

Ethyl Levulinate Synthesis from Levulinic Acid and Furfuryl Alcohol by Using Modified Carbon Cryogels

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The research on ethyl levulinate synthesis is now increased due to its potential to be derived from biomass and for applications in biofuel. In the present work, model compound of biomass-derived intermediates, levulinic acid and furfural alcohol, were utilized for ethyl levulinate synthesis using modified carbon cryogel. Carbon cryogel produced from urea and furfural (UCC) mixtures was modified via sulfonation (UCC-S) and subsequently doped with Fe (UCC-S-Fe) to increase the surface chemistry of the reaction. In order to study the acidity and phase structure of the catalyst, the UCC-S and UCC-S-Fe were characterized by using NH_3 -TPD and XRD. The ethanolysis of levulinic acid and furfuryl alcohol were conducted in a batch reaction system for the catalytic testing experiment by study the effect of reaction time and catalyst loading. At the selected conditions, with UCC-S as the catalyst, a high ethyl levulinate yield of 99.5 mol% was obtained from ethanolysis of levulinic acid using 10 wt% of a catalyst loading for 4 h. Although UCC-S catalyst gives low ethyl levulinate yield from ethanolysis of furfuryl alcohol, a high yield ethyl levulinate of 97.8 mol% was observed within 5 h of reaction time by applying 20 wt% of UCC-S-Fe catalyst loading. Thus, the modification of urea-furfural carbon cryogel via sulfonation and Fe-doping have improved the properties of carbon cryogel and performed as a promising solid acid catalyst for ethyl levulinate production. However, different activity performances were demonstrated by the two catalysts in the ethanolysis reactions of levulinic acid and furfuryl alcohol.

1. Introduction

Lignocellulosic biomass as the second generation of biomass is continuously generated throughout many countries in the world. This becomes a problem and required an alternative way to reduce biomass capacity. Researchers have focussed and put an effort on biomass utilization by converting it into chemicals and other materials as an alternative to reduce the waste generated. Many processes have been applied to derive chemical from biomass including thermochemical and biochemical process. Acid hydrolysis of biomass is one of the thermochemical processes that can convert biomass into chemicals.

Levulinic acid (LA) is a platform chemical that can be derived via hydrolysis of lignocellulosic biomass (Liu et al., 2018). Levulinic acid is a derived product of 5-hydroxymethylfurfural (HMF) from C6 sugar (hexose) of biomass (Neves et al., 2013). Currently, the LA derivatives to alkyl levulinate has attracted an attention of researchers to synthesis alkyl levulinates via esterification reaction with alcohol (Varkolu et al., 2016). In addition, Wang et al. (2014) has mention that a wide range of biomass sources such as cellulose, saccharides, HMF, and furfuryl alcohol can be utilized for the production of alkyl levulinates through catalytic reaction with various acids in alcohols. Furfuryl alcohol (FA) can be produced from furfural which is a chemical derived product from C5 sugar (pentose) of biomass (Cai et al., 2014). Furfuryl alcohol can further applied for synthesis of alkyl levulinate by acid-catalyzed reaction (Neves et al., 2013). This gives a direction to produce alkyl levulinate from biomass components (from C5 and C6 sugar) or directly from raw biomass. The conversion of biomass to alkyl levulinate via one-pot conversion process has been conducted (Tiong et al., 2017). A good performance catalyst should be obtained for high conversion of chemical components from both C5 and C6 sugar to alkyl levulinate in one pot reaction system. Thus, the catalyst performance and

reaction study on the biomass derived components such as LA and FA is important to be understood for next application on raw biomass to alkyl levulinate.

