# Synthesis of Renewable Jet Fuel Precursors from C-C Bond Condensation of Furfural and Ethyl Levulinate in Water

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**Abstract** – Biomass derived jet fuel is proven as a potential alternative for the currently used fossil oriented energy. The efficient production of jet fuel precursor with special molecular structure is prerequisite in producing biomass derived jet fuel. We synthesized a new jet fuel precursor containing branched $C_{15}$ framework by aldol condensation of furfural (FA) and ethyl levulinate (EL), where the latter of two could be easily produced from lignocellulose by acid catalyzed processes. The highest yield of 56% for target jet fuel precursor could be obtained at the optimal reaction condition (molar ratio of FA/EL of 2, 323 K, 50 min) by using KOH as catalyst. The chemical structure of $C_{15}$ precursor was specified as (3E, 5E)-6-(furan-2-yl)-3-(furan-2-ylmethylene)-4-oxohex-5-enoic acid ($F_2E$). For stabilization, this yellowish solid precursor was hydrogenated at low temperature to obtain C=C bonds saturated product, and the chemical structure was proposed as 4-oxo-6-(tetrahydrofuran-2-yl)-3-(tetrahydrofuran-2-yl)-methyl hexanoic acid ($H$-$F_2E$). The successful synthesis of the new jet fuel precursors showed the significance that branched jet fuel could be potentially produced from biomass derived FA and EL via fewer steps.

Key words: Aldol Condensation, Furfural, Ethyl Levulinate, Jet Fuel Precursor, Biomass

## 1. INTRODUCTION

With continuous depletion of fossil resources and environmental problems of increasing concern, the production of clean and renewable hydrocarbon fuels has drawn considerable attention [1-3]. Jet fuel composed of branched long chain alkanes is an important part of today's energy chart, but its production is mainly dependent on non-renewable fossil energy. This results in the great significance for searching for a new jet fuel production technology from renewable biomass resources [4,5].

For producing jet fuel with branched carbon numbers of 8~16 from biomass, the following routes have been usually utilized. Hydrodeoxygenation of vegetable/animal oils followed by hydroisomerization, Fischer-Tropsch technology of syngas from biomass gasification followed by hydroisomerization, and 1-butene (produced by dehydration of 1-butanol which originates from sugar fermentation) oligomerization followed by hydroisomerization [6-9]. These routes, however, show obvious disadvantages for vegetable oil feedstock due to limited resources, for Fischer-Tropsch synthesis and 1-butene oligomerization technology due to multi-step tranformations, high cost and low productivity (for the last route). Moreover, additional hydroisomeri-

zation is necessary for obtaining the branched alkanes suitable for jet fuel application [10,11].

The alternative route for producing jet fuel is to use biomass derived platforms such as furfural (FA), 5-hydroxymethyl furfural (HMF) and levulinic acid derivatives by C-C bond condensation followed by hydrodeoxygenation in liquid phase. Among those steps, the efficient synthesis of condensation intermediate/precursor from biomass derived platform is the key. Dumesic [12-14] and Huber [15,16] synthesized the oxygenated precursors with adjustable carbon numbers ($C_8$-$C_{16}$) by aldol condensation of lignocellulose derived FA/HMF and acetone. In addition, the other condensation pathways containing hydroxylalkylation-alkylation, ketonization and self-condensation, etc. [17-21] were also extensively investigated by using heterogeneous and/or homogeneous base or acid catalysts. However, the often used small aldehydes/ketones such as acetone and butanal originate from fossil resources and/or survive from biomass by multi-step syntheses. This results in the production of jet fuel with low yield and low efficiency [22-24]. Therefore, exploring new starting materials which are produced directly and facilely from biomass for jet fuel precursor is of importance but still presents an open challenge.

