

Formation of Humin and Alkyl Levulinate in the Acid-catalyzed Conversion of Biomass-derived Furfuryl Alcohol

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To avoid undesired polymerization and maximize the selectivity of alkyl levulinate from the acid-catalyzed conversion of biomass-derived furfuryl alcohol, the effects of catalyst and reaction parameters on the formations of humin and alkyl levulinate were investigated. The results show that Amberlyst 15, of moderate acidic strength, was more favorable for the selective conversion of furfuryl alcohol to alkyl levulinate, and heteropolyacids of strong acidic strength tended to promote furfuryl alcohol polymerization. Compared with water as a reaction medium, alcohol significantly lowered humin formation and enhanced the yield of the resulting products. The formations of humin and alkyl levulinate were both favored at high catalyst loadings and reaction temperatures. An augmentation in initial furfuryl alcohol concentration caused an increase in humin formation and a decrease in alkyl levulinate yield. A high alkyl levulinate yield of up to 94% (100% furfuryl alcohol conversion) was achieved at 110 °C for 4 h with 5 g/L Amberlyst 15 catalyst and an initial furfuryl alcohol concentration of 0.1 mol/L. At this point, about 5% furfuryl alcohol was polymerized to form the humin, and its polymerization occurred mainly during the initial reaction stage.

Keywords: *Furfuryl alcohol; Acid catalysis; Alkyl levulinate; humin; Alcohol*

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INTRODUCTION

With diminishing fossil resources as well as the deprivation of the global environment and climate, abundant and renewable biomass is considered to be a promising alternative for the sustainable supply of fuels and chemicals that can serve as replacements for fossil-based products (Corma *et al.* 2007; Zhou *et al.* 2011). Furfuryl alcohol, one of the most important furan derivatives, is industrially produced *via* the hydrogenation of furfural derived from the hydrolysis and dehydration of xylan contained in lignocellulosic biomass (Sharma *et al.* 2013; Perez and Fraga 2014). Furfuryl alcohol has been regarded as a significant commodity, and it is the preferred building block for conversion to more useful chemicals. One attractive option is the one-pot synthesis of alkyl levulinate by acid catalysis in an alcohol medium. Alkyl levulimates are versatile platform chemicals with numerous potential industrial applications as fuel additives, flavorings, and solvents, as well as in the field of chemical synthesis (Windom *et al.* 2011; Démolis *et al.* 2014; Tang *et al.* 2014).

On the industrial scale of this technology, an economically feasible and highly selective process is strongly in demand. To meet this challenge, the research and

development of a catalyst is thought to be crucial, and solid acid catalysts have attracted considerable interest because of their high catalytic activity, easy separation from the reaction mixture, and environmental friendliness. For instance, several kinds of solid acid catalysts, including macroreticular resins (Lange *et al.* 2009), methylimidazolebutylsulfate phosphotungstate (Zhang *et al.* 2011), sulfonic acid functionalized ionic liquids (Hengne *et al.* 2013; Wang *et al.* 2014), and propylsulfonic acid-functionalized mesoporous silica (Demma Carà *et al.* 2014), have been demonstrated to be effective in the conversion of furfuryl alcohol to alkyl levulinate. In general, these previous studies mainly focused on the optimization of alkyl levulinate production by developing novel and proper acid catalysts. Minimal attention has been given to the formation of by-product humin during this transformation process. It is known that furfuryl alcohol tends to polymerize to form insoluble solid substances in the presence of an acid catalyst (Bertarione *et al.* 2009; Kim *et al.* 2011, 2013). This polymerization is particularly undesirable toward our goal, as it diminishes the utilization efficiency of furfuryl alcohol. On the other hand, when using solid acids as catalysts, the formed humin mainly deposits on the surface (Peng *et al.* 2011; Hu *et al.* 2015). This occurrence results in the deactivation of catalysts and consequently impacts their recycling (Neves *et al.* 2013; Zhao *et al.* 2014). Hence, integrated exploration of the formation rules of humin and alkyl levulinate is essential for seeking appropriate approaches to avoid unwanted side reactions and enhance the effective conversion of furfuryl alcohol.

In view of this purpose, the current study was conducted to provide insight into the effects of several common solid acid catalysts (heteropolyacids, acidic resins, and zeolites) and multiple process parameters (catalyst loading, initial furfuryl alcohol concentration, reaction medium, temperature, and time) on humin formation and product distribution in furfuryl alcohol conversion. Based on the experimental findings, reaction pathways for the formations of humin and alkyl levulinate in an alcohol medium are proposed.

EXPERIMENTAL

Materials

Heteropolyacids ($\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$) and two polymeric resin-based acids (Amberlite 732 and Amberlyst 15) were purchased from Aladdin Reagent (Shanghai, China). Zeolites, including HY, H-mordenite, and ZSM-5, were obtained from Nankai University Catalyst Co., Ltd. (Tianjing, China). Other chemicals were all of analytical grade and were used without further purification or treatment.

Methods

General experimental procedure

The reactions were carried out in a cylindrical stainless steel pressurized reactor with a total volume of 50 mL. Using a typical experiment for the conversion of furfuryl alcohol, *n*-butanol (19.47 mL) and furfuryl alcohol (6 mmol, 0.53 mL) were introduced into the reactor, along with 0.1 g Amberlyst 15 solid catalyst. The above mixture was then brought to a temperature of 110 °C by oil-bath heating and was continuously stirred at 800 rpm with a magnetic stirrer. After running the reaction, the reactor was quenched in an ice water bath to terminate the reaction. The humin formed in the acid-catalyzed

conversion of furfuryl alcohol exists as solid particles adhering to the reactor's inner wall, suspended in the reaction solution, or/and deposited on the solid catalyst. For this, the solid material was scraped off the reactor's inner wall and collected by filtration for the reaction solution. The combined solid material was dried to a constant weight at 105 °C, and the amount of humin was calculated by subtracting the solid catalyst weight (Hu *et al.* 2011). Meanwhile, the liquid sample was preserved from filtration for further analysis.

