DEVELOPMENT OF GREEN PROCESS FOR PRODUCTION OF SECOND AND THIRD GENERATION DERIVATIVES FROM CASTOR OIL

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by

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Certificate

This is to certify that the thesis entitled **"Development of Green Process for Production of Second and Third Generation Derivatives from Castor Oil,"** submitted by Mr. Sagarkumar Yogesh Dhanuskar to the Indian Institute of Technology Delhi for the award of the degree of Doctor of Philosophy, is a record of the original bonafide research work carried out by him. He has worked under my supervision and has fulfilled the requirements, which, to my knowledge, has reached the requisite standard for submitting this thesis. The results in this thesis have not been submitted in part or full to any University or Institute for the award of any degree or diploma.

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Abstract

Castor oil has the potential to be a renewable resource for the synthesis of high-value-added chemicals. Currently, the first-generation castor oil derivatives such as sulfonated castor oil-turkey red oil, ethoxylated castor oil, and hydrogenated castor oil are produced in India. These second and third generation derivatives has more values than the first-generation products. The technological challenges are higher temperature for conversion, development of suitable catalyst, and green process for production. The thesis focuses on conversion of castor oil derivatives from methyl ricinoleate to sebacic acid, 2-octanol, heptaldehyde and methyl undecenaote by using thermal-catalytic cracking, and alkali-splitting reaction. Transesterification of castor oil to convert into methyl ricinoleate for the physico-chemical characteristics and fatty acid composition of methyl ricinoleate and castor oil have been studied by conventional and modern techniques. It was observed that castor oil contained 86.4 % ricinoleic acid in its fatty acid composition.

This work focuses on the thermal cracking of methyl ricinoleate, the major component of castor oil, in a micro fixed bed reactor that was used to produce methyl undecenoate and heptaldehyde. Methyl undecenoate and heptaldehyde have wide applications in polymers, cosmetics, and drug industries. The effect of flow rate, sweeping gas flow rate, preheating, and reaction temperatures were examined briefly. Thermal cracking of methyl ricinoleate at a preheating temperature of 350 °C and reaction temperatures of 550 °C, the highest yields of methyl ricinoleate, 46.7 wt.%, and heptaldehyde 27.3 wt.% were achieved. The increase in sweep flow rate from 15 ml min^{-1} to 25 ml min^{-1} enhanced the production of pyrolytic oil yield to 92.6 wt.%. Density functional theory (DFT) was performed to examine the experimental results and distribution of the products involved in the dissociation of methyl ricinoleate. Assuming C-C bond scission followed by the cleavage of the OH bond, the reaction energy of methyl undecenoate and heptaldehyde thermal cracking is computed using

DFT. This research may provide an alternative pathway to produce important chemicals from castor oil for upscaling and process development for the industry.

Furthermore, methyl undecenoate and heptaldehyde formation are enhanced in the presence of a catalyst. It has been demonstrated that lanthanum supported on zeolite HZSM-5 is effective at converting methyl ricinolate to bio-oil. The synthesis of lanthanum-loaded on HZSM-5 has been further confirmed through the characterizations of the catalyst. The experimental results indicate that the optimum condition for achieving maximum yield conversion was attained at 500 °C for 150 mins with 2 gm of 5 wt.% La/HZSM-5. The bio-oil obtained at the optimal condition was comprised around 97.5 wt.% with methyl undecenoate (76.5 wt.%) and heptaldehyde (54.7 wt.%) alongside other minor aromatic hydrocarbons.

Methyl ricinoleate was used as the raw material for alkali splitting to prepare sebacic acid and 2-octanol. The reaction parameters, including catalyst, the ratio of oleochemicals/NaOH, reaction time, and reaction temperature, were optimized. It was found that 10wt.% Fe/HZSM-5 showed the best catalytic performance, and 280 ^{o}C was considered the most suitable reaction temperature. The oleochemicals/NaOH ratios 10:15, 12:15, 14:15, and 15:15 were determined as the optimal ratio for alkali-splitting of methyl ricinoleate. In addition, the optimal reaction time of alkali-splitting of methyl ricinoleate was 4 hr, and the maximum yield was 5 wt.% Fe/HZSM-5 of 29.7 wt.% of 2-octanol and 56.8 wt.% of sebacic acid, 10 wt.% Fe/HZSM-5 of 39.4 wt.% of 2-octanol and 68.1wt.% of sebacic acid, 15 wt.% Fe/HZSM-5 of 42.3 wt.% of 2-octanol and 71.8 wt.% of sebacic acid, respectively. FT-IR and NMR confirmed high purity of sebacic acid and 2-octanol.

