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## Insights into the metal salt catalyzed ethyl levulinate synthesis from biorenewable feedstocks

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### ABSTRACT

Ethyl levulinate (EL) synthesis from biorenewable feedstocks in the presence of metal salts and under non-microwave instant heating reaction environment has been studied. Initial screening suggested  $\text{CuCl}_2$  and  $\text{FeCl}_3$  as an efficient catalyst for EL synthesis from 5-hydroxymethylfurfural (HMF), thereby resulting into 47.5% and 43.3% EL yield respectively at 160 °C in 5 min. Interestingly, environmentally benign and widely available metal salt,  $\text{AlCl}_3$ , was found to yield comparable EL (39.0%) when experiments were performed under identical reaction conditions. Therefore, further study was performed using  $\text{AlCl}_3$  to estimate the effect of operating parameters and catalyst concentration over EL yield and HMF conversion. Thereafter, a comparative study on the effect of microwave vs non-microwave instant heating reaction environment has been done to develop a sustainable process for EL synthesis. Consequently, mechanistic insights on reactant conversion and product yield have been attempted to understand various pathways followed. Thereafter, effect of reaction temperature, catalyst loading, ethanol concentration and heating rates were explored. EL synthesis from HMF under instant heating reaction conditions in the presence of metal salts is reported for the first time. We anticipate that present work would be helpful in providing insights on effects of instant heating method and operating conditions for EL synthesis from HMF.

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### 1. Introduction

Rapid growth of modern society has intensified the usage of conventional fossil fuel, thereby causing swift decline in the fuel reserves and substantial increase in environmental damages. Therefore, current research focus has been shifted towards development of sustainable process to obtain fuel and chemicals from biorenewable resources [1–11]. In this regard, lignocellulosic biomass consisting of lignin, cellulose and hemicellulose is widely used to produce an array of chemicals and fuel [12]. However, lignin acts as binding material that prevents cellulose and hemicellulose from taking part in further reactions to produce desired chemicals. Therefore, lignin is removed at first step using various technologies. Thereafter, cellulose and hemicellulose are depolymerized to produce HMF and furfural (FA) respectively via a series of reactions [13]. Both HMF and FA are considered among to be important class of building block chemicals for high value applications [14]. On fur-

ther dehydration under acidic conditions, HMF yields levulinic acid (LA) which itself is a major building chemical [15]. However, separation of levulinic acid and HMF is challenging task which may limit its feasibility for scale up [16].

Albeit HMF is a major platform chemical obtained from biomass resources, its applicability as a biofuel is yet to be proven. However, HMF may be used to produce a wide range of fuel additives such as 2,5-dimethylfuran, 5-ethoxymethylfurfural (EOMF) and alkyl levulinates [17]. Specifically, biomass derived alkyl levulinates are widely used as fuel and fuel additive [18,19]. In this regard, ethyl levulinate has shown considerable promises, both as fuel and building block chemical. On blending 10% EL with regular diesel, 41% reduction in engine out smoke number is measured [20]. In addition, significant reduction in cloud point (4–5 °C), pour point (3–4 °C) and cold filter plugging point (3 °C) is measured with 20% EL blend [21]. Moreover, it is possible to reduce sulfur emission in diesel engines by addition of EL with other co-additives [22]. Alternatively, EL can be upgraded to produce a diverse platform chemical gamma valerolactone via hydrogenation reaction [23–25]. In general, EL is conventionally used in plasticizers, flavor and fragrance industry in very less quantity [26]. A catalytic method for bulk pro-

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duction of EL may open up a window of opportunity in the area of biorenewable energy and chemicals research.

Interestingly, an array of catalytic materials have been used for the synthesis of EL from various bio renewable feedstocks [27–34]. In this regard, a recent review by our group can be referred for further study on catalytic and mechanistic insights on EL synthesis [35]. On the contrary, HMF as feedstock is least explored, necessitating the development of a sustainable process to produce EL from it. For example, Neves et al. have reported a maximum 21% EL yield from HMF using zeolite based catalyst for 48 h at 140 °C [36]. Authors have measured 100% HMF conversion, albeit EL yield remained low in all reaction conditions. The possible reason could be attributed to formation of by-products such as lactides. The authors have also summarized, major catalysts applied for EL synthesis from HMF, such zeolites, MCM, zirconia, sulfated zirconia, SBA-15, heteropolyacids, and ionic liquids. A maximum 75% EL yield was measured using sulfonated SBA-15 catalysts in 24 h at 140 °C by Riisager and coworkers [37].

On the contrary, up to 80% and 97% EL yield obtained when metal salt catalyzed experiments were performed on furfural alcohol (FAL) and LA respectively, under microwave irradiation [38,39]. It is reported that microwave heating have several advantages that leads to higher product yield. For example, rapid heating suppresses formation of byproducts whereas conventional heating promotes by-product formation due to slow heating and increased time to reach the desired temperature [40,41]. In contrast, Dutta et al. have observed formation of EL in significant quantity (25% EL yield) in an oil bath reactor for 8 h in the presence of metal salt based catalyst [42]. This indicates that metal salts can be effective catalyst for EL synthesis from HMF under non-microwave reaction conditions for a short reaction time. Moreover, Yang et al. have obtained 12% EL yield under microwave irradiation in 15 min at 160 °C which is comparatively lower than the EL yield obtained by conventional heating method [43]. Nevertheless, microwave irradiation based EL synthesis technologies are yet to be tested for a large scale production. Thus, it is essential to develop non-microwave based sustainable technologies which has greater acceptance at industrial scale. To best of our knowledge, no efforts has been made to attempt EL synthesis in the presence of metal salts under non-microwave instant heating conditions.