Ethyl levulinate (EL) and FA can be easily produced by hydrolysis and dehydration from cellulose in ethanol and from hemi-cellulose in water, respectively [25]. E.S.Olson patent introduced such simple synthesis routes, however, no scientific insights into kinetic parameters, products controlling mechanism, and also analysis of condensation structure were proposed [19]. Here, we used EL and FA as the
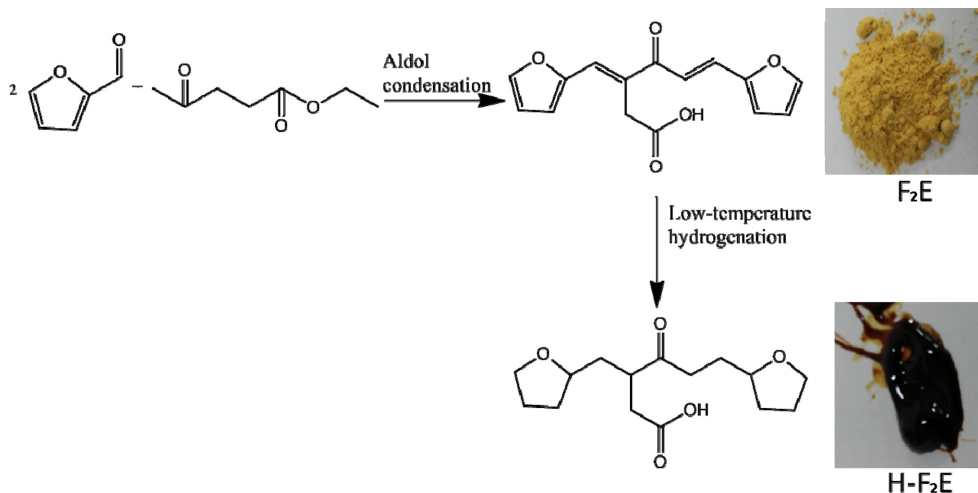
**Fig. 1. Scheme of oxygenated $C_{15}$ precursor production by aldol condensation of furfural and EL and hydrogenation at low temperature.**

feedstock to produce the oxygenated $C_{15}$ precursor by aldol condensation in water over base catalyst (Fig. 1), This new precursor was further hydrogenated over supported metal catalyst to obtain the stabilized product (this hydrogenation at low temperature is necessary because the direct hydrodeoxygenation of the pristine precursor at high temperature is prone to coking due to the active C=C and C=O bonds in the precursor [25]). Particularly, this new precursor presents the intrinsic branched carbon framework, which is favorable to produce branched hydrocarbons for jet fuel after hydrodeoxygenation. Kinetic parameters, products controlling mechanism and analysis of condensation structure were concretely analyzed.

## 2. Experimental

### 2-1. Materials

FA (≥99.5%, analytical reagent) was purchased from Tianjin Damao Chemical Reagents Factory. EL (≥99.5%, analytical reagent) and 5%Pd/C catalysts were purchased from Aladdin industrial Co. Ltd. Methanol (≥99.5%, analytical reagent) was purchased from Tianjin Fuyu Fine Chemical Co. Ltd. KOH, NaOH, LiOH, Ba(OH)$_2$, Ca(OH)$_2$ and Na$_2$CO$_3$ were purchased from Tianjin Fuchen Chemical Reagents Factory. All of these materials were used as received.

### 2-2. Catalyst and product analysis

The surface area and pore size distribution of Pd/C were carried out over an automated surface area and pore size analyzer by Quantachrome at 77 K. The catalyst was degassed at 343 K for 10 h prior to measurement. The surface area was calculated by Brunauer-Emmett-Teller (BET) method and the pore size distribution was calculated by Barret-Joyner-Halenda (BJH) measurement.

X-ray powder diffraction (XRD) pattern was obtained on a Rigaku D/max-rC X-ray diffractometer operated at 40 kV and 40 mA using Cu K$_\alpha$ radiation (λ=0.154 nm), and the data were collected in the 2θ range of 5º~80º at each step of 0.02º.

$^{13}$C Chemical shift of product was measured in solvent CD$_3$OD

with tetramethyl silane (TMS) as reference. Structure of the product was analyzed by Fourier transform infrared (FT-IR) spectrometer NICOLET iS50. Before measurement, the samples were mixed with KBr, fully ground and compressed into slices. Elemental analyses of products were conducted on an elemental analyzer (vario-ELI) with a thermal conductivity detector (TCD) and helium as carrier gas. LC-MS analysis was performed in an Agilent 1290~6540 instrument. Thermogravimetric analysis was carried out in air on Linseis TG system with the temperature range of 303~1273 K and the ramp of 293 K/min, respectively. GC analysis was performed in Agilent 7890 instrument with HP-INNOWAX column.

