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# Optimization by Box–Behnken experimental design for synthesis of *n*-hexyl levulinate biolubricant over hierarchical H-ZSM-5: An effort towards agricultural waste minimization

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ABSTRACT

The present study is devoted to develop efficient catalytic process for conversion of agricultural waste feedstock to value added chemicals. In this context, the *n*-hexyl levulinate, a renewable biolubricant was synthesized by esterification of biomass derived levulinic acid (LA) with *n*-hexanol in a closed batch system. Hierarchical-HZ-5 (modified H-ZSM-5) was used as a heterogeneous acid catalyst. There are no reports available on the synthesis of *n*-hexyl levulinate biolubricant using renewable levulinic acid.

The process variables such as catalyst to LA ratio ($X_1$), *n*-hexanol to LA molar ratio ($X_2$), reaction time ($X_3$) and reaction temperature ($X_4$) were optimized by response surface methodology (RSM), using the Box–Behnken model. Analysis of variance was done to check the suitability and significance of the quadratic model. The yield of *n*-hexyl levulinate obtained was 97% with 100% selectivity at optimum process parameters.

The RSM analysis predicted that catalyst to LA ratio is most significant (value of $p < 0.0001$) and *n*-hexanol to LA molar ratio is least significant (value of $p = 0.0064$) process parameter in esterification. The quadratic model established was revealed to be suitable and statistically precise with correlation value ($R^2$) of 0.9837 to predict the yield of *n*-hexyl levulinate.

## 1. Introduction

The progressive depletion of fossil fuels and hike in fuel price has drawn attention of researchers to look in to the utilization of alternative feedstock such as renewable waste biomass. Waste stream like agriculture waste having low or no value would be preferred, as it does not compete with food and does not create issue of food Vs fuel (Galletti et al., 2012). Sugarcane is recognized as one of the most promising agricultural sources of biomass energy. Sugarcane produces mainly two types of waste biomass, cane trash and bagasse. Cane Trash is the field residue remaining after harvesting the Cane stalk while bagasse consists of fibrous residue left over after milling of the Cane. Bagasse contains mainly cellulose, hemi-cellulose, pentosans, lignin, sugars, wax and minerals (Yan et al., 2008). Large quantities of bagasse are either thrown away or taken away for use as fuel or for compost making. In Indian context, a several sugar factories produces surplus bagasse waste and faces the disposal problems. The prices of bagasse in India are very low and varied in the range of $ 0 to 7 per tonne.

The key challenges is to convert (especially heterogeneous catalytically) these abundant available agricultural waste

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*Abbreviations:* ANOVA, analysis of variance; BJH, Barrett–Joyner–Halenda; BBD, Box–Behnken design; BET, Brunauer–Emmett–Teller; FID, flame ionization detector; LA, levulinic acid; XRD, powder X-ray diffraction; RSM, response surface methodology; TPAD, temperature programmed ammonia desorption; 3D, three dimensional; 2D, two dimensional.

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sugarcane bagasse in to important renewable chemicals such as glucose, xylose, levulinic acid (LA) (platform chemical), levulinic esters or levulinates (ethyl, butyl, hexyl, octyl) which are considered as alternative biofuels to fossil fuel (Zhu et al., 2014). This gives sustainable supply of lubricants in the future economy (Oh et al., 2013). In this context, the traditional mineral-oil based lubricants, creating numerous adverse environmental concerns such as groundwater contamination, soil contamination, air pollution, food and agricultural product contamination, demanded to be replaced by renewable, biodegradable and eco-friendly lubricants (Akerman et al., 2011; Oh et al., 2013; Salimon et al., 2010). Renewable, biobased lubricants (biolubricants) bear potential advantages over conventional synthetic and mineral-oil based lubrication products. Biolubricants are biodegradable, carbon-neutral, non-toxic (Lathi and Mattiasson, 2007; Oh et al., 2013) and no need to mix with additives such as anti-oxidants, pour point depressants, viscosity index improvers, detergents and emulsion stabilizers etc. (Vasudevan and Briggs, 2008). Most of the biolubricants were synthesized by transesterification of edible and non-edible vegetable oil or esterification of free fatty acid such as oleic acid with higher alcohols ($C_8$ to $C_{14}$) (Akerman et al., 2011; Avisha et al., 2013; Bokade and Yadav, 2007, 2009; Oh et al., 2013; Wai et al., 2013).

As per our knowledge, there is only one report available on the use of biomass derived LA for the synthesis of biolubricant (Nandiwale et al., 2014). Very recently, we have studied the catalytic performance of the desilicated H-ZSM-5 and heteropolyacid supported on desilicated H-ZSM-5 (Nandiwale et al., 2013) as heterogeneous catalysts in esterification of renewable LA with lower alcohols such as ethanol to ethyl levulinate biodiesel. The present work is an effort in this direction to catalytically convert synthetic levulinic acid with *n*-hexanol to *n*-hexyl levulinate (biofuel), which can be effectively employed to levulinic acid derived from actual agricultural waste feedstock.