Analytic methods

Furfuryl alcohol, 2-alkoxymethylfuran, and alkyl levulinate were analyzed by gas chromatography (GC) on an Agilent 6890 instrument equipped with a DB-5 capillary column (30.0 m × 320 μm × 0.25 μm) and a flame-ionization detector (FID). The following operating conditions were used in the analysis: the carrier gas was nitrogen with a flow rate of 1.0 mL/min, the injection port temperature was 250 °C, the oven temperature was programmed from 60 °C to 90 °C (6 min) at a heating rate of 5 °C/min, then to 190 °C (5 min) at a heating rate of 20 °C/min, and the detector temperature was 270 °C. The amounts of furfuryl alcohol and alkyl levulinate were calculated based on external standard curves constructed with their authentic standards. The 2-alkoxymethylfuran identified by GC-MS is not commercially available, and its amount was calculated using calibration data of the corresponding alkyl levulinate while assuming a similar carbon response factor. The formed solid material was characterized by FT-IR, UV-Vis spectroscopy, and elemental analysis. The FT-IR spectrum was recorded using a Bruker TENSOR 27 FT-IR spectrophotometer. The sample was combined with KBr containing 0.5 wt% solid material, and data were collected from 4000 to 400 cm⁻¹ with a scan step of 2 cm⁻¹. The UV-Vis spectrum was monitored using a Purkinje TU-1950 UV-Vis spectrophotometer. Cyclohexane was used as a solvent for the solid material, and data were recorded from 800 to 190 nm with a scan step of 1 nm. The elemental analysis was performed on a PerkinElmer 2400 Series II CHNS/O analyzer. Furfuryl alcohol conversion and product yields were defined as follows:

- Furfuryl alcohol conversion (%) = (1 – moles of furfuryl alcohol after reaction / moles of furfuryl alcohol loaded in feed) × 100%
- 2-Alkoxymethylfuran yield (%) = (moles of 2-alkoxymethylfuran produced / moles of furfuryl alcohol loaded in feed) × 100%
- Alkyl levulinate yield (%) = (moles of alkyl levulinate produced / moles of furfuryl alcohol loaded in feed) × 100%
- Humin yield (%) = (mass of humin obtained / mass of furfuryl alcohol loaded in feed) × 100%.

RESULTS AND DISCUSSION

Humin Characterization

In the course of the experiments, the dark-brown insoluble solid material known as humin was observed and was adhering to the inner wall of the reactor, suspended in the reaction solution and/or adsorbed on the surface of the solid catalyst. The formed humin was characterized by FT-IR, UV-Vis spectroscopy, and elemental analysis. The FT-IR spectrum of the humin is shown in Fig. 1a, and the corresponding assignments of the peaks are given in an inset. A wide range of functional groups existed in the humin,

which contained hydroxyl groups, aliphatic carbon-hydrogen bonds, carbonyl groups, carbon-carbon double bonds, and carbon-oxygen bonds. The UV-Vis spectroscopy (Fig. 1b) shows a strong absorption band from 210 to 240 nm of the wavelength, suggesting that the humin contains large conjugated π -bonded systems. These observations showed that the humin is probably mainly a product of side-reaction of the acid-catalyzed polycondensation of furfuryl alcohol. The elemental analysis of the humin shown in Table 1 further indicates that the C content in the humin was higher than that of furfuryl alcohol, while the H and O contents were relatively lower. It can be understood that this was caused by the condensation dehydration and polymerization of furfuryl alcohol for the formation of humin. Also, the high O content in the humin demonstrates that the oxygen-based functional groups, such as the hydroxyl group and carbonyl groups, play important roles in the polymerization reaction.

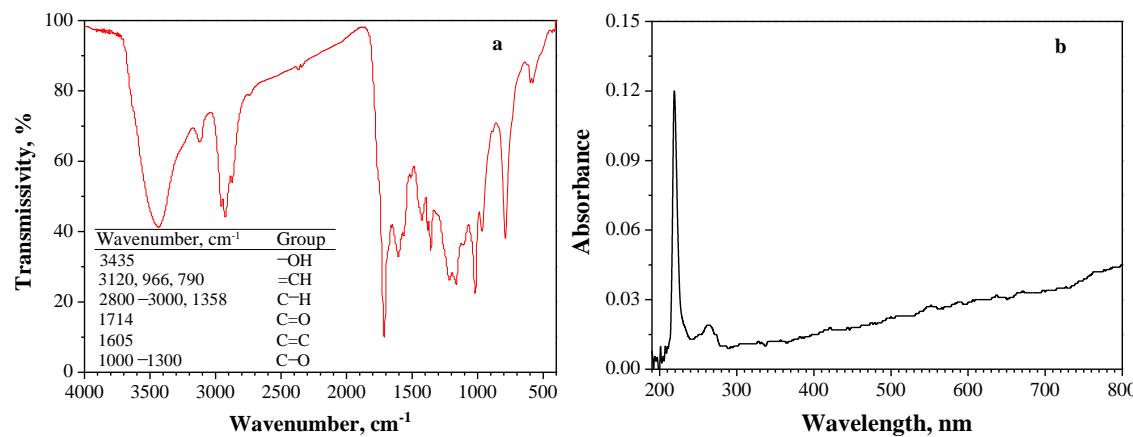


Fig. 1. FT-IR (a) and UV-Vis (b) spectra of the humin formed from the acid-catalyzed conversion of furfuryl alcohol in alcohols. Reaction conditions of the sample: 0.3 mol/L furfuryl alcohol in n-butanol; Amberlyst 15 as the catalyst; catalyst loading of 5 g/L; reaction temperature of 110 °C; reaction time of 4 h

Table 1. Elemental Composition of Furfuryl Alcohol and Humin

Sample	Elemental Composition (wt.%)		
	C	H	O
Furfuryl alcohol	61.2	6.1	32.7
Humin	69.6	5.0	25.4

Catalytic Effects of Various Solid Acid Catalysts

During the acid-catalyzed conversion of furfuryl alcohol to alkyl levulinate, there were likely several intermediates and/or by-products formation. Indeed, the study of Maldonado *et al.* (2012b) indicated that three possible intermediates (2-ethoxymethylfuran, 4,5,5-trithoxypentan-2-one, and structure for one as yet undetermined) in the conversion of furfuryl alcohol to ethyl levulinate were detected, and multiple pathways for the production of ethyl levulinate were proposed. Furthermore, a range of soluble by-products (furyl and C6 aromatic compounds, and cyclic and linear aliphatic compounds with different types of functional groups such as ether, acetal, and ester) were also identified by Neves *et al.* (2013). It is thus clear that the reaction pathway

and product composition from the acid-catalyzed conversion of furfuryl alcohol in alcohols are quite complicated. This study was focused on monitoring the formations of alkyl levulinate and humin. Alkyl levulinate is a target chemical derived from the alcoholysis of furfuryl alcohol, while the humin is a dominating and insoluble by-product of furfuryl alcohol polymerization that significantly affects the utilization efficiency of furfuryl alcohol. Moreover, a key intermediate 2-alkoxymethylfuran derived from the etherification of furfuryl alcohol and alcohols was analyzed.