### 2-3. Aldol condensation of FA and EL

The aldol condensation of FA and EL was carried out in a 150 ml, round-bottomed flask provided with a reflux device and a magnetic stirrer. Typically, 50 ml deionized water and 0.06 mol NaOH were put into the flask until NaOH was completely dissolved by stirring. 0.06 mol FA was then added to the flask. After 0.5 h, 0.03 mol EL was introduced tropwise with the molar ratio of FA to EL of 2 through a peristaltic pump. The reaction was controlled at 323 K for 50 min. After reaction, the reactor was cooled to ambient temperature. Aqueous HCl solution was used to adjust the reaction solution until the pH of 5~6 and a tawny solid condensation product (F$_2$E) was formed. F$_2$E was obtained by filtration, purification with deionized water and dried at 313 K for 12 h in vacuum. F$_2$E was analyzed by $^{13}$C NMR, FT-IR and TGA techniques.

The conversion of reactant and the yield of product was determined by the following formula and the weight data of remnant reactant can acquired by GC analysis.

Conversion of reactant (%)

$$= \left(1 - \frac{\text{Weight of Remnant Reactant}}{\text{Weight of Reactant Input}}\right) \times 100\%$$

$$\text{Yield of F}_2\text{E}(\%) = \left(\frac{\text{Dry Weight of F}_2\text{E}}{\text{Weight of Reactant Input}}\right) \times 100\%$$
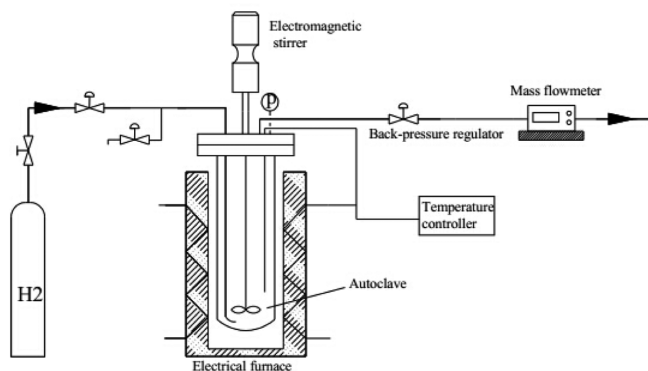
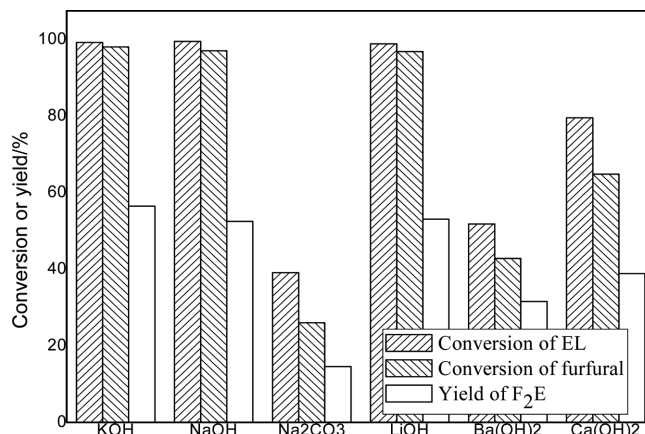**Fig. 2. Schematic diagram of experiment apparatus.**



**Fig. 3. EL and FA condensation to $F_2E$ over different base catalysts. Reaction conditions: 323 K, 50 min; 0.06 mol FA, 0.03 mol EL (the molar ratio of EL/FA 2:1), 0.06 mol base, 50 ml $H_2O$.**

### 2-4. $F_2E$ Hydrogenation at low temperature

Hydrogenation of $F_2E$ was in a 100 ml stainless autoclave equipped with a mechanical stirrer (Fig. 2). For each reaction, 0.5 g of 5% Pd/C catalyst, 4.4 g of freshly produced $F_2E$ and 50 ml methanol were introduced into the autoclave. After eliminating the air residue within the reactor by $H_2$ flushing, the reactor was pressurized by $H_2$ and was heated to a certain temperature for a certain period. During hydrogenation process, the $H_2$ pressure was kept at the constant 3 MPa by supplying $H_2$ when it was consumed. After reaction, the reaction system was cooled, the catalyst was removed by filtration, and the dark brown hydrogenated product (H-$F_2E$) was obtained by removing methanol via vacuum distillation. LC-MS, FT-IR, $^{13}$C NMR technologies were used to analyze H-$F_2E$.