Thus, objective of present study was to synthesize EL from HMF under instant heating under non-microwave reaction environment in the presence of a suitable metal salt catalyst. Thereafter, effect of operating conditions such as reaction time and temperature, catalyst and feedstock concentration, effect of alcohol chain length on EL yield were studied. In addition, effect on EL yield with other biorenewable feedstocks such as LA, glucose, fructose and FAL was studied. Moreover, effects of heating ramp rate in non-microwave reaction environment have been explored. Consequently, attempts have been made to develop a plausible reaction mechanism for EL production from HMF under different heating conditions. Finally, a comparative study on the effect of non-microwave reaction environment vs. microwave reaction environment for HMF conversion and EL yield have been attempted. We believe that the present study would be helpful in providing insights on advantage of instant heating process and basis for further study under non-microwave instant heating condition for ethanolsis of HMF to produce EL.

## 2. Experimental

### 2.1. Materials

The metal salts ( $\text{AlCl}_3$ ,  $\text{CrCl}_3$ ,  $\text{FeCl}_3$ ,  $\text{SnCl}_4$ ,  $\text{ZnCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{ZrOCl}_2$ ,  $\text{LiCl}$ ) tested herein were procured from Thermo-Fischer scientific, India and used without further modifications. On

the contrary, HZSM-5 with varying silica alumina ratio and Lanthanum loaded HZSM-5 were synthesized in our lab. All feedstocks, Ethyl levulinate, Levulinic acid, 5-hydroxymethylfurfural, 5-ethoxymethylfurfural and furfural alcohol were purchased from Sigma-Aldrich, USA and used without further purification. Methanol, ethanol, butanol and other alcohols were procured from Merck, India and used directly for the esterification reaction.

### 2.2. Experimental setup and esterification reaction

All experiments were performed in a non-microwave synthesis reactor supplied by Anton Paar, USA (Model: Monowave-50). The reactor consists of a 315W stainless steel heating jacket along with integrated pressure and temperature control system (Refer to Fig. S-1 in SI). Experiments using non-microwave instant heating reactor (Monowave 50) is employed for the first time. In a typical experimental procedure, desired amount of HMF (0.5 mmol, 63 mg) and catalysts (0.2 mmol) were charged into the high pressure quartz vials. Thereafter, 4.5 ml ethanol was added into feed-catalyst mixture and a magnetic bead was kept inside the vials for stirring purpose. The reactor temperature was set to 160 °C and as fast as possible mode of heating was selected to reach the desired temperature. In general, it took 2 min to reach the desired temperature. Thereafter, 5–10 min hold time was set for the reaction to occur. Consequently, reaction mixture was cooled down by inbuilt cooling system provided with the reactor. Post this, ethanol concentration was varied to study the effect of feed to ethanol ratio. Similarly, catalyst concentration, reaction temperature, reaction time and stirring speed were varied to study their effect on EL yield. Moreover, feedstock and alcohols composition was varied to study the effect on EL yield. For a comparative study, experiments were also performed using Anton Paar, USA, (model: Monowave 300) microwave reactor. All experiments were repeated twice for accuracy of the results and average values are reported herein. In some cases, like with zeolite catalysts, reactions were performed thrice to recheck the activity of the catalysts.

### 2.3. Product analysis

Product mixture obtained after ethanolsis reaction were charged into a rotary evaporator (Make: Buchi, Switzerland, Model: R210) for separation of the catalysts. Earlier studies by prominent research groups in this area suggest that DB-5 and DB-5MS capillary columns are suitable for EL and related compounds determination using gas chromatography technique [44–49]. Thus, product mixture was analyzed in a GC-FID system (Nucon, India, Model: 5765) provided with DB-5MS capillary column (30 m length  $\times$  0.25 mm id  $\times$  0.25  $\mu\text{m}$  film, Agilent India) and flame ionization detector. The injector and detector temperature was kept at 250 °C and 240 °C respectively approximately close to previously reported methods [47,48]. Minor changes in reported program were made based on different preliminary studies at our lab for temperature optimization and an optimized program was developed. Initial temperature was set to 60 °C and thereafter, gradually increased to 180 °C with a ramp rate of 10 °C/minute. The oven temperature was held for 1 min at 180 °C. Post this, final oven temperature i.e. 240 °C was achieved in 4 min with a ramp rate of 15 °C/minute and held for 3 min at the final temperature. Nitrogen (30 ml/min) was used as a carrier gas whereas hydrogen and zero air were used as flame generation gases with a flow rate of 30 ml/min and 300 ml/min respectively. The split ratio of the sample was 1:30 in GC-FID system. The GC-FID was calibrated using external standard method. All samples were analyzed thrice for the better accuracy in results and averaged val-

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