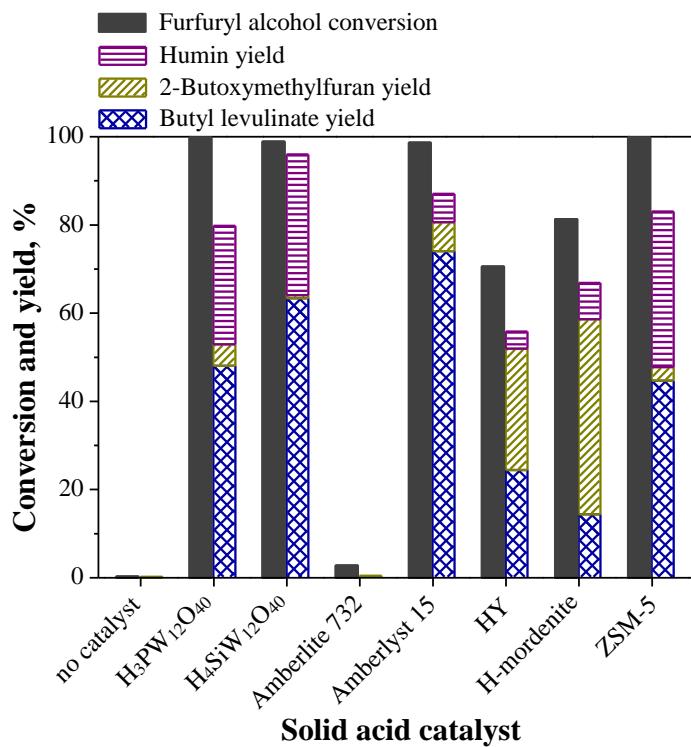


Fig. 2. Catalytic effects of various solid acid catalysts on furfuryl alcohol conversion, product distribution, and humin formation. Reaction conditions: 0.3 mol/L furfuryl alcohol in *n*-butanol; catalyst loading of 5 g/L; reaction temperature of 110 °C; reaction time of 4 h

Table 2. Acidic and Catalytic Properties of the Tested Solid Acid

Solid acid	Acidity ^a , mmol/g	H ₀ ^b	TOF ^c , h ⁻¹
H ₃ PW ₁₂ O ₄₀	1.04	< -13.0	6.9
H ₄ SiW ₁₂ O ₄₀	1.39	< -13.0	6.8
Amberlite 732	4.50	-3.0 ~ -2.1	0
Amberlyst 15	4.70	-3.0 ~ -2.1	2.4
HY	2.60	-5.6 ~ -3.0	1.4
H-mordenite	1.88	< -3.0	1.1
ZSM-5	1.19	-5.6 ~ -3.0	5.6

^a Acidity of heteropolyacids is a theoretical value. Acidity of resins was provided by manufacturer. Acidity of zeolites was estimated from temperature-programmed desorption of ammonia.

^b H₀ was determined by Hammett indicator method.

^c TOF denoted as moles of butyl levulinate produced (data from Fig. 2) per mole of acid protons per hour.

Here, various types of solid acid catalysts, including heteropolyacids, acidic resins, and zeolites were investigated for the catalytic conversion of furfuryl alcohol in an *n*-butanol medium at 110 °C for 4 h. No catalyst was used as the reference. The results of furfuryl alcohol conversion, product distribution, and humin formation are depicted in Fig. 2. Hardly any conversion of furfuryl alcohol was observed in the absence of the catalysts. With the use of an acid catalyst, furfuryl alcohol conversion became easy to perform, but the distribution of products was appreciably different for all investigated solid acid catalysts. Heteropolyacids, *i.e.* H₃PW₁₂O₄₀ and H₄SiW₁₂O₄₀, are known as a kind of fine solid acid catalyst, with Brønsted acidity ($H_0 < -13.0$) even stronger than that of sulfuric acid (Deng *et al.* 2011), and were found to be effective for the conversion of furfuryl alcohol in *n*-butanol. However, the yields of butyl levulinate were lower than expected, giving moderate yields of 48% and 63%, respectively. It can be noted that the polymerization of furfuryl alcohol was favored under the circumstances, providing a humin with yields of 27 to 32%. Hence, the loss of butyl levulinate yield could be caused by the formation of a relatively large amount of humin. The above results lead to the conclusion that strong Brønsted acids are more likely to facilitate the polymerization of furfuryl alcohol. Regarding acidic resins, Amberlite 732 (gel-type resin) was inactive for the transformation of furfuryl alcohol, possibly because of its microporous structure, offering acid groups that are much less accessible for the less polar furfuryl alcohol (Lange *et al.* 2009). By contrast, the macroreticular resin Amberlyst 15 offers more accessible acid sites, and it is almost equivalent in acidic strength to 40% sulfuric acid (Fărcașiu *et al.* 1997). As a result, Amberlyst 15 exhibited superior catalytic performance for the alcoholysis of furfuryl alcohol, affording a 74% yield of butyl levulinate and a relatively low yield of humin (6%). However, the TOF for Amberlyst 15 was significantly lower than that for heteropolyacids due to its weak acidic strength ($H_0 = -3.0 \sim -2.1$) (Table 2). This indicated that higher acid strength accelerated the production rate of butyl levulinate but tended to promote furfuryl alcohol polymerization as well. For Amberlyst 15, the combined yield of butyl levulinate and humin was about 20% less than furfuryl alcohol conversion, implying that there may be many intermediates in the reaction products. The major intermediate of the reaction by far was 2-butoxymethylfuran, which accounted for about 7% of the product mixture. In that case, a higher yield of butyl levulinate could be produced by optimizing reaction parameters. Furthermore, the reusability of Amberlyst 15 was examined. After filtering the liquid-phase fraction, the residue could catalyze the next run, giving almost unchanged product yields. Therefore, the catalyst species appeared not to become shielded due to the slight deposition of formed humin on the catalyst and not to decompose in the reaction. Among tested zeolites, it was found that ZSM-5 was efficient for the conversion of furfuryl alcohol to afford a high TOF. Unfortunately, the polymerization of furfuryl alcohol to form a solid humin was observed clearly, and the humin yield reached up to 35%. As a consequence, only a moderate yield of butyl levulinate of *ca.* 44% was reached. Similar yields of alkyl levulinate in the presence of other alcohols were also obtained in previous studies (Lange *et al.* 2009; Demma Carà *et al.* 2014). For HY and H-mordenite, furfuryl alcohol cannot be fully consumed under the same reaction conditions and exhibited poor catalytic activities for the formation of butyl levulinate (TOF 1.4 for HY, and TOF 1.1 for H-mordenite in Table 2). Butyl levulinate and humin were both obtained at lower yields, while a larger amount of an intermediate (2-butoxymethylfuran) was detected, likely because of the lack of suitable acid sites (Peng *et al.* 2011). Generally speaking,

