हाइड्रोडेक्सीजेशन (एचडीओ) (ऑक्सीजन को हटाने के लिए) शामिल हैं; हालांकि, यह कठोर प्रतिक्रिया परिस्थितियों में काम करता है, जिसके परिणामस्वरूप C1 light C4 प्रकाश ऑक्सीकारक अंशों (5-15%) की हानि होती है, जो गैर-संघनन योग्य गैसों के रूप में होती है जो जैव ईंधन और रसायनों के ताप मूल्य को बढ़ाने में योगदान दे सकती थीं। इस नुकसान को लिग्निन-व्युत्पन्न फेनोलिक यौगिकों के सत्यापन द्वारा दबाया जा सकता है, सी-सी युग्मन के माध्यम से एक क्षारीय प्रतिक्रिया के साथ इस तरह के प्रकाश ऑक्सीजन के साथ सी 10-सी 13 ईंधन रेंज एल्काइफेनोल्स का उत्पादन करने के लिए एचडीओ से पहले। वर्तमान कार्य m-cresol के एल्केलाइजेशन पर केंद्रित है, पाइरोलिसिस जैव-तेल में एक प्रचुर मात्रा में, आइसो-प्रोपेनोल (प्रकाश ऑक्सीटेज के रूप में) धातु लोड किए गए जिओलाइट्स के साथ स्थिर C10 अग्रदूत और महत्वपूर्ण मूल्य वर्धित रसायन, थाइमोल बनाने के लिए है।

थर्मोडायनामिक रूप से नियंत्रित और काइनेटिक नियंत्रित प्रतिक्रियाओं का आकलन करने के लिए सभी संभावित दुष्प्रभावों के साथ-साथ आइसो-प्रोपेनोल के साथ एम-क्रेसोल अल्काइलेशन प्रतिक्रिया की थर्मोडायनामिक सीमाओं को समझने के लिए एक थर्मोडायनामिक विश्लेषण किया जाता है। इस प्रतिक्रिया की थर्मोडायनामिक सीमाओं की पहचान करने के बाद, जिओलाइट्स HZSM5, HMC22,

HBEA, और HY के पास अलग-अलग मध्यम और बड़े ताकना वास्तुकला और विविध अम्लता है जो वांछित मोनो-सी-अल्कीलेटेड उत्पाद, थाइमोल को अधिकतम प्रवाह में अधिकतम करने के लिए उत्प्रेरक के रूप में जांचा जाता है। वायुमंडलीय पैक बिस्तर रिएक्टर। इस प्रतिक्रिया के लिए संरचना-गतिविधि संबंध अत्यधिक महत्वपूर्ण पाया जाता है। इसलिए, विभिन्न धातुओं के साथ आयन एक्सचेंज द्वारा ब्रॉस्टेड और लुईस अम्लता और जिओलाइट उत्प्रेरक के ताकना आयामों की ट्यूनिंग की जाती है और धातु की मात्रा को अनुकूलित किया जाता है, जो सम-विषम रूपांतरण के साथ *m*-cresol के रूपांतरण को बढ़ाता है और चयनात्मक गठन के साथ होता है। अजवाइन का सत्व। जिओलाइट ढांचे की संरचना और स्थिरता में व्यवधान और इसके अपमानित उत्प्रेरक प्रदर्शन को धातु लोडिंग की बहुत अधिक मात्रा में मनाया जाता है। होनहार उत्प्रेरक को चुनने के बाद, प्रयोगों के सांख्यिकीय डिजाइन का उपयोग प्रतिक्रिया तापमान, वजन प्रति घंटा अंतरिक्ष वेग, आइसो-प्रोपेनॉल से लेकर एम-क्रेसोल तिल अनुपात जैसे महत्वपूर्ण प्रक्रिया मापदंडों के प्रभाव की जांच करने के लिए किया जाता है, और एम के रूपांतरण पर उनके व्यक्तिगत और इंटरैक्टिव प्रभाव। सबसे होनहार उत्प्रेरक पर प्रक्रिया मापदंडों के अनुकूलन के लिए क्षारीय प्रतिक्रिया में क्रेकोल और थाइमोल चयनात्मकता।

मेटल लोडेड ज़ोलाइट पर इस प्रतिक्रिया तंत्र में यंत्रवत अंतर्दृष्टि की जाँच डेंसिटी फंक्शनल थ्योरी (डीएफटी) गणनाओं का उपयोग करके की जाती है और प्रतिक्रिया तंत्र पर अम्लता के प्रभाव को अभिभावक जिओलाइट के साथ परिणामों की तुलना करके स्पष्ट किया जाता है। थाइमोल की प्रतिक्रिया और थर्मोडायनेमिक स्थिरता की दर इस उत्प्रेरक की उच्च अम्लता के परिणामस्वरूप धातु लोड किए गए बड़े छिद्रयुक्त ज़ोलाइट के मामले में अधिक पाई जाती है। अंत में, इस प्रतिक्रिया के कैनेटीक्स की जांच एक बाहरी और अंतर्गर्भाशयी जन प्रसार-मुक्त शासन में सबसे आशाजनक उत्प्रेरक से अधिक की जाती है। समय पर धारा व्यवहार से पता चलता है कि उत्प्रेरक सक्रिय साइट के नुकसान के कारण विशेष रूप से उच्च तापमान (~ 300 डिग्री सेल्सियस) पर निष्क्रिय हो जाता है और कोक द्वारा छिद्रण करता है। हालांकि, इस संशोधित उत्प्रेरक को निष्क्रिय करने की दर माता-पिता जिओलाइट के निष्क्रिय होने की

दर से काफी कम है। उत्पाद वितरण के आधार पर, एक प्रतिक्रिया नेटवर्क को स्पष्ट किया जाता है और एक गतिज मॉडल विकसित किया जाता है। गतिज मापदंडों को 200 डिग्री सेल्सियस से 300 डिग्री सेल्सियस के तापमान रेंज में अनुमानित किया जाता है। उत्प्रेरक निष्क्रियकरण मापदंडों के तापमान निर्भरता की जांच करने के लिए उत्प्रेरक निष्क्रियकरण को भी मॉडल में शामिल किया गया है।

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