

CATALYTIC CONVERSION OF BIO-OIL BY STEAM REFORMING TO HYDROGEN

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CATALYTIC CONVERSION OF BIO-OIL BY STEAM REFORMING TO HYDROGEN

by

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CERTIFICATE

This is to certify that the research thesis entitled “**CATALYTIC CONVERSION OF BIO-OIL BY STEAM REFORMING TO HYDROGEN**” submitted by **Mr. Ritesh Mittal** to the **I.I.T- Delhi** for award of **Doctor of Philosophy** degree is original bonafide research work done by Mr. Ritesh Mittal under my guidance. Thesis has fulfills standards as per regulatory requirements of **I.I.T- Delhi** for awarding degree. Research report and results presented in the thesis had not been submitted, partially / full, to any university / institute.

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*“Let Noble Thoughts come to us from all sides”
– “RIG VEDA”*

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ABSTRACT

Mitigation in global warming and issues of India's energy security, self-sufficiency and diversification of energy basket are key factors to propagate need for alternative clean fuel like hydrogen. Hydrogen contributes very significantly to the refining industry globally. It is also one of the most expensive molecule and requires valuable naphtha or gas to produce it via steam reforming route. As is foreseen in the future, its demand will expand in both technology end use and requirement for product up gradation. Ligno-cellulosic-biomass derived bio-oil is more sustainable carbon dioxide neutral energy source precursor without raising food and fuel debate. It is considered second generation fuel source and offers diverse utilization routes with hydrogen production as one of them by catalytic steam reforming of bio-oil. Steam reforming is promising route as it gives high hydrogen yield with low CO₂ emission. Therefore, development of a stable and selective catalyst for high hydrogen yield and CO minimization at optimum reaction conditions is prudent area of research globally.

The present research work explores the role of catalysis in steam reforming of bio-oil with Ni/CeO₂-ZrO₂ and doped Ni/CeO₂-ZrO₂-La₂O₃ catalyst. Initially, Ni/Al₂O₃ catalyst was used for experimental investigations but the level of deactivation was very high leading to short run time and therefore further studies were only done using ceria-zirconia supported doped and undoped catalysts. The catalysts were prepared by impregnation co-precipitation method and were characterized using various techniques viz, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD), Brunauer Emmett Teller (BET) Surface Area, Temperature Programmed Reduction (TPR), Raman Spectroscopy (RS), Thermo Gravimetric Analysis-Differential Thermal Analysis (TGA-DTA), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), H₂-Chemisorption, NH₃-Temperature Programmed Desorption (NH₃-TPD), Fourier Transform Infra Red (FTIR) spectroscopy.

Catalyst support characterization results revealed that ZrO_2 content in catalyst lattice improved the oxygen storage capacity of support and thereby improving catalyst activity. Also, characterization of nickel impregnated catalyst ($\text{Ni/CeO}_2\text{-ZrO}_2$) and doped catalyst ($\text{Ni/CeO}_2\text{-ZrO}_2\text{-La}_2\text{O}_3$) showed reducibility of NiO at lower temperature. Wheat straw was used as a ligno-cellulosic biomass for preparing bio-oil by fast pyrolysis at 500°C . Effect of temperature and sweep gas flow rate on bio-oil yield were studied in producing bio-oil for the further detailed steam reforming experiments of the bio-oil prepared. Physiochemical characterization of bio-oil was done by various techniques viz, Density, Ash, Moisture and CHNO analysis, Fourier Transform Infra Red (FTIR) spectroscopy, Gas Chromatography-Mass Spectrometry (GC-MS) and Nuclear Magnetic Resonance (NMR) Spectroscopy (^1H -NMR and ^{13}C -NMR).

The effects of temperature, space time and S/B on bio-oil conversion and product selectivity were investigated in a tubular fixed bed reactor at atmospheric pressure. Initial theoretical trends were obtained using thermodynamic analysis with Aspen plus simulator for reactor parameters optimization for reforming. Experiments in the temperature range of $600\text{-}850^\circ\text{C}$, space time of $650\text{-}1900 \text{ g}_{\text{cat.s}}/\text{g}_{\text{bio-oil}}$ and S/B (steam to bio-oil molar ratio) of $3.5\text{-}7.5:1$ was performed for the two set of catalysts. Gaseous products obtained from reforming were mainly H_2 , CO , CO_2 and CH_4 . Overall conversion, hydrogen yield and product selectivity for both catalysts were analyzed and compared. After optimized reaction parameters, further experimental runs were done with different S/B and Ni wt % for the doped catalyst. Ceria wt % in the doped catalyst was also varied. Experimentally, effect of Ce loading on hydrogen yield at different temperatures at W/F_{A0} of $1900 \text{ g}_{\text{cat.s}}/\text{g}_{\text{bio-oil}}$ and S/B of 5 for doped $\text{Ni/CeO}_2\text{-ZrO}_2\text{-La}_2\text{O}_3$ catalyst (Ni 20 wt% and La_2O_3 3 wt%) was studied and variation in hydrogen yield with varying Ce was not significant and therefore equi-molar $\text{CeO}_2\text{:ZrO}_2$ composition in