Amberlyst 15 of moderate acidic strength was more favorable for the selective conversion of furfuryl alcohol to alkyl levulinate, and heteropolyacids of high acidic strength tended to promote the formation of the humin. Therefore, Amberlyst 15 was chosen as the most suitable catalyst for the purpose of this study.

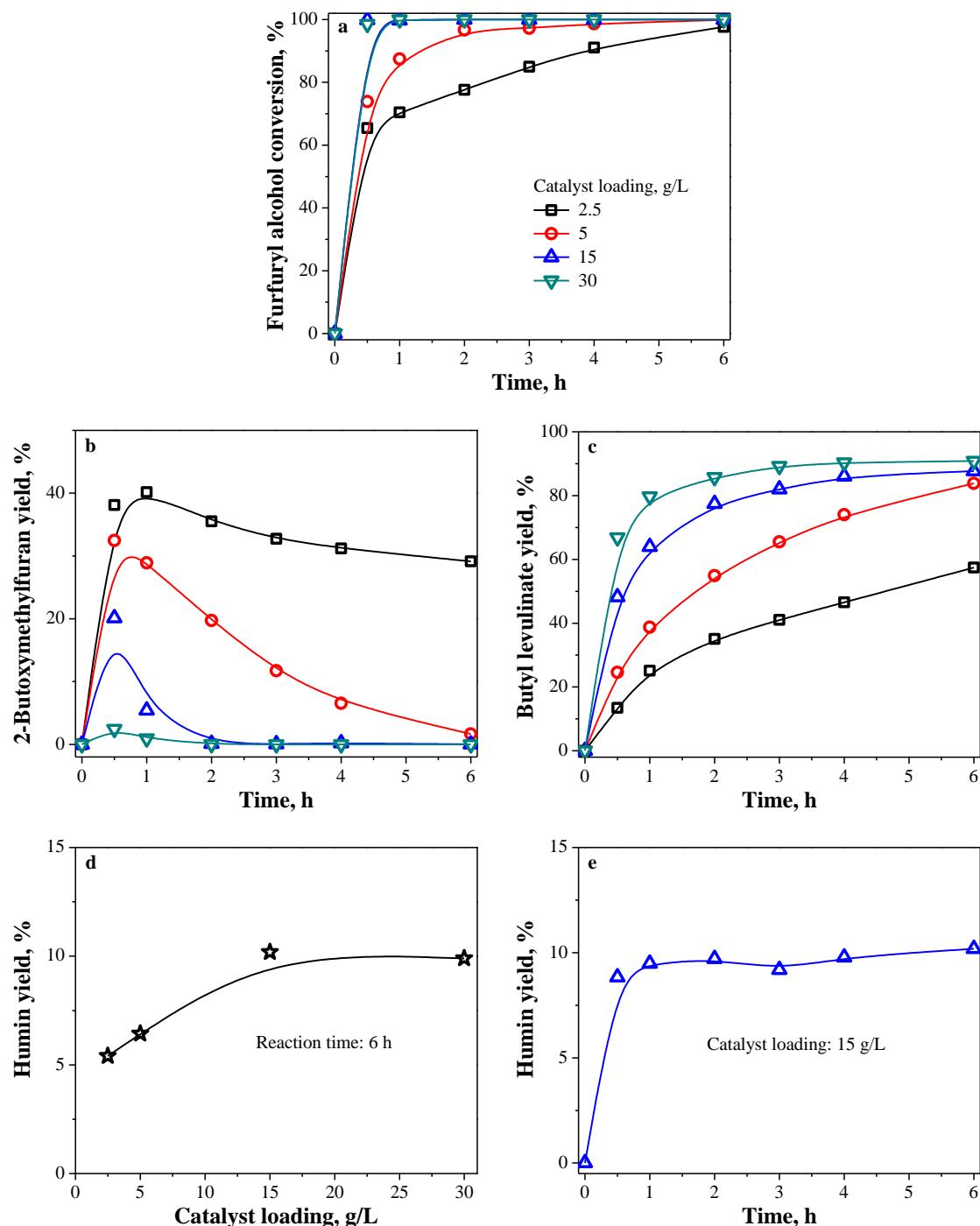


Fig. 3. Effect of catalyst loading on furfuryl alcohol conversion, product distribution, and humin formation. Reaction conditions: 0.3 mol/L furfuryl alcohol in *n*-butanol; reaction temperature of 110 °C; Amberlyst 15 as the catalyst