This research may provide an alternative pathway to produce important chemicals from castor oil for upscaling and process development for the industry.

सारांश

इस थीसिस में वर्णित शोध कार्य में मिथाइल रिकिनोलिएट की दो सबसे महत्वपूर्ण प्रतिक्रियाएं शामिल हैं। हेप्टाल्डिहाइड, मिथाइल अनडेसीनोएट, सेबासिक एसिड और 2-ऑक्टेनॉल, औद्योगिक रूप से महत्वपूर्ण उच्च मूल्यवान ओलेओकेमिकल्स की अधिकतम पैदावार प्राप्त करने के लिए थर्मल और कैटेलिटिक क्रैकिंग और क्षार विभाजन।

मिथाइल रिसिनोलेट और अरंडी के तेल की भौतिक-रासायनिक विशेषताओं और फैटी एसिड संरचना के लिए अरंडी के तेल को मिथाइल रिसिनोलेट में परिवर्तित करने के लिए अरंडी के तेल का ट्रांसएस्टरीफिकेशन पारंपरिक और आधुनिक तकनीकों द्वारा अध्ययन किया गया है। यह देखा गया कि अरंडी के तेल में फैटी एसिड संरचना में 86.4% रिसिनोलिक एसिड होता है।

अरंडी के तेल में उच्च मूल्यवर्धित रसायनों के संश्लेषण के लिए एक नवीकरणीय संसाधन होने की क्षमता है। यह कार्य मिथाइल रिसिनोलेट के थर्मल क्रैकिंग पर केंद्रित है, जो माइक्रो फिक्स्ड बेड रिएक्टर में अरंडी के तेल का प्रमुख घटक है जिसका उपयोग मिथाइल अनडेसीनोएट और हेप्टाल्डिहाइड का उत्पादन करने के लिए किया जाता था। मिथाइल अनडेसीनोएट और हेप्टाल्डिहाइड का पॉलिमर, सौंदर्य प्रसाधन और दवा उद्योगों में व्यापक अनुप्रयोग है। प्रवाह दर, व्यापक गैस प्रवाह दर, प्रीहीटिंग और प्रतिक्रिया तापमान के प्रभाव की संक्षेप में जांच की गई। 350 डिग्री सेल्सियस के प्रीहीटिंग तापमान और 550 डिग्री सेल्सियस के प्रतिक्रिया तापमान पर मिथाइल रिकिनोलेट की थर्मल क्रैकिंग, मिथाइल रिकिनोलेट 46.7 wt.% और हेप्टाल्डिहाइड 27.3 wt.% की उच्चतम उपज प्राप्त की गई। स्वीप प्रवाह दर को 15 मिली मिनट-1 से बढ़ाकर 25 मिली मिनट-1 करने से पायरोलाइटिक तेल उपज का उत्पादन 92.6 डब्ल्यूटी% तक बढ़ गया। मिथाइल रिकिनोलेट के पृथक्करण में शामिल उत्पादों के प्रयोगात्मक परिणामों और वितरण की जांच करने के लिए घनत्व कार्यात्मक सिद्धांत

(डीएफटी) का प्रदर्शन किया गया था। सी-सी बांड विखंडन को ओएच बांड के दरार के बाद मानते हुए, मिथाइल अनडेसीनोएट और हेप्टाल्डिहाइड थर्मल क्रैकिंग की प्रतिक्रिया ऊर्जा की गणना डीएफटी का उपयोग करके की जाती है। यह शोध उद्योग के लिए अपस्केलिंग और प्रक्रिया विकास के लिए अरंडी के तेल से महत्वपूर्ण रसायनों का उत्पादन करने के लिए एक वैकल्पिक मार्ग प्रदान कर सकता है।