support was selected for future experiments with Ni 20 wt% in doped catalyst. Weight ratio (Ce:Zr) for CeO₂-ZrO₂ were taken as 0.6:0.4, 0.5:0.5 and 0.4:0.6. Ni 20 wt% was selected after varying and testing catalyst with different Ni wt% of 10%, 15%, 20% and 25% for Ni/CeO₂-ZrO₂-La₂O₃ catalyst (CeO₂:ZrO₂ molar ratio 1:1 and La₂O₃ 3 wt%) at different temperatures in the range of 600 °C to 850 °C. At initial temperatures till 650 °C, variation in hydrogen yield was not significant with changing Ni wt% but at higher temperatures wide variation in yield was reported. At 850 °C, variation in hydrogen yields for Ni 20 wt% and Ni 25 wt% are very close and therefore Ni 20 wt% is chosen for further experiments. Spent catalyst was also characterized using BET, XRD TEM, SEM, TPH, TPO, TGA and RS, to analyze the extent of coking and carbon deposition particular to the reforming reaction of bio-oil. Results reveal that Ni aids to cleave the C-C and C-H bonds of oxygenated compounds of bio-oil to produce hydrogen and CO. La₂O₃ further reduces CO concentration in product stream by promoting water gas shift reaction and reduced coking. Bio-oil conversion and hydrogen selectivity increased with increasing contact time while CO and CH₄ selectivity decreased. Investigation revealed that La₂O₃ promoted catalyst has better catalytic activity with reduced coking than that of Ni/CeO₂-ZrO₂ catalyst. It was deduced that with optimized reaction parameters of temperature, space time and S/B, Ni/CeO₂-ZrO₂-La₂O₃ can be a promising catalyst for bio-oil steam reforming.

सार

ग्लोबल वार्मिंग में कमी और भारत की ऊर्जा सुरक्षा, आत्मनिर्भरता और ऊर्जा टोकरी के विविधीकरण के मुद्दे हाइड्रोजन जैसे वैकल्पिक स्वच्छ ईंधन की आवश्यकता का प्रचार करने के लिए महत्वपूर्ण कारक हैं। विश्व स्तर पर परिष्कृत उद्योग के लिए हाइड्रोजन बहुत महत्वपूर्ण योगदान देता है यह सबसे महंगी अणु में से एक है और इसे वाष्प सुधारन मार्ग के माध्यम से उत्पादित करने के लिए मूल्यवान नाफ्था या गैस की आवश्यकता होती है। जैसा कि भविष्य में सोच रहा है, इसकी मांग प्रौद्योगिकी के अंत उपयोग और उत्पाद उन्नयन के लिए आवश्यकता दोनों में विस्तारित होगी। लिग्ना-सेल्यूलोसिक-बायोमास व्युत्पन्न जैव-तेल खाद्य और ईंधन बहस को बढ़ाए बिना अधिक टिकाऊ कार्बन डाइऑक्साइड तटस्थ ऊर्जा स्रोत के अग्रदूत हैं। यह दूसरी पीढ़ी के ईंधन स्रोत माना जाता है और हाइड्रोजन उत्पादन के साथ विविध उपयोग मार्ग प्रदान करता है क्योंकि इनमें से एक जैव-तेल की उत्प्रेरक भाप सुधार वाष्प सुधार, मार्ग का वादा कर रहा है क्योंकि यह कम सीओ₂ उत्सर्जन के साथ उच्च हाइड्रोजन उपज देता है। इसलिए, उच्च हाइड्रोजन उपज के लिए एक स्थिर और चयनात्मक उत्प्रेरक का विकास और इष्टतम प्रतिक्रिया की स्थिति में कम से कम होना वैश्विक स्तर पर अनुसंधान के विवेकपूर्ण क्षेत्र है।