Effect of Catalyst Loading

Catalyst loading determines the availability of acid sites that were expected to catalyze both the production of desirable alkyl levulinate and undesirable humin from furfuryl alcohol. Hence, the effect of catalyst loading ranging from 2.5 to 30 g/L (based on total volume of reactants, similarly hereinafter) on the conversion of furfuryl alcohol in *n*-butanol medium was investigated using Amberlyst 15 as the catalyst, and the results are given in Fig. 3. Higher catalyst loadings accelerated the conversion of furfuryl alcohol, but the influence was relatively small (Fig. 3a). Furfuryl alcohol was almost entirely consumed for all used catalyst loadings at the end of the tests. However, the degradation of 2-butoxymethylfuran as a key intermediate was affected significantly, and the results were sensitive to catalyst loading. The degradation was favored at higher catalyst loadings (Fig. 3b). Consequently, a higher amount of butyl levulinate was produced when employing higher catalyst loadings (Fig. 3c). This influence was prominent, and butyl levulinate yield increased from 57 to 84% after a reaction time of 6 h when increasing the catalyst loading from 2.5 to 5 g/L. This indicates that a catalyst loading of 2.5 g/L does not offer enough acid sites for the formation of butyl levulinate in a short time, thus giving rise to a low conversion rate. The higher catalyst loading resulted in a greater availability of acid sites, promoting a faster conversion of furfuryl alcohol and the degradation of intermediates to butyl levulinate. The equilibrium conversion for the formation of butyl levulinate was nearly reached after 4 and 3 h and at catalyst loadings of 15 and 30 g/L, respectively. The humin formation after 6 h presented in Fig. 3d shows that there was a significant increase in humin yield when the catalyst loading was increased from 2.5 to 15 g/L, and then it remained almost constant. This indicates that more acid sites also contributed to promoting the polymerization of furfuryl alcohol. The influence of catalyst loading on humin formation was very similar to that of the formation of butyl levulinate. It is thus clear that the alcoholysis of furfuryl alcohol to alkyl levulinate was accompanied by its polymerization, just in various selectivities. Further, humin formation may be affected by residence time, and the change of humin formation with residence time was investigated. Figure 3e shows that the amount of humin formation grew very rapidly in the first stage of 0.5 h, and then it was observed to rise slightly with prolonged reaction time. It can be inferred that humin formation is more likely and directly caused by furfuryl alcohol, and its derived products, such as 2-butoxymethylfuran, are not the main precursors of humin.

Effect of Reaction Temperature

The effect of reaction temperature on furfuryl alcohol conversion, product distribution, and humin formation was studied *versus* reaction time, and the tests were carried out at 90, 100, 110, and 120 °C, respectively. Figure 4a shows that almost complete conversion of furfuryl alcohol was achieved within 0.5 h under all tested temperatures. The yield of intermediate 2-butoxymethylfuran was particularly high during the initial stage of the reaction because of the speedy etherification of furfuryl alcohol and *n*-butanol. However, the maximum yield of 2-butoxymethylfuran declined at 0.5 h with increased temperature (Fig. 4b). At the same reaction time, butyl levulinate yield was increased when employing higher temperatures, as shown in Fig. 4c.

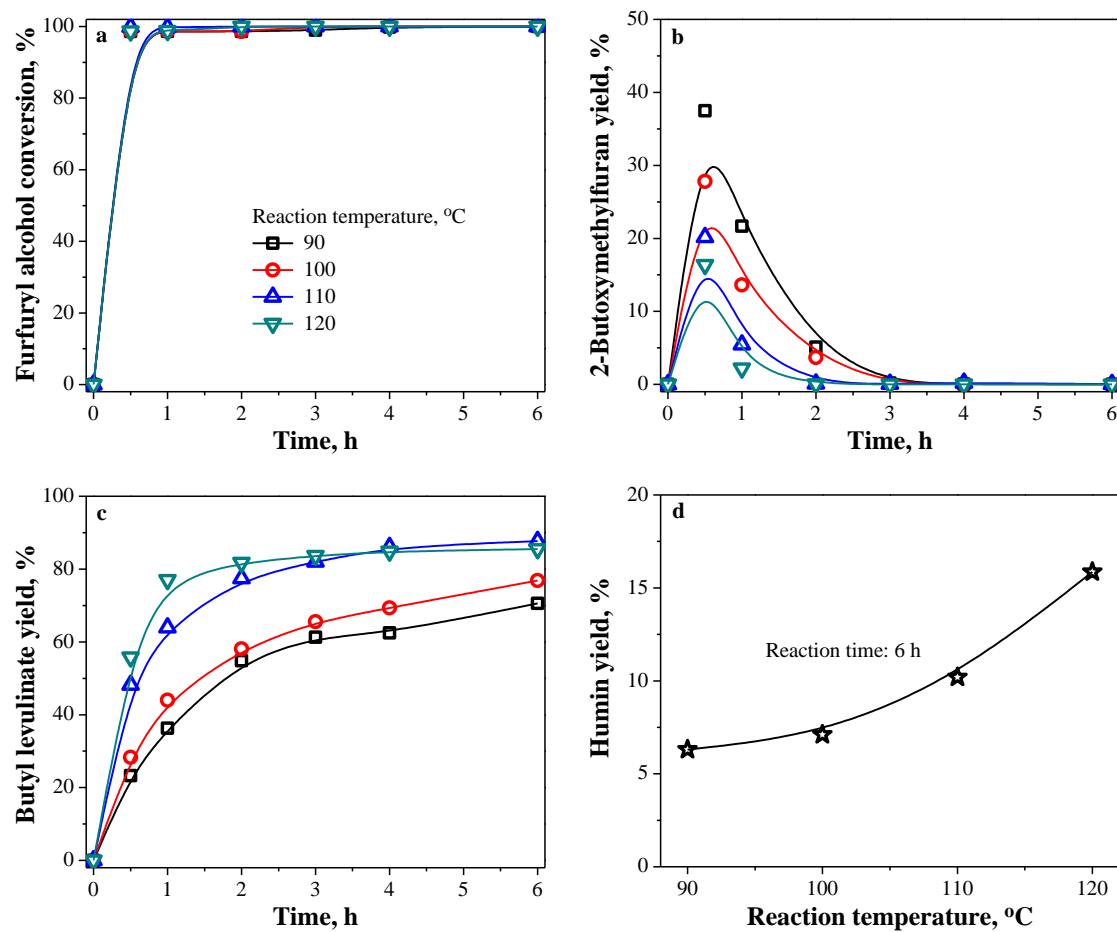


Fig. 4. Effect of reaction temperature on furfuryl alcohol conversion, product distribution, and humin formation. Reaction conditions: 0.3 mol/L furfuryl alcohol in *n*-butanol; Amberlyst 15 as the catalyst, and catalyst loading of 15 g/L