Ethyl levulinate (EL) is one of alkyl levulinate that mainly synthesized from various feedstocks such as levulinic acid (Yadav and Yadav, 2014) and furfuryl alcohol (Kong et al., 2017) via catalytic reaction with ethanol. Besides, EL synthesis from levulinic acid is possible through a non-catalytic reaction by using high temperature reactive distillation as provided by Silva et al. (2018). Ethyl levulinate has a wide range of applications in chemicals industries including flavoring, fragrance, and as additive in biodiesel fuels (Windom et al., 2011). Ethyl levulinate can be used for blending with biodiesel to improve the engine performance and solve the issue on gas emission. As example, diethyl succinate and 1-octanol was designed for blending with B5 to have a greener emission (Phoon et al., 2017). The ethanolsis of LA and FA to EL was carried out in the presence of heterogeneous acid catalyst as an alternative to replace the homogeneous catalyst due to problem of catalyst recyclability. Many heterogeneous catalysts have been applied for the ethanolsis of LA and FA to EL. This includes the sulfonation of the catalyst to provide high Brønsted acid sites on the reaction. The catalyst properties especially the catalyst acidity is important to provide the active sites and enhance the reaction. As studied by Tominaga et al. (2011), the mixed catalysts of Brønsted and Lewis acid could provide high product yield of methyl levulinate from cellulose. Previously, iron modified catalyst such as Fe/HY (Ramli and Amin, 2015), Fe/USY (Kong et al., 2017), and Fe/ β zeolite (Xia et al., 2018) have provide both Brønsted and Lewis acid for the reaction and shown its capability on the conversion of biomass components.

The current synthesis of carbon cryogel from urea-furfural has shown good potential to be modified as a catalyst for the ethanolsis reaction. The combination of Brønsted and Lewis acid from sulfonation and Iron doping may enhance the reaction to provide high product yield. Thus, this study was conducted for modification of the synthesis of carbon cryogel from urea and furfural for the application as an acid catalyst. The modified carbon cryogel was characterized to study important properties which are the acidity and phase structure of the catalyst. Our study includes the parameters studies on the synthesis of EL via LA and FA by varied the reaction time and catalyst loading.

2. Methodology

2.1 Chemicals and reagents

In carbon cryogel synthesis, urea was purchased from Sigma-Aldrich Co., U.S and furfural was purchased from Merck, Germany. Sulfuric acid, H_2SO_4 (95-97%) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were purchased from QRec, New Zealand and used for modification of carbon cryogel. Furfuryl alcohol ($\text{C}_5\text{H}_6\text{O}_2$, 98 %), levulinic acid ($\text{C}_5\text{H}_8\text{O}_3$), and ethanol ($\text{C}_2\text{H}_5\text{OH}$, 99 %) were purchased from Merck, Germany for the reaction testing. The standard of ethyl levulinate ($\text{C}_7\text{H}_{12}\text{O}_3$, 99 %) was purchased from Merck, Germany for product analysis. All the chemicals were used as received.

2.2 Carbon cryogel synthesis and modification as catalyst

Method of carbon cryogel synthesis was referred from previous work (Zainol et al., 2019a) and applied on urea and furfural feedstocks with some changes on the synthesis condition. The gels were synthesized by mixing urea and furfural at 0.5 molar ratio with the addition of distilled water as diluent followed by additional of H_2SO_4 as acid catalyst. The mixture was stirred for 30 min at room temperature. Then, the gel was pre-frozen in a refrigerator for 2 h and freeze-dried at $-60\text{ }^\circ\text{C}$ for 4 h to form cryogel. The cryogel was calcined at $500\text{ }^\circ\text{C}$ for 2 h to produce urea-furfural carbon cryogel (UCC). The UCC was firstly modified via sulfonation in concentrated H_2SO_4 at $150\text{ }^\circ\text{C}$ for 15 h. Then, continuous washing process via vacuum filtration was conducted until the pH of the filtrate is around 6.7 to 7. The sulfonated carbon cryogel (UCC-S) was used for the ethanolsis of levulinic acid. However, further modification of UCC-S is required for the ethanolsis of furfuryl alcohol to provide high ethyl levulinate yield. The UCC-S was further impregnated with 5 wt% of Fe via mixing of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 50 mL of distilled water for 2 h at room temperature. After that, the mixture was filtered and dried in the oven overnight at $110\text{ }^\circ\text{C}$. The produce Fe doped UCC-S catalyst (UCC-S-Fe) was obtained after calcination at $400\text{ }^\circ\text{C}$ for 5 h.

2.3 Characterization of catalyst

The phase structure and crystallinity peak of UCC-S and UCC-S-Fe were studied by using X-ray diffraction (XRD) analysis (Rigaku SmartLab X-ray diffractometer system) using Cu K α radiation at 40 kV and 30 mA for angle 2θ of 10° to 80° . The acidity of the UCC-S and UCC-S-Fe were determined by using ammonia-temperature programmed desorption (NH $_3$ -TPD) analysis which performs via Micromeritics AutoChem II 2920 V4.03 apparatus. In this analysis, the thermal conductivity detector (TCD) was used with 10% NH $_3$ /He of gas flow and the heating of desorption process was carried out up to $900\text{ }^\circ\text{C}$.