सेबासिक एसिड और 2-ऑक्टेनॉल तैयार करने के लिए क्षार विभाजन के लिए कच्चे माल के रूप में मिथाइल रिकिनोलिएट का उपयोग किया जाता था। उत्प्रेरक, ओलेओकेमिकल्स/NaOH का अनुपात, प्रतिक्रिया समय और प्रतिक्रिया तापमान सहित प्रतिक्रिया मापदंडों को अनुकूलित किया गया था। यह पाया गया कि 10wt.% Fe/HZSM-5 ने सबसे अच्छा उत्प्रेरक प्रदर्शन दिखाया, और 280 oC को सबसे उपयुक्त प्रतिक्रिया तापमान माना गया। ओलेओकेमिकल्स/NaOH अनुपात 10:15, 12:15, 14:15, 15:15 को मिथाइल रिकिनोलेट के क्षार-विभाजन के लिए इष्टतम अनुपात के रूप में निर्धारित किया गया था। इसके अलावा, मिथाइल रिसिनोलेट के क्षार-विभाजन का इष्टतम प्रतिक्रिया समय 4 घंटे था, और 5 wt.% Fe/HZSM-5 की अधिकतम उपज, 29.7 wt.% 2-ऑक्टेनॉल और 56.8 wt.% सेबासिक एसिड, 10 wt.% Fe/HZSM-5, 39.4 wt.% 2-ऑक्टेनॉल और 68.1 wt.% सेबासिक एसिड, 15 wt.% Fe/HZSM-5, 42.3 wt.% 2-ऑक्टेनॉल और 71.8 wt.% क्रमशः सेबासिक एसिड का। सेबासिक एसिड और 2-ऑक्टेनॉल की उच्च शुद्धता की पुष्टि एफटी-आईआर और एनएमआर द्वारा की गई थी।

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NOMENCLATURE

W	Weight of the catalyst (g)
D	The internal diameter of reactor
d_p	Catalyst particle size
E_a	Activation energy (kJ/mol)
E_{TS}	Energy of transition state (kJ/mol)
E_{IS}	Energy of reactant state (kJ/mol)
E_{ads}	Adsorption energy (kJ/mol)
E_{diss}	Dissociation energy (kJ/mol)
S_{BET}	BET surface area (m^2/g)
S_{micro}	Micropore surface area (m^2/g)
S_{ext}	External surface area (m^2/g)
V_{micro}	Micropore volume (cm^3/g)
I_D	Intensity of D band in Raman spectra
I_G	Intensity of G band in Raman spectra
T_{ref}	Reference temperature (ºC)

Greek letters

λ	X-ray wavelength (1.54 Å)

θ	Diffraction angle

Acronyms

CA	Castor oil
SA	Sebacic Acid
MU	Methyl Undecenoate
HEP	Heptaldehyde
MR	Methyl Ricinoleate
RA	(12R,9Z)-hydroxyoctadecenoic acid
RA	Ricinoleic Acid
GHG	Greenhouse Gas
HFA	Hydroxy Fatty Acid
DCO	Dehydrated Castor Oil
UDA	10-Undecenoic Acid
CTH	Catalytic Transfer Hydrogenation
MTTP	Methyl Tri-n-octyl Ammonium
ECO	Epoxidized Castor Oil
PU	Polyurethane
HDO	Hydrodeoxygenation
OA	Oleic Acid

DFT	Density functional theory
DNP	Double numerical plus polarization
GGA	Generalized gradient approximation
PW91	Perdew and Wang 91
TS	Transition state
SAR	Silica alumina ratio (SiO_2/Al_2O_3)
ZSM-5	Zeolite Socony Mobil-5
CAT 1	HZSM-5
CAT 2	5wt.% La/HZSM-5
MFI	Framework code (International zeolite association)
BET	Brunauer-Emmett-Teller
MHz	Megahertz
FESEM	Field Emission Scanning Electron Microscope
EDX	Energy-dispersive X-ray spectroscopy
TPD	Temperature programmed desorption
TPR	Temperature programmed reduction
TPO	Temperature programmed oxidation
HR-TEM	High Resolution-Transmission electron micrographs
TGA	Thermal Gravimetric Analysis

TCD	Thermal Conductivity Detector
FID	Flame Ionization Detector
GHSV	Gas hourly space velocity
GCMS	Gas chromatography–mass spectrometry