वर्तमान अनुसंधान कार्य Ni/CeO₂-ZrO₂ और Ni/CeO₂-ZrO₂-La₂O₃ उत्प्रेरक के साथ जैव-तेल में सुधार के लिए भाप में कटैलिसिस की भूमिका की व्याख्या करता है। शुरू में, Ni/Al₂O₃ उत्प्रेरक प्रयोगात्मक जांच के लिए इस्तेमाल किया गया था लेकिन निष्क्रियता का स्तर बहुत ही कम था, जिसके कारण कम रम का समय था और इसलिए आगे पढ़ा गया था केवल सिरीया-ज़िरकोनिया का उपयोग किया गया था जो डीओड और अंडेड उत्प्रेरक समर्थित है। उत्प्रेरक संसेचन सह-वर्षा पद्धति द्वारा तैयार किया गया था और विभिन्न तकनीकों जैसे स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी (एसईएम), ट्रांसमिशन इलेक्ट्रॉन माइक्रोस्कोपी (तेम), एक्स-रे विवर्तन (एक्सआरडी), ब्रुनेर एमेट्ट टेलर (बीईटी) सतह क्षेत्र, तापमान का उपयोग किया गया था प्रोग्रामिंग कमी (टीपीआर), रमन स्पेक्ट्रोस्कोपी (आरएस), थर्मो ग्रेविमेट्रिक विश्लेषण-विभेदक थर्मल विश्लेषण (टीजीए-डीटीए), इंडक्टेडिव कम्प्लेटेड प्लाज़्मा-मास स्पेक्ट्रोमेट्री (आईसीपी-एमएस), एच-2 केमिस्मोरॉप्शन, एनएच₃-तापमान प्रोग्रामेड डेस्ट्रॉप्शन (एनएच₃-टीपीडी)), फूरियर ट्रांसफॉर्म इन्फ्रा रेड (एफटीआईआर) स्पेक्ट्रोस्कोपी।

उत्प्रेरक समर्थन लक्षण वर्णन के परिणाम बताते हैं कि उत्प्रेरक जाली में ZrO₂ सामग्री ने ऑक्सीजन भंडार क्षमता में सुधार किया और उत्प्रेरक गतिविधि में सुधार किया। इसके अलावा, निकल गर्भवती उत्प्रेरक (Ni/CeO₂-ZrO₂) और डीएड उत्प्रेरक (Ni/CeO₂-ZrO₂-La₂O₃) के लक्षण वर्णन ने निम्न तापमान पर एनआईओ की न्यूनता दिखाई। 500°सी में तेजी से जैव-तेल की तैयारी के लिए गेहूं का भूरा एक लिग्ना-सेल्यूलोसिक बायोमास के रूप में इस्तेमाल किया गया था। जैव-तेल की पैदावार पर तापमान और स्वीप गैस प्रवाह की दर का

प्रभाव बायो-ऑयल के उत्पादन में अध्ययन किया गया था ताकि जैव-तेल के अधिक विस्तृत भाप सुधार के प्रयोगों को तैयार किया जा सके। जैव-तेल के भौतिक-रासायनिक लक्षण वर्णन विभिन्न तकनीकों जैसे घनत्व, ऐश, नमी और चलो विश्लेषण, फूरियर ट्रांसफॉर्म इन्फ्रा रेड (एफटीआईआर) स्पेक्ट्रोस्कोपी, गैस क्रोमैटोग्राफी-मास स्पेक्ट्रोमेट्री (जीसी-एमएस) और परमाणु चुंबकीय अनुनाद (एनएमआर) स्पेक्ट्रोस्कोपी द्वारा किया गया था (¹एच-एनएमआर और ¹³सी-एनएमआर)।