2.4 Catalytic testing and product analysis

All reactions were conducted in a batch reaction system. As for the ethanolsis of levulinic acid, the reflux reaction setup was used at fixed temperature of 80 °C. However, the ethanolsis of furfuryl alcohol was conducted in a stainless steel pressurized reactor due to high reaction temperature is required. Based on the reaction screening conducted, the reaction temperature of the ethanolsis of furfuryl alcohol was fixed at 200 °C. The effect of reaction time was studied up to 5 h for both reactions. As for the effect of catalyst loading, low catalyst loading range of UCC-S (3–15 wt%) was used for EL synthesis from LA as compared to catalyst loading of UCC-S-Fe (10-40 wt%) that was used for EL synthesis from FA. The molar ratio of LA and FA to ethanol were fixed to 10 and 20. The reaction mixture was heated with stirring at 200 rpm. After the reaction, the mixture was cooled and the liquid-phase fraction was separated via filtration and collected for analysis by using GC-FID. The EL peak was detected by gas chromatography with flame ionization detector (GC-FID) using Agilent Technology 7820A gas chromatography system equipped with a DB-Wax column (30 mm × 0.25 mm × 0.25 μm). The GC-FID was conducted with the following conditions: the carrier gas is nitrogen with a flow rate of 1.0 mL/min; the injection port temperature is 250 °C; the oven temperature is programmed from 50 °C at a heating rate of 5 °C/min until 170 °C and then to 240 °C at a heating rate of 15 °C/min; the detector temperature is 270 °C. The concentration of EL was determined based on standard calibration curves and the EL yield was calculated using Eq(1).

$$\text{Ethyl levulinate yield (mol\%)} = [(C_{\text{EL}} \times V_{\text{P}})/1000/M_{\text{EL}}]/(W_{\text{F}}/M_{\text{F}}) \times 100 \quad (1)$$

where, C_{EL} is the ethyl levulinate concentration (mg/L), M_{EL} is the molecular weight of ethyl levulinate (g/mol), V_{P} is the final volume (mL), M_{F} is the molecular weight (g/mol) and W_{F} is the initial weight (g) of the feedstocks used (levulinic acid and furfuryl alcohol) in the reaction.

3. Results and discussion

Figure 1a presents the NH_3 -TPD thermograph of the UCC-S and UCC-S-Fe. Based on the NH_3 -TPD thermograph, the acidity of the catalyst is represented into three regions, this is, low, moderate and strong acidity. As shown by UCC-S, high total acidity of 52.1 mmol/g is obtained, which contributes by 8.8, 21.9, and 21.4 mmol/g of low, moderate, and strong acidity. The acidity present is attributed by the acid modification from the sulfonation in UCC-S. This high acidity of the catalyst is applied for the ethanolsis of LA to obtain high EL yield. The acid presented in the UCC-S is donated by the sulfonate group as Brønsted acid sites for the reaction. As for the reaction of FA to EL, the further modification of UCC-S with Fe is conducted to enhance the surface acidity of the catalyst (UCC-S-Fe). Iron-doped is contributed to the Lewis acid sites of the catalyst (Kong et al., 2017). Based on these results, the modification of UCC-S with Fe has shown the increase of total acidity of UCC-S-Fe. Total acidity of 75 mmol/g of UCC-S-Fe is obtained after the modification mainly contributed by strong acid (67.5 mmol/g). The high total acidity of UCC-S-Fe includes low and strong acidity only since the moderate acidity of UCC-S-Fe is lower as their acid strength is increased with the modification of Fe. Kong et al. (2017) stated that the modification of catalyst to increase the acidic properties is important to reduce the production of by-product. They have also stated that the strong acidic of catalyst provides higher catalytic activity for the oligomerization of FA. The acidic properties of UCC-S and UCC-S-Fe are improved through the modification step for the catalytic reaction to obtain high EL yield. The Fe doped on the UCC-S is changing its acidic distribution by increase the acid strength of UCC-S-Fe for ethanolsis reaction.