It is speculated that furfuryl alcohol not only forms the intermediate 2-butoxymethylfuran, but it is also converted to butyl levulinate simultaneously. With prolonged residence time, the formed 2-butoxymethylfuran continued to degrade into other products, and a significant amount of butyl levulinate was produced at this point. Increasing the temperature to 110 and 120 °C caused the formation rate of butyl levulinate to accelerate noticeably. Interestingly, the eventual yield of butyl levulinate remained nearly constant as the reactants had reached their near-equilibrium conversion (Fig. 4c). Also, humin formation was found to be closely related to reaction temperature, which was favored at higher temperatures. In particular, humin yield increased almost linearly from 7 to 16%, with an increase in temperature from 100 to 120 °C (Fig. 4d). Clearly, higher temperatures accelerated the reaction rate of alcoholysis, but unwanted side reactions for humin formation became more serious simultaneously. Hence, elevated temperature is unfavorable for the extent of the reaction. At lower temperatures, the combined yield of detected products and humin was clearly below that of the furfuryl alcohol conversion under the same reaction conditions, implying that some other and more complex intermediates exist in the reaction products. This was thoroughly investigated during the acid-catalyzed conversion of furfuryl alcohol to ethyl levulinate

using liquid chromatography-mass spectrometry (LC-MS) and 1D and 2D nuclear magnetic resonance (NMR) spectroscopy, as presented in the study of Maldonado *et al.* (2012b). Furthermore, Fig. 4b shows that 2-butoxymethylfuran was completely consumed after 4 h. This indicates that the conversion of other possible intermediates into butyl levulinate is slower and more difficult than the conversion of 2-butoxymethylfuran.

Effect of Initial Furfuryl Alcohol Concentration

One of the important process parameters is substrate concentration, which affects the utilization efficiency of furfuryl alcohol and the final concentration of alkyl levulinate. In practice, a higher concentration is desired because not only can it enhance the production efficiency of alkyl levulinate but also cut down the energy consumption that occurs during the purification of the product. Here, the experiments were conducted by varying the initial furfuryl alcohol concentration from 0.1 to 1 mol/L, and the results are depicted in Fig. 5. As can be seen from Fig. 5a, the initial furfuryl alcohol concentration had less influence upon furfuryl alcohol conversion, and the conversion was mainly focused on the initial stage of the reaction. However, the effect of initial furfuryl alcohol concentration on product distribution and humin formation became very conspicuous, suggesting that the substrate inhibited kinetics substantially. Both the degradation rate of 2-butoxymethylfuran and the formation rate of butyl levulinate decreased with increasing initial furfuryl alcohol concentration (Figs. 5b and c). When the initial furfuryl alcohol concentration was 0.1 mol/L, butyl levulinate yield reached a maximum of 94% after the reaction. However, butyl levulinate concentration in the resulting product mixture was fairly low (0.09 mol/L). When the initial furfuryl alcohol concentration was increased to 0.3 and 0.6 mol/L, although a moderate drop in butyl levulinate yield was observed, butyl levulinate concentration increased significantly to 0.26 and 0.47 mol/L, respectively. Further increasing of the substrate concentration resulted in increased furfuryl alcohol available for conversion, which means higher obtainable butyl levulinate concentrations. Unfortunately, butyl levulinate yield was found to decline markedly, and its concentration increased disproportionately when the initial furfuryl alcohol concentration increased from 0.6 to 1 mol/L. A similar effect of substrate concentration on the chemical reaction was also observed in some previous reports (Girisuta *et al.* 2007; Yu and Wu 2011; Peng *et al.* 2012). This probably occurred because of product feedback inhibition and/or reactivity diminution for additional furfuryl alcohol, resulting in the transformation of reaction pathways. It is known that butyl levulinate yield decreased when applying higher initial furfuryl alcohol concentrations. Although 2-butoxymethylfuran yield increased accordingly, humin formation also increased significantly with increasing initial furfuryl alcohol concentration. Concretely, humin yield increased by 2.1 times (*ca.* 17%), with an increase in the initial furfuryl alcohol concentration from 0.1 to 1 mol/L (Fig. 5e), suggesting that the reactivity ratio of furfuryl alcohol polymerization to its alcoholysis increased. The above results indicate that the efficient conversion of furfuryl alcohol to alkyl levulinate is highly sensitive to initial furfuryl alcohol concentration. The yield and concentration of alkyl levulinate formed is often contradictory, and compromises have to be made between them for practical usage in order to reduce production cost.