वायुमंडलीय दबाव में ट्यूबलर फिक्स्ड बिल्ला रिएक्टर में तापमान, अंतरिक्ष समय और जैव-तेल रूपांतरण और उत्पाद चुनिंदा पर एस/बी के प्रभाव की जांच की गई। सुधार के लिए रिएक्टर मापदंडों के अनुकूलन के लिए एस्पेन प्लस सिम्युलेटर के साथ थर्मोडायनामिक विश्लेषण का उपयोग करके प्रारंभिक सैद्धांतिक रुझान प्राप्त किए गए थे। 600-850 डिग्री सेल्सियस के तापमान सीमा, 650-1900 के जी(उत्प्रेरक).एस/जी_{तेल} और एस/बी (वाष्प से जैव-तेल दाढ़ अनुपात) के तापमान 3.5-7.5:1 के तापमान के दो सेटों के लिए किया गया था उत्प्रेरक। सुधार से प्राप्त गैसीय उत्पादों मुख्य रूप से एच-2, सीओ, सीओ-2 और सीएच-4 थे। कुल मिलाकर रूपांतरण, दोनों उत्प्रेरक के लिए हाइड्रोजन उपज और उत्पाद चयन का विश्लेषण किया गया और तुलना की गई। अनुकूलित प्रतिक्रिया मापदंडों के बाद, अतिरिक्त प्रयोगात्मक रन डीएड उत्प्रेरक के लिए अलग एस/बी और नी वेट% के साथ किया गया था। डीएड उत्प्रेरक में सीरिया का% भी विविध था। प्रयोगात्मक रूप से, 1900 जी(उत्प्रेरक).एस/जी_{तेल} के डब्ल्यू/एफएफ और डीपीड Ni/CeO₂-ZrO₂-La₂O₃ उत्प्रेरक (नी 20वेट% और La₂O₃ 3 वेट La₂O₃ के लिए एस/बी के अलग-अलग तापमान पर हाइड्रोजन उपज पर सीई लोड करने का प्रभाव % का अध्ययन किया गया और हाइड्रोजन उपज में भिन्नता के साथ भिन्नताएं महत्वपूर्ण नहीं थीं और इसलिए समरूपता CeO₂ समर्थन में ZrO₂ संरचना भविष्य में प्रयोग के लिए चुना गया था, जो कि 20 डिग्री सेल्सियस डीएपी उत्प्रेरक में है।

CeO₂-ZrO₂ के लिए वजन अनुपात (सीई:जेआर) 0.6: 0.4, 0.5: 0.5 और 0.4: 0.6 के रूप में लिया गया था। Ni/CeO₂-ZrO₂-La₂O₃ उत्प्रेरक (CeO₂-ZrO₂ दाढ़ अनुपात 1:1 और La₂O₃-3%) वेट के लिए 10%, 15%, 20% और 25% के विभिन्न नी विल्ट% के साथ अलग-अलग परीक्षण और परीक्षण के बाद नी 20% 600 डिग्री सेल्सियस से 850 डिग्री सेल्सियस की सीमा में अलग-अलग तापमान पर 650 डिग्री सेल्सियस तक प्रारंभिक तापमान पर, हाइड्रोजन उपज में अंतर नी नीले रंग की मात्रा को बदलने के साथ महत्वपूर्ण नहीं था, लेकिन उच्च तापमान पर उपज में व्यापक विविधता की सूचना मिली थी। 850 डिग्री सेल्सियस में, नी 20 वें% और नी 25 वें% के लिए हाइड्रोजन पैदावार में अंतर बहुत करीब है और इसलिए नी 20 वें% आगे प्रयोगों के लिए चुना जाता है। बायो-ऑयल के सुधार की प्रतिक्रिया के लिए विशेष रूप से कोकिंग और कार्बन ब्योरा की मात्रा का विश्लेषण करने के लिए बीएटी, एक्सआरडी मंदिर, एसईएम, टीपीएच, टीपीओ, टीजीए और आरएस का प्रयोग किया गया था। परिणाम बताते हैं

कि नी हाइड्रोजन का निर्माण करने के लिए जैव-तेल के ऑक्सीजन युक्त यौगिकों के सी-सी और सी-एच बंधन को ढंकने में सहायता करता है और सीईओ-2 ओ पानी की गैस की प्रतिक्रिया को कम करने और कम कोकिंग का प्रचार करके उत्पाद धारा में सीओ एकाग्रता को कम करता है। जैव-तेल रूपांतरण और हाइड्रोजन चुनिंदा बढ़ते संपर्क समय के साथ बढ़े जबकि सीओ और सीएच-4 चुनिंदा कमी हुई। जांच से पता चला है कि La_2O_3 की उत्पत्ति उत्प्रेरक में $\text{Ni/CeO}_2\text{-ZrO}_2$ उत्प्रेरक की तुलना में कम कोकिंग के साथ बेहतर उत्प्रेरक गतिविधि है। इसका अनुमान लगाया गया कि तापमान, अंतरिक्ष समय और एस/बी, $\text{Ni/CeO}_2\text{-ZrO}_2\text{-La}_2\text{O}_3$ के अनुकूलित प्रतिक्रिया पैरामीटर के साथ जैव-तेल भाप सुधार के लिए एक आशाजनक उत्प्रेरक हो सकता है।

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CHAPTER – 1

INTRODUCTION