X-ray diffraction spectra of UCC, UCC-S and UCC-S-Fe are depicted in Figure 1(b) have shown the phase structure of catalyst precursor with sulfonated followed by Fe-doped. Based on the XRD pattern, the broad peak observed between 10° and 30° showing that all UCC, UCC-S and UCC-S-Fe consist of non-crystalline structures as the amorphous of carbon-based from urea and furfural. The amorphous phase structure relates to the random aromatic carbon arrangement (Hara, 2010). Sulfonation of UCC that produces UCC-S did not show any formation of crystal peak and presented a small change as compared to UCC, which remains as amorphous structure. As observed, the crystallinity of amorphous peak of UCC is reduced after sulfonation. This shows that the modification of the carbon surface properties via sulfonation step can reduces the crystallinity of amorphous phase structure due to effect of strong acid on the carbon structure. The small peak of iron oxide (Fe_2O_3) is observed between 30° and 40°. The other crystalline peaks of iron oxide could not be observed from XRD pattern due to low Fe dosage used for modification. The previous studies also mentioned that the peak of iron oxide is not detected due to low iron dosage used or there is a possibility that iron oxide presents as non-crystalline (Turapan et al., 2012, Shwan et al., 2014). Based on the characterization, the acidic properties of both UCC-S and UCC-S-Fe catalysts contributed by sulfonation and followed by Fe doping is applied to study the performance on the ethanolsis of LA and FA.

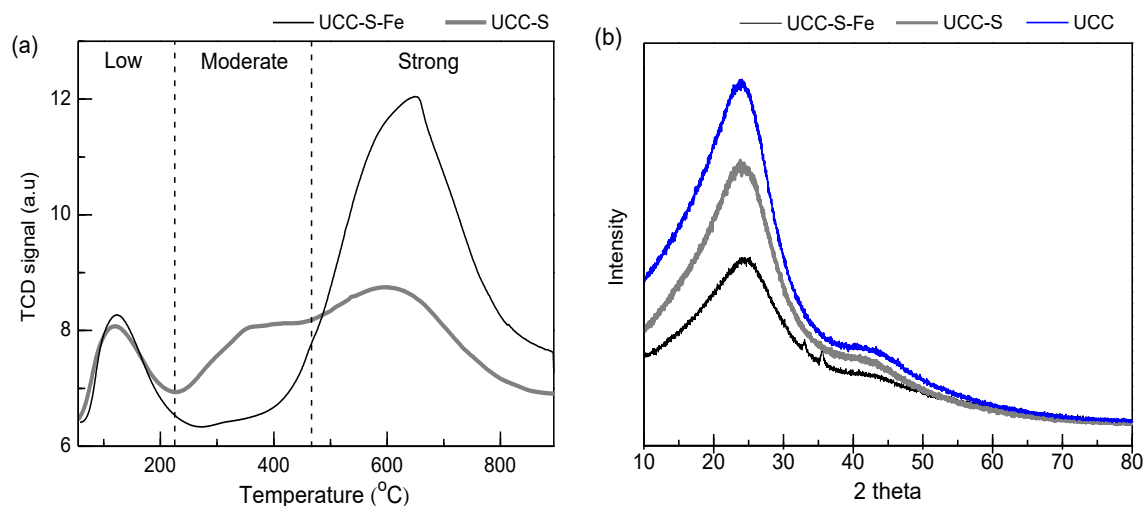


Figure 1: (a) NH₃-TPD thermographs of UCC-S and UCC-S-Fe, (b) XRD spectra of UCC, UCC-S and UCC-S-Fe.

As for the ethanolysis of levulinic acid using UCC-S, the results of parameters studies on reaction time and catalyst loading are shown in Figure 2. As in Figure 2a, the EL yield was increased from 17.7 to 99.5 mol%, as reaction time increases from 2 to 4 h. The EL yield is slowly reduced to 76.7 mol% by increasing the reaction time to 5 h. The similar trend on reduction in the EL yield has been reported by previous studies (Maheria et al., 2013). The reducing of EL yield at long reaction time may be due to the hydrolysis and reversible process caused by the formation of water from the ethanolysis reaction process. As stated by Maheria et al. (2013), long reaction time may cause the additional of water formation from reaction to break the ester link into their parent components of carboxylic acid and alcohol. Therefore, long reaction time is not feasible for the reaction to obtain high EL yield. The reaction time of 4 h is selected as optimum time for the next testing of ethanolysis of LA using UCC-S.