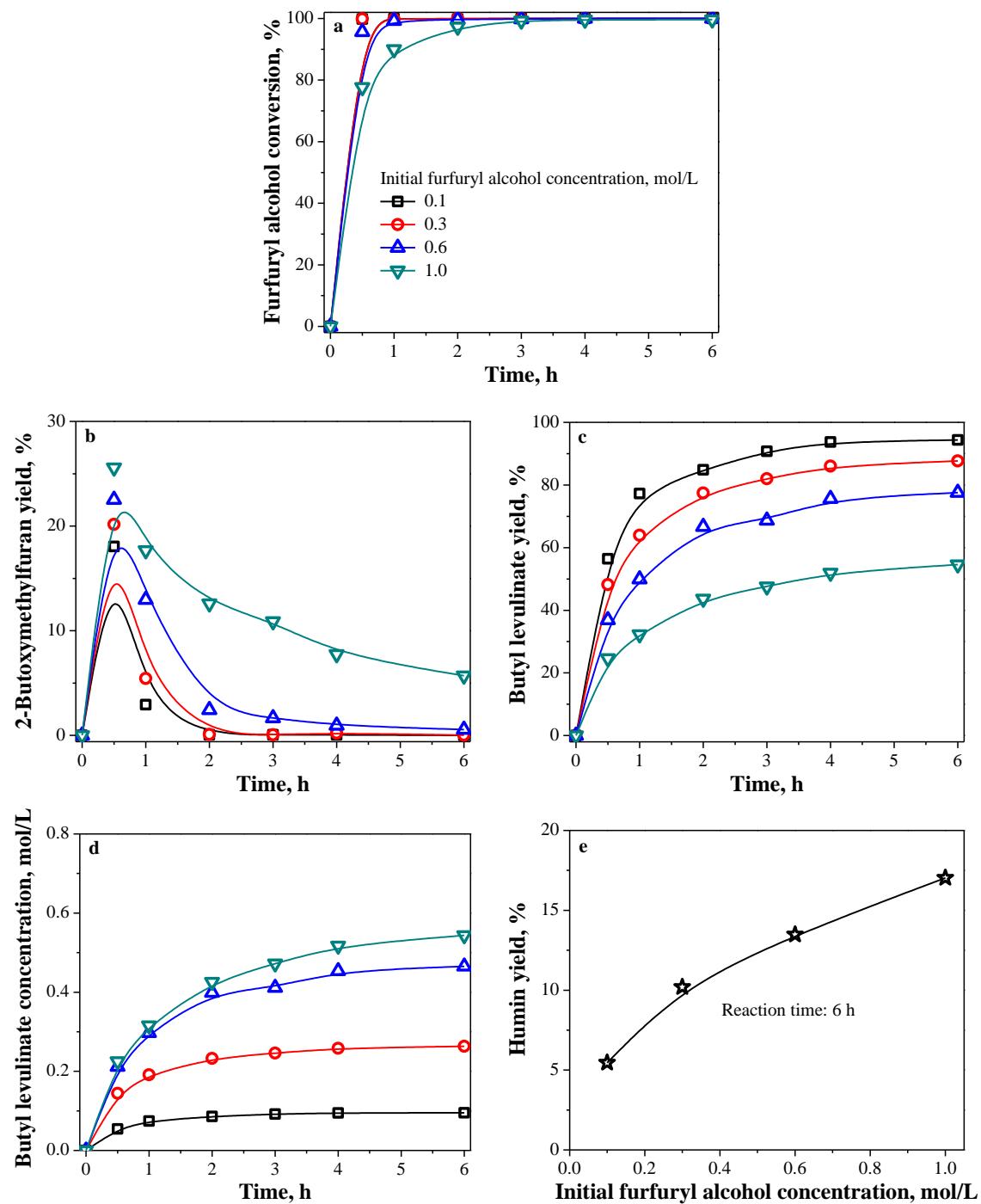


Fig. 5. Effect of initial furfuryl alcohol concentration on furfuryl alcohol conversion, product distribution, and humin formation. Reaction conditions: Amberlyst 15 as the catalyst; catalyst loading of 15 g/L; reaction temperature of 110 °C

Screening of Reaction Medium

It has been well known that a variety of alkyl levulimates can be formed by carrying out the alcoholysis of furfuryl alcohol in the presence of various alcohols, and levulinic acid is derived from furfuryl alcohol hydrolysis in a water medium (Maldonado

et al. 2012a; Wang *et al.* 2014). To gain insight into reaction characteristics in various media, the results for the conversion of furfuryl alcohol in water and different alcohols media catalyzed by Amberlyst 15 are presented in Fig. 6. It is shown that a consistent conversion of furfuryl alcohol in *ca.* 98% was achieved for water and all alcohols studied in this work. Moreover, similar yields of humin (about 6%) and alkyl levulinate (74 to 80%) were detected for production of the investigated alcohols. The existing little difference most likely results from the boiling point and steric effect of the alcohols (Wang *et al.* 2014). However, the conversion of furfuryl alcohol to form humin in a water medium could be as high as 20%, which is significantly higher than that in the alcohol medium. Similar results were also presented for the acid-catalyzed conversion of carbohydrates in a methanol/water medium (Hu and Li 2011; Hu *et al.* 2012). Accordingly, it was also found that the obtained yield of levulinic acid (42%) for the water medium was distinctly lower than that of alkyl levulinate (74 to 80%) for the investigated alcohols. These findings indicate that alcohols instead of water as a reaction medium can effectively protect the reactive hydroxyl groups *via* the etherification of furfuryl alcohol and alcohols, likely stabilizing them and lowering their tendency toward polymerization. This observation further confirms that humin formation is more likely and more directly formed with furfuryl alcohol than its derived compounds, such as 2-alkoxymethylfuran. It follows that alcohols have potential as media in the conversion of biomass-derived compounds to efficiently produce specific platform chemicals.

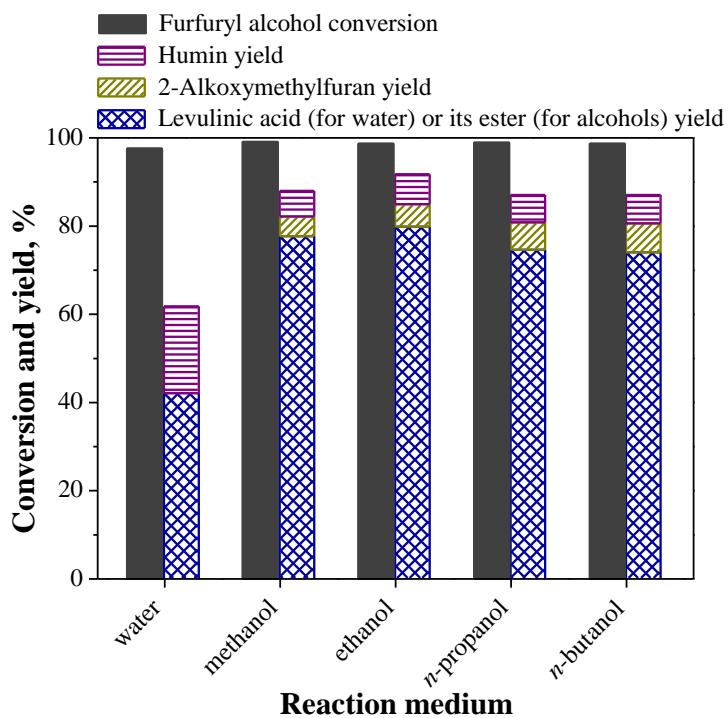


Fig. 6. Screening of the reaction medium in the acid-catalyzed conversion of furfuryl alcohol. Reaction conditions: 0.3 mol/L furfuryl alcohol in a reaction medium; Amberlyst 15 as the catalyst, and a catalyst loading of 5 g/L; reaction temperature of 110 °C; reaction time of 4 h

Formation Pathways of the Humin and Alkyl Levulinate

According to the present findings and the related literature (Bertarione *et al.* 2009; Zhang *et al.* 2011; Maldonado *et al.* 2012b; Kim *et al.* 2013), simplified pathways for the formation of humin and alkyl levulinate from the acid-catalyzed conversion of furfuryl alcohol in alcohols are proposed, as depicted in Fig. 7.