## 3. Results and Discussion

### 3-1. Aldol condensation of EL and FA

Fig. 3 gives the results of aldol condensation between EL and FA in the presence of various basic catalysts. The reactions were carried out at the mild temperature of 323 K and the time of 50 minutes in water. As indicated from Fig. 3, both the high conversion of more than 95% for EL and FA and the high yield of more than 50% for yellowish solid product could be observed when using KOH, NaOH and LiOH as the catalysts. Among these base catalysts, KOH showed superior performance in this process by obtaining the highest condensation product yield of 56%. Meanwhile, using $Na_2CO_3$, $Ca(OH)_2$ and $Ba(OH)_2$ as the catalysts, both of the EL and FA conversion, and the yield of condensation product yield were significantly reduced. The sequence of activities for the base catalysts decreased in the order of KOH>NaOH>LiOH>$Ca(OH)_2$>$Ba(OH)_2$>$Na_2CO_3$. Aldol condensation of FA and EL is a typical base catalyzed process by coupling of the carbon atoms having α-H in EL and the carbonyl group in FA via carbanion mechanism. The basicity of catalysts plays the essential role in obtaining the target condensation product. The higher product yields gained over the water soluble KOH, NaOH and LiOH are dependent on their strong basic properties [24]. While, the inferior performance over $Na_2CO_3$, $Ca(OH)_2$ and $Ba(OH)_2$ is possibly responsi-

ble for the weak basicity ($Na_2CO_3$) and the limited water solubility ($Ca(OH)_2$ and $Ba(OH)_2$), which results in very limit basic sites for triggering this reaction.

We collected the solid product and analyzed its composition and structure by using different technologies. Elemental Analysis showed that the molecular formula of the resultant condensation product was $CH_{0.81}O_{0.34}$, which is very similar to the theoretical $C_{15}H_{13}O_5$ (simplified formula $CH_{0.87}O_{0.33}$) produced by condensation of two FA and one levulinic acid. This indicated that the $F_2E$ was successfully synthesized and EL transferred to LA by hydrolysis during the condensation process. The structure of $F_2E$ was analyzed by $^{13}$C NMR spectra (Fig. 4). All fifteen carbon atoms could be identified by the $^{13}$C NMR spectrum recorded after 50 K scans (rd=2.0 s). The peaks at 112, 115, 145 and 151 ppm were assigned to the furan ring and the carboxyl and ketone peaks were observed at 173 and 190 ppm, respectively. We continued to confirm the existence of carboxylic group by using FT-IR (Fig. 5), considering the absorption at 1706 cm$^{-1}$. Taking into account that base could possibly counteract with EL and remain metal in the final condensation product, the TGA was implemented in air (Fig. S1). The result showed that $F_2E$ was burned up at about 923 K and no any solid residue was detected, indicating no metal was combined with $F_2E$ (Fig. 1).

Fig. 6 shows the influence of reaction time on aldol condensation of FA and EL with the molar ratio of 2 over KOH at 323 K. The $F_2E$ yield as well as FA and EL conversion increased with increasing reaction time, and obtained the highest $F_2E$ yield of 56% at 50 min and nearly complete FA and EL conversion. This indicated that such condensation is quite easy and could get high target product at short time. As reaction time further increased, the yield of $F_2E$ and the conversion of FA and EL changed a little by stabilizing the constant 50% and 90%, respectively.

As shown in Fig. 7, the yield of $F_2E$ over KOH continuously increased as the reaction temperature increased from 303 K to 343 K, and then stabilized upon the reaction temperature of above 343 K. This result also could be explained by our observations that the reac-