The effect of UCC-S loading on EL yield (Figure 2b) shows that EL yield increases from 85.0 to 99.5 mol% with increasing the catalyst loading from 3 to 10 wt%. The EL yield reduces when the reaction is conducted by using 15 wt% of UCC-S. The same trend has been reported by previous work where the EL is reduced as the catalyst loading is increasing (Zainol et al., 2019b). The decreasing of EL yield may be due to high concentration of catalyst that can increase the reaction viscosity and limit the mass transfer rate. Previous studies have reported that the increase in reaction mixture viscosity and mass transfer limitation could hinder the catalytic activity (Li et al., 2019). Based on the graph in Figure 2b, the catalyst loading of 5 wt% is sufficient to give high EL yield of 97.1 mol%. The catalyst loading is selected at 5 wt% for the ethanolysis of LA using UCC-S.

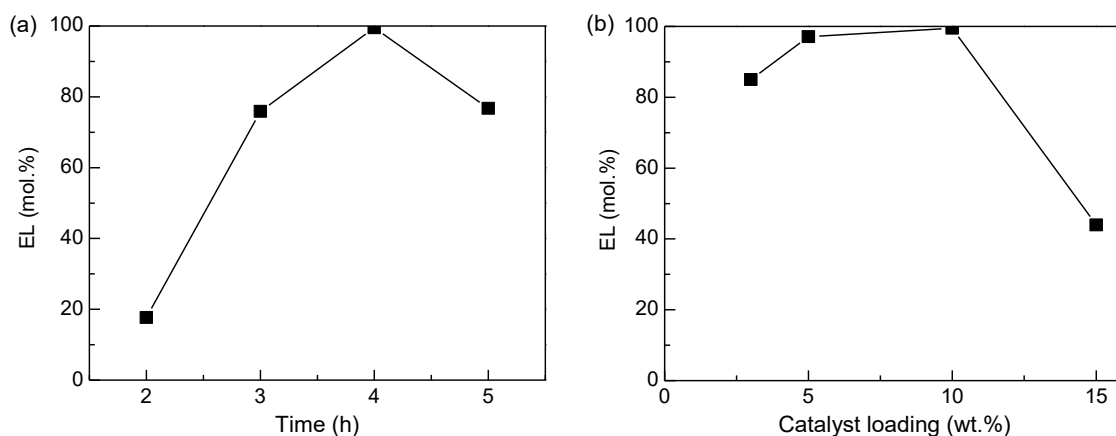


Figure 2: Effect of (a) reaction time (1:10 of LA:EtOH, 80 °C, 10 wt% catalyst) and (b) catalyst loading (1:10 of FA:EtOH, 80 °C, 4 h) on EL yield from LA by using UCC-S catalyst.

The further modification of UCC-S with Fe is required to improve the acidic properties of UCC-S-Fe. The reaction performance of UCC-S-Fe on the ethanolsis of FA are shown in Figure 3. As shown in Figure 3a, the reaction time was varied from 1 to 5 h to observe the reaction performance of the UCC-S-Fe. The EL is significantly increased from 43.2 to 97.8 mol% when the reaction time is increased from 1 to 2 h. Then, the EL yield is slightly reduced when the ethanolsis reaction of FA is further conducted up to 5 h. The reducing of EL yield at long reaction time may be affected by the formation of reaction intermediate before convert to EL. As stated by Wang et al. (2014), low yield of EL obtained at prolonged reaction time is speculated by the formation of intermediates from the reaction of furfuryl alcohol with ethanol as the rate-determining step before converted into the final product. Thus, the optimum reaction time for the ethanolsis of FA to EL by using UCC-S-Fe is selected at 2 h.

