



Improved levulinic acid production from agri-residue biomass in biphasic solvent system through synergistic catalytic effect of acid and products

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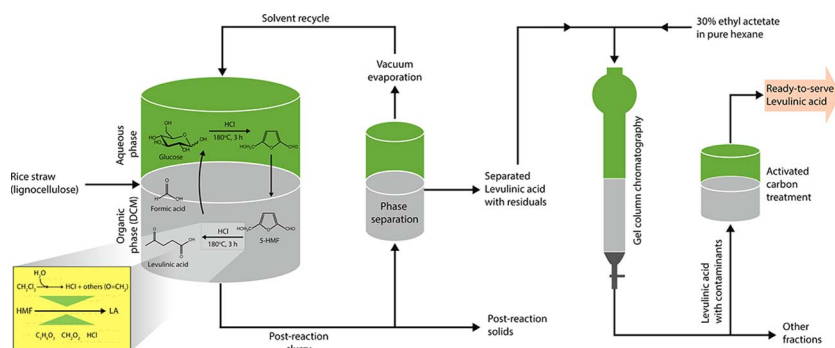
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GRAPHICAL ABSTRACT



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ABSTRACT

In this study, levulinic acid (LA) was produced from rice straw biomass in co-solvent biphasic reactor system consisting of hydrochloric acid and dichloromethane organic solvent. The modified protocol achieved a 15% wt LA yield through the synergistic effect of acid and acidic products (auto-catalysis) and the designed system allowed facile recovery of LA to the organic phase. Further purification of the resulting extractant was achieved through traditional column chromatography, which yielded a high purity LA product while recovering ~85% wt. Upon charcoal treatment of the resultant fraction generated an industrial grade target molecule of ~99% purity with ~95% wt recovery. The system allows the solvent to be easily recovered, in excess of 90%, which was shown to be able to be recycled up to 5 runs without significant loss of final product concentrations. Overall, this system points to a method to significantly reduce manufacturing cost during large-scale LA preparation.

1. Introduction

Of the platform molecules identified by US DOE, levulinic acid (LA) or 4-oxopentanoic is of considerable economic interest due to its bi-functional nature, i.e., keto- and carboxyl-groups, which allow it to

perform many catalytic transformations towards synthesis of industrially important green solvents (γ -valerolactone, GVL) and fuel chemicals (butene, 5-nonanone, 2-methyl-tetrahydrofuran (MTHF)) (Caes et al., 2015; Pileidis and Titirici, 2016). This five-carbon molecule is commonly produced from glucose in the presence of acid catalyst.

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After glucose isomerization, the process first delivers 5-hydroxymethylfurfural (HMF) as principal intermediate product via dehydration reaction ($-3\text{H}_2\text{O}$) and further, it is rehydrated ($+2\text{H}_2\text{O}$) to produce LA and formic acid (FA) at equal proportions along with H_2O (Chen et al., 2017; Weiqi and Shubin, 2017). An undesirable insoluble by-product, humins, are also formed during the sequential transformation reactions, reducing the final LA yield to 2/3 or lower than the theoretical yield. Therefore, the extent of the degradation reactions generally determines the final LA concentration under the modest reaction conditions (Rackemann and Doherty, 2011). To date, several studies have demonstrated LA production through both homogeneous and heterogeneous catalyzed reactions using nearly all possible forms of carbohydrate substrates (e.g., lignocellulose, cellulose, cellobiose, glucose, fructose, inulin, cassava etc.) (Elumalai et al., 2016b; Girisuta et al., 2013; Mukherjee et al., 2015; Runge and Zhang, 2012; Zhao et al., 2017). The most widely investigated method is homogeneous reaction using inorganic mineral acids, mainly H_2SO_4 , HCl , H_3PO_4 owing to its high efficiency and easy operation. Despite its highly corrosive nature, HCl exhibits promise due to its high dissociation constant (Shen and Wyman, 2012; Victor et al., 2014). However, separation of final product compounds from aqueous acidic solutions is considered one of the main challenges during LA preparations. Due to the presence of a carboxyl group, LA has the strongest interaction with water forming hydrogen bonds with H_2O molecules. Also, LA dissociated ions can be solvated by H_2O (Szabolcs et al., 2013). Furthermore, in typical reaction, many of these acidic reagents lead to the production of unwanted by-products, which negatively impact LA yield. In order to avoid these limitations, later studies have introduced co-solvent reactor setup consisting of either biphasic or monophasic system. The goal of this setup is improving overall conversion efficiency through continuous extraction of furans, preferentially HMF to the organic phase, thereby reducing the residence time of HMF in aqueous medium. This approach helps protect HMF from further degradation to humic species, and allows easy product separation (Alonso et al., 2013).

