Esterification of levulinic acid with butanol over ion exchange resins

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A R T I C L E   I N F O

A B S T R A C T

Alkyl levulinates are biobased chemicals with a great number of applications and great biofuel potential for blending to conventional diesel or gasoline. The present work focuses on the liquid-phase synthesis of butyl levulinate (BL) by esterification of levulinic acid (LA) with 1-butanol (BuOH) using a set of acidic ion-exchange resins. Experiments were performed at 80 °C and 2.5 MPa in a batch reactor by using an initial molar ratio AL/BuOH of 1/3 and a catalyst loading of 0.8%. It has been found that BL could be successfully obtained over ion-exchange resins with a selectivity higher than 99.5%. LA conversions ranged from 64% (Amberlyst 46, macroreticular, surface sulfonated) to 94% (Dowex 50Wx2, gel-type resin, conventionally sulfonated) at 8 h reaction time. By comparing their catalytic behavior, it was seen that resins morphology plays a very important role in the synthesis of BL making easier the access of reactants to acid sites. Accessibility of LA and BuOH to acid centers was high over highly swollen and low polymer density resins. Thus, gel-type resins with low divinylbenzene (DVB) content have been found as the most suitable to produce BL, e.g. Dowex 50Wx2, Dowex 50Wx4 and Purolite® CT224. Among them, Dowex 50Wx2 (2% DVB) is the most efficient catalyst tested.

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1. Introduction

In the search for alternative and renewable energy sources, attention has gravitated towards biofuels. Despite the interest, biofuels in their current form present a number of issues. First Generation Biofuels (FGB) are produced from classic food crops with well-known technologies. FGB are unsustainable in the long term because of the stress their generalized production would place on food commodities [1]. Second Generation Biofuels (SGB) are derived from non-food crops, preferably from lignocellulosic feedstocks from agricultural wastes. Yet there are obstacles to commercial scale production of SGB, most prominently that the hydrolysis process for the release of sugars from their lignocellulose matrix economically and in high yields still contributes to more than 45% of biofuel cost production [2].

The transformation of lignocellulosic biomass can yield a number of valuable products that can be used by the chemical industry as platform chemicals. Available techniques to transform lignocellulose into sugars are gasification, pyrolysis and hydrolysis. Hydrolysis requires the lignocellulose to be broken into its constituent parts: cellulose (40–50%), hemicellulose (25–35%) and lignin (15–20%). The hydrolysis of cellulose and hemicellulose

catalyzed by H_2SO_4 gives place to C_5 and C_6 sugar monomers such as xylose, glucose, and fructose, and it is today the most important route for obtaining monosaccharides [1]. Fast pyrolysis is also a promising technology. It allows the transformation of the cellulosic fraction of biomass into anhydrosugars (levoglucosan, cellobiosan) which can be hydrolyzed to glucose [3–5]. Levulinic acid (LA) is amongst the platform chemicals obtained from the chemical transformation of lignocellulose-derived sugars, and was highlighted by the United States Department of Energy as a promising building block for chemistry in 2004 and 2010. It can be considered one of the most important platform chemicals derived from biomass because of its reactive nature and the fact that it can be produced at low cost by the Biofine process since 1996 [6,7]: currently 5–8 $/kg, but prices can be expected to drop to 1$/kg once relevant conversion technologies have been successfully commercialized [8]. As a versatile building block, LA and its derivates have a wide number of applications [9–12].

Alkyl esters of levulinic acid are the most notable of LA derivates with a good number of commercial uses [13–16], including their potential application as green solvents [10]. They have the potential to substitute compounds currently derived from petrochemical routes for blending to conventional diesel or gasoline because of their low toxicity and physicochemical properties; exhibiting characteristics that make them appropriate for use as cold-flow improvers in biodiesel or oxygenate additives for gasoline and diesel fuel, given that oxygenates and fuel blends must comply with

Nomenclature

BL	Butyl levulinate
BuOH	1-Butanol
DBE	Dibutyl ether
d_{bead}	Mean bead diameter (mm)
d_{pore}	Mean macropore diameter (nm)
DVB	Divinylbenzene
EL	Ethyl levulinate
EOE	Ethyl octyl ether
FGB	First generation biofuel
HPA	Heteropolyacid
ISEC	Inverse steric exclusion chromatography
LA	Levulinic acid
n_{BL}	Mole of butyl levulinate (mol)
PS-DVB	Polystyrene-divinylbenzene
$R_{BuOH/LA}$	Molar ratio BuOH/LA
r_{BL}	Reaction rate of butyl levulinate synthesis (mol/(h·kg of dry catalyst))
SGB	Second generation biofuel
S_{BuOH}^{BL}	Selectivity to butyl levulinate
S_{pore}	Surface area (m^2/g)
t	Time (h)
T_{max}	Maximum working temperature (°C)
TOF	Turnover frequency (mol/(h·eq H$^+$))
V_{pore}	Pore volume (cm^3/g)
V_{sp}	Specific volume of swollen polymer (cm^3/g)
w	Catalyst mass (g)
X_{LA}	Levulinic acid conversion
ρ_s	Skeletal density (g/(cm^3 of dry catalyst))
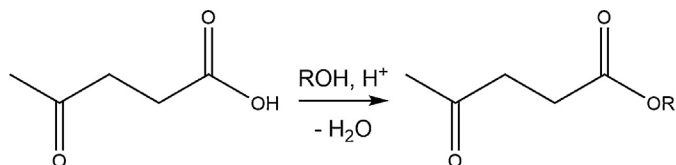
Scheme 1. Acid catalyzed reaction of esterification of levulinic acid.

the increasingly stringent specifications of the European Union (Directive 2009/30/EC).