Response surface methodology (RSM) has been widely adopted for optimization of various parameters in esterification and transesterification process (Boey et al., 2013; Nandiwale et al., 2014). RSM is a combination of mathematical and statistical methods which is beneficial to improve the process, where interested response is influenced by multiple variables and the goal is to optimize this response (Boey et al., 2013; Nandiwale et al., 2014). It also analyse the influence of independent variables in combination and produces a mathematical model to analyse catalytic processes (Boey et al., 2013). RSM has been successfully applied for process optimization of numerous biodiesel, esters and other processing methods using enzyme or heterogeneous catalysts (Boey et al., 2013; Chang et al., 2012; Kansedo et al., 2009; Nandiwale et al., 2014; Wang et al., 2007; Yin et al., 2013).

In present study, RSM was used for the optimization of process parameters for esterification of LA with *n*-hexanol over Hierarchical-HZ-5 catalyst with four important variables such as catalyst to LA ratio ($X_1$), *n*-hexanol to LA molar ratio ($X_2$), reaction time ($X_3$) and reaction temperature ($X_4$). The effect of these variables on the yield of *n*-hexyl levulinate (response) was studied using Box–Behnken model and subsequently an empirical mathematical model was developed to correlate the response with the process variables. This study also emphasis on the identification of crucial process parameter which is responsible for maximizing yield of *n*-hexyl levulinate. The study was also extended on validation of theoretical and experimental data.

## 2. Materials and methods

### 2.1. *Materials*

Levulinic acid (99%) and *n*-hexanol (99%) were obtained from M/s E. Merck, Mumbai (India). All the reagents were used as received.

### 2.2. *Catalyst synthesis and characterization*

The procedure reported by Shiralkar et al. (1991) was used to synthesize H-ZSM-5 with Si/Al ratio of 37. The hierarchical H-ZSM-5 (Hierarchical-HZ-5) was obtained by post alkali treatment method. Typically, 100 g of H-ZSM-5 was mixed in 3000 mL of 0.2 M aq. NaOH and kept at 339 K for 30 min. The sample was filtered and subjected to threefold ion exchange with aq. 0.1 M ammonium nitrate (in the proportion 10 mL $g^{-1}$) at 338 K for 5 h. After threefold ion exchange, the protonic form of sample was obtained by calcination at 823 K for 5 h. The obtained sample was designated as Hierarchical-HZ-5.

The phase purity and crystallinity of catalyst samples were determined by powder X-ray diffraction (PXRD) system, Model X-Pert PRO-1712 using CuKα radiation at a scanning rate of 0.0671 $s^{-1}$ in the 2θ ranging from 5 to 50° (Fig. 1(a)). The degree of crystallinity was obtained by taking the ratio of summation of integrated peak areas of the peaks appearing at $2\theta = 22.5–25°$ of the Hierarchical-HZ-5 sample to the summation of the integrated peak area of the same peaks in the H-ZSM-5 parent sample. Low temperature (77 K) nitrogen adsorption and desorption isotherms of H-ZSM-5 and Hierarchical-HZ-5 catalysts were obtained by using SA 3100 analyser (Beckman Coulter, CA, USA) (Fig. 1(b)). The specific surface area and pore diameter of catalysts was calculated using Brunauer–Emmett–Teller (BET) method and Barrett–Joyner–Halenda (BJH) model, respectively (Table 1). The total acidity of H-ZSM-5 and Hierarchical-HZ-5 were obtained with Temperature Programmed Ammonia Desorption (TPAD) by Micrometics AutoChem (2910, USA) with thermal conductivity detector (Table 1).

### 2.3. *Catalytic evaluation and analysis of product*

The experiments of *n*-hexyl levulinate synthesis were carried out in a 100 mL stainless steel batch reactor, under autogeneous pressure (25–65 psi). LA, *n*-hexanol and catalyst were mixed in the reactor totalling to 30 mL. The reactor was sandwiched with electric heater. The temperature was maintained within an accuracy of ±0.5 K by PID controller. The reactions were conducted at a temperature range of 363–403 K, catalyst to LA ratio of 0.10–0.25, *n*-hexanol to LA molar ratio of 4–10 and reaction time of 1–5 h. The liquid reaction product were quantified by Chemito GC-1000, capillary column, BP-1 (50 m length and 0.3 mm film thickness) with nitrogen as a carrier gas and Flame Ignition Detector (FID) in programmable temperature range of 313 to 473 K. The reaction products were confirmed by gas chromatography mass spectroscopy (GC–MS) (Shimadzu-QP 5000).

### 2.4. *Box–Behnken experimental design*

An experimental design for the reaction parameters used in the esterification of LA with *n*-hexanol over Hierarchical-HZ-5 to synthesize *n*-hexyl levulinate biolubricant was performed by RSM with Design-Expert® Version 8.0.7.1 (Stat-Ease, Inc.,