In this regard, an ideal solvent is one which is suited for substrate conversion, increases the product yield and selectivity, and poses no, or minimal, adverse ecological impacts. Various studies have employed a range of polar protic and aprotic solvents with different polarities, including methyl isobutyl ketone (MIBK), MTHF, GVL, dichloromethane (DCM), 2-butanol, tetrahydrofuran (THF), dimethylsulfoxide, 2-sec-butylphenol etc. forming monophasic or biphasic systems in combination with mineral acid reagents (aqueous), and showed furans extraction to be dependent on the polarity of the solvents (Byun and Han, 2016; Chheda et al., 2007; Elumalai et al., 2016a; Gürbüz et al., 2012; Morone et al., 2015). THF (polarity index, $P = 4.2$) exhibited excellent performance during carbohydrates conversion to HMF (partition coefficient, $R_{\text{HMF}} = 3.1$), ascribed to its greater affinity for HMF due to the similarity in chemical structure (Cai et al., 2013; Yang et al., 2012). Several studies have also demonstrated the use of DCM and proposed that it could be a suitable extraction agent for HMF due to its attractive affinity (Chheda et al., 2007), despite having the comparatively low P value of 3.1. Therefore, the polarity is not the only factor affecting furans distribution to the organic phase. In fact, distribution of HMF to the organic phase is relatively poor due to its high polarity and therefore, it tends to be retained in the aqueous phase (Gallo et al., 2013). Later studies have attempted to improve the HMF distribution through the addition of salts, commonly NaCl , KCl , and Na_2SO_4 , into the co-solvent systems but the movement of salts into the extractant medium could not be easily controlled (Mukherjee et al., 2015). In theory, these approaches could potentially prevent further rehydration of 5-HMF to LA due to the low availability of H_2O molecules. Due to these constraints, only a few studies have been focused on LA synthesis in co-solvent systems using carbohydrate sources. For instance, Dumesic and co-workers (Alonso et al., 2013; Wettstein et al., 2012) have extensively investigated the deconstruction of both cellulose and lignocellulose in monophasic or biphasic systems consisting of GVL, as an extraction

solvent, and mineral acids, particularly H_2SO_4 and HCl (with the addition of salts). The main interest of these studies is the production of GVL through continuous extraction of LA into organic medium. Interestingly, maximum LA conversion (between 18 and 66% depending on the acid and substrate concentrations) and recovery to the organic medium were achieved under modest reaction conditions, where complete transformation to GVL took place. The lack of residual concentration of HMF in GVL medium might be attributed to its instability in GVL and therefore, achieving high LA conversion in the aqueous phase is mainly due to its complete water miscibility property.

The present study employed a biphasic system consisting of dilute HCl (aqueous) and DCM (organic extraction solvent) for the deconstruction of secondary agriculture residue (rice straw) to LA with the objective of establishing a cost-effective processing method by achieving maximum product recovery to the organic phase. Rice straw is considered one of the abundantly available biomass around the world (~ 900 million tons produced per year globally), is relatively inexpensive and is currently underutilized due to its recalcitrant nature, low proteinaceous matter and high silica content (Sarkar et al., 2012). This approach would enable facile product separations, and solvent recovery for reuse due to its highly volatile and low boiling properties (boiling point 39.6°C).

2. Experimental methods

2.1. Chemicals

All reagents and chemicals (including cellulose, glucose, dichloromethane (DCM), methanol, levulinic acid (LA), formic acid (FA), 5-hydroxymethylfurfural (HMF), furfural (FF), activated carbon, and carbohydrate standards) were purchased from Sigma Aldrich India as analytical grade and used as received without any modifications.

2.2. Feedstock preparation

Native rice straw sample was collected from the agricultural field near Mohali, Punjab State, India. It was air dried under sunlight to a final moisture content of $< 6\%$ wt, ground to a final particle size ranging between 5 and 4 mm using a commercial grinder machine (Kinematica PX-MFC 90 D) and followed by, sieved to obtain a uniform particle size of 0.5 mm (30 mesh).

2.3. Fractional composition determination

The fractional compositional analysis was performed on the solvent pre-extracted rice straw using standard National Renewable Energy Laboratory (NREL) protocol in order to determine its primary constituents, such as carbohydrate sugars, lignin, and ash (Elumalai et al., 2016a). Solvent pre-extraction was done on native rice straw using a solvent mixture of ethanol/benzene at 80:20 ratio in a Soxhlet extraction apparatus for overnight (or at least 8 siphons). The solids collected were then oven dried for overnight at 105°C .

2.4. Single-pot reaction of rice straw fiber

Powdered rice straw (30 mesh) or cellulose was soaked using dilute HCl solution (aqueous) and fresh organic solvent (DCM) in 100 mL stainless steel autoclave vessel containing Teflon liner. A magnetic stirring bead was added to the vessel and sealed tightly to avoid any solvent escape. The vessel was heated to the desired temperature (up to 200°C) using a magnetic stirring hot plate (Thermofisher). After completion of reaction (3h), the post-reaction medium was collected and transferred to a separating funnel. Approximately 2 volumes of fresh DCM was added externally into the dark brown colored medium in order to achieve a clear separation of organic and aqueous phases. Further, the separated organic phase was evaporated under vacuum

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