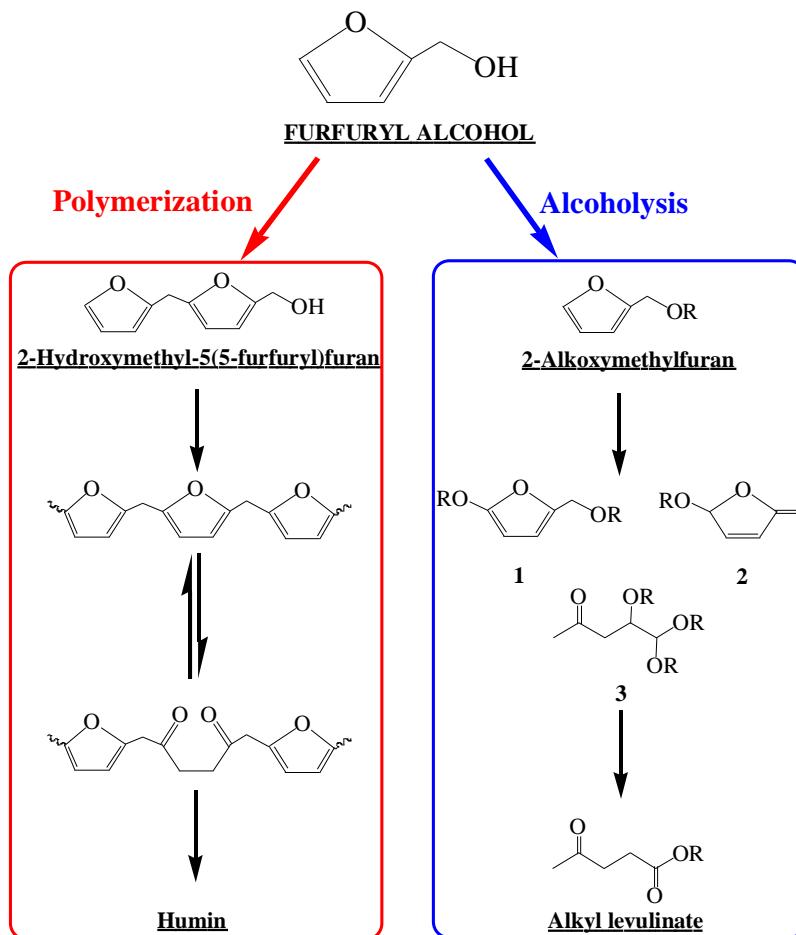


Fig. 7. Proposed formation pathways of humin and alkyl levulinate from the acid-catalyzed conversion of furfuryl alcohol in alcohols

In an alcohol medium, the alcoholysis of furfuryl alcohol plays a dominant role throughout the reaction. To begin with, the hydroxyl group of furfuryl alcohol is protonated and reacts with the hydroxyl group of alcohol by the condensation reaction in the presence of an acid catalyst to form the key intermediate 2-alkoxymethylfuran. This process is both easy to perform and rapid, as shown in Figs. 3 to 5. However, the further conversion of 2-alkoxymethylfuran to its final form alkyl levulinate becomes much slower and more complex. The reaction rate is thus controlled by this stage. The process likely involves the formation of several intermediates (1, 2, and 3) because of the addition and discharge of alcohol in various locations of 2-alkoxymethylfuran and its derived compounds. Subsequently, these intermediates are converted to alkyl levulinate *via* a series of transformations including protonation, elimination, and isomerization. During the course of the reaction, the humin is formed in a parallel mode directly from furfuryl

alcohol, not from its derived compounds, as previously discussed. However, only a small proportion of the furfuryl alcohol undergoes inter-molecular condensation due to the effective protection of the reactive hydroxyl group of furfuryl alcohol by etherification with alcohol. The conversion of furfuryl alcohol to 2-alkoxymethylfuran is probably easier and faster than that of furfuryl alcohol condensation. The formation of humin from furfuryl alcohol is considered to be complicated. The generally accepted pathway primarily involves the formation of -CH₂- bridges from the acid-catalyzed reaction of two furfuryl alcohol molecules (Bertarione *et al.* 2009; Kim *et al.* 2011). The oligomers undergo hydride ion exchanges from the carbon atom linking two furan rings with the carbenium ion, formed by water elimination from a protonated methylol termination of another oligomer. Simultaneously, the formation of γ -diketone structures *via* the furan ring opening is likely to occur. Ultimately, the resulting solid humin with multiple conjugated sequences and carbonyl groups that cause the dark-brown color is formed.

CONCLUSIONS

1. The choices of catalyst and reaction parameters were of importance for avoiding the formation of undesired humin to upgrade the production of alkyl levulinate from furfuryl alcohol. Amberlyst 15 of moderate acidic strength was more favorable for the formation of alkyl levulinate, and heteropolyacids of high acidic strength tended to promote furfuryl alcohol polymerization.
2. High catalyst loadings and temperatures could have accelerated the conversion of furfuryl alcohol to alkyl levulinate, but humin formation was also favored. Alkyl levulinate yield decreased with the enhancement of initial furfuryl alcohol concentration due to an increase in humin formation and the accumulation of intermediates. The use of alcohol instead of water as a reaction medium can effectively protect the reactive hydroxyl group of furfuryl alcohol *via* etherification, likely stabilizing them and lowering their tendency toward polymerization.
3. A high alkyl levulinate yield of up to 94% (100% furfuryl alcohol conversion) was achieved at 110 °C for 4 h with 5 g/L Amberlyst 15 catalyst and an initial furfuryl alcohol concentration of 0.1 mol/L. At this point, about 5% furfuryl alcohol was polymerized to form humin, and its polymerization mainly occurred during the initial stage of the reaction.
4. This study can provide guidance for the choice of appropriate conditions to improve the selective conversion of furfuryl alcohol to alkyl levulinate. For practical applications, more attention may need to be paid to the efficient conversion of high concentrations of furfuryl alcohol into alkyl levulinate.

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