The presence of catalyst is important to enhance the reaction and the optimum of UCC-S-Fe loading is required for obtaining high EL yield. The effect of catalyst loading for ethanolsis of FA to EL is shown in Figure 3b. The UCC-S-Fe loading is studied by using up to 40 wt% of catalyst loading and optimum EL yield of 97.8 mol% is obtained by applied 20 wt% of UCC-S-Fe. The EL yield is increased from 42.4 mol% by applying 10 wt% of UCC-S-Fe up to the optimum yield. High EL yield is obtained in the ethanolsis of LA to EL by using 5 to 10 wt% of UCC-S as compared to catalytic reaction of FA to EL by using 10 wt% of UCC-S-Fe that gives low EL yield. This is due to insufficient of UCC-S-Fe catalyst to provide an active site for the reaction. Then, the result shows that EL yield is reduced when the catalyst loading is increased above 20 wt%. The higher catalyst loading provides more active sites which could drive the reaction by minimizing the reaction time. However, higher catalyst loading in the reaction medium could affect the reaction for EL formation. This is also related to high concentration of catalyst that can increase the reaction viscosity which can limit the mass transfer rate. Therefore, the catalyst loading of 20 wt% is observed to be optimum for the catalyst loading. Catalytic ethanolsis of furfuryl alcohol involves the adsorption of furfuryl alcohol on the Brønsted or Lewis acid sites of catalyst. The modification of Fe on UCC-S has increased the strength of acidity which enhances the reaction for EL production. The catalyst properties are important to provide good reaction performances for both reaction of LA and FA to EL by using UCC-S and UCC-S-Fe. The positive results obtained by using UCC-S and UCC-S-Fe for EL synthesis via LA and FA, show a potential of modified carbon cryogel as strong acid catalyst. This finding may provide a future direction on the derivation of EL from the lignocellulosic biomass.

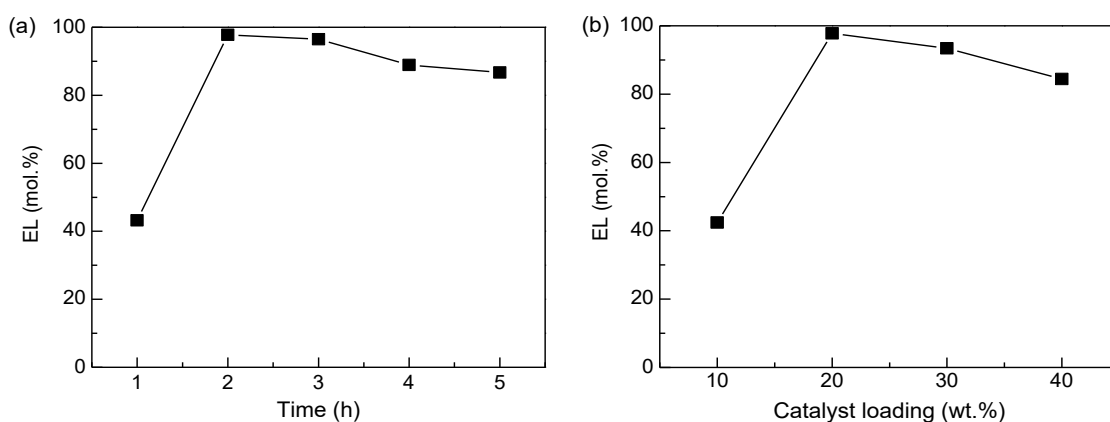


Figure 3: Effect of (a) reaction time (1:20 of FA:EtOH, 200 °C, 20 wt% catalyst) and (b) catalyst loading (1:20 of FA:EtOH, 200 °C, 2 h) on EL yield from FA by using UCC-S-Fe catalyst.

4. Conclusions

Both modified urea-furfural carbon cryogels, UCC-S and UCC-S-Fe are prepared and characterized accordingly. High acidity of the UCC-S and UCC-S-Fe provides good performance on ethanolsis of LA and FA to EL. The acid strength of UCC-S is improved by further modification with Fe to enhance the ethanolsis reaction. The Fe doping was confirmed via XRD spectra of UCC-S-Fe where the peak of iron oxide was detected. High EL yield was obtained from both reactions at the selected reaction time and catalyst loading. Conversion of LA to EL required moderate reaction condition (temperature: 80 °C and reaction time: 4 h) with low catalyst loading (10 wt%) used to obtain high EL yield (99.5 mol%). On the contrary, even though the ethanolsis of FA is conducted at short time (2 h) to provide high yield of EL (97.8 mol%), the reaction conditions required high temperature (200 °C) and catalyst loading (20 wt%). High EL yield obtained from LA

and FA as biomass-derived chemical have given a positive outlook towards the derivation of EL from lignocellulosic biomass by using modified carbon cryogel catalysts.

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