Levulinate esters can be obtained by direct esterification of levulinic acid with alcohols, typically acid catalyzed (Scheme 1). Sah [17], and later Schuette [18] and Cox [19] were the first to synthesize alkyl levulinates by direct reaction between the acid and the alcohol; publishing the formation of a number of alkyl levulinates in excess of the corresponding alcohol in the presence of HCl. These early studies employed mostly homogeneous catalysis, and reported yields were low (35–75%). Heterogeneously catalyzed esterification of LA has been attempted more recently, using most often solid Brønsted acids. It has been proposed that the mechanism for the esterification of LA on acidic surfaces involves the adsorption through the protonated carbonyl group (carboxyl group) enabling a nucleophilic attack of the alcohol assisted by an oxygen atom from the catalyst structure [20,21].

The most widely studied alkyl levulinate is ethyl levulinate (EL), both its synthesis pathways and possible applications have been explored thoroughly. Traditionally EL was synthesized by using homogeneous catalysts such as HCl, H$_3$PO$_4$ and H$_2$SO$_4$. Very recently, this reaction has been re-examined extensively with more robust and industrially benign greener catalysts. For this purpose solid acid catalysts have been tested, including supported heteropoly acids [20–23], zeolites [21,24], hybrid catalysts [25–27],

sulfated carbon nanotubes [28], Starbon® mesoporous materials functionalized with sulfonated groups [29], sulfated metal oxides [26] and silicas [30,31], and immobilized lipases [32]. It has also been synthesized using commercial acidic sulfonic polystyrene-codivinylbenzene (PS-DVB) resins as reference catalysts, usually Amberlyst 15 and Amberlyst 70 [1,21,22,28,30]. At the same time, there have been studies aimed at improving the conversion of lignocellulose, glucose or fructose directly into ethyl levulinate in a one-step process catalyzed by either H$_2$SO$_4$ or ZrO$_2$-based sulfonated catalysts [33–36].

Comparatively, the potential of butyl levulinate (BL) has been left untapped. EL has been considered often in recent years, and was investigated as a novel, bio-based cold flow improver for use in biodiesel fuels [37,38]. As an additive for diesel, BL is even more promising than EL [39]. Both reduce vapor pressure in diesel blends [37], have a freezing point below −60 °C, their boiling point and flash point are in the acceptable range for diesel fuel, improve lubricity, conductivity and reduce particulate emissions in diesel blending. On the other hand, BL is only sparingly soluble in water (up to 1.3 wt.%) unlike EL (up to 15.6 wt.%). Although they both exhibit less energy per volume unit than conventional diesel fuel by 31% (EL) and 25% (BL), respectively, this is already an improvement on bioethanol blends. In diesel blends containing 20% (v/v) levulinate, EL tends to form a separate liquid phase in most diesel fuels at temperatures significantly above the cloud point of diesel fuel, while BL remains completely soluble in diesel down to the diesel cloud point (around −25.8 °C). Nonetheless, both esters exhibit a very low cetane number, which means blending with these components requires cetane-enhancing additives.

Literature on BL synthesis is sparse: first attempts at synthesis were undertaken with homogeneous catalysts [17–19], and a kinetic model for the esterification of LA with butanol (BuOH) was proposed by Bart et al. [37]. Some work has been made in BL production directly from cellulose with homogeneous catalysis [41]. Esterification of LA with butanol over several types of solid catalysts such as zeolites [42,43], Zr-containing MOFs [44], and heteropolyacid (HPA) supported on acid-treated clay montmorillonite (K10) [45] has been described in literature since then. There have also been sporadic but successful attempts at production and kinetic modelling of BL by esterification of LA via immobilized lipase catalysis [46]. Surprisingly the catalysis with acidic ion-exchange resins has never been studied before.

Since to the best of our knowledge the synthesis of butyl levulinate by esterification of levulinic acid with 1-butanol is not reported over acidic ion-exchange resin, a widely available and inexpensive catalyst, in the open literature. Therefore, the present paper is devoted to the study of the liquid phase synthesis of BL from LA and BuOH over sulphonated PS-DVB resins. A catalyst screening is carried out in order to select suitable catalysts for obtaining BL. Moreover, it is also desired to elucidate the effect of the resins morphology on their catalytic activity.

2. Experimental

2.1. Chemicals

Levulinic acid (≥98%, Acros Organics) and 1-butanol (≥99.5%, Acros Organics) were used as reactants. Distilled water, butyl levulinate (≥98%; Sigma Aldrich) and dibutyl ether (≥99%, Acros Organics) were used for analysis purposes.

2.2. Catalysts

Tested catalysts were acidic PS-DVB ion exchange resins supplied by Rohm and Haas (Amberlyst 15 [A15], Amberlyst 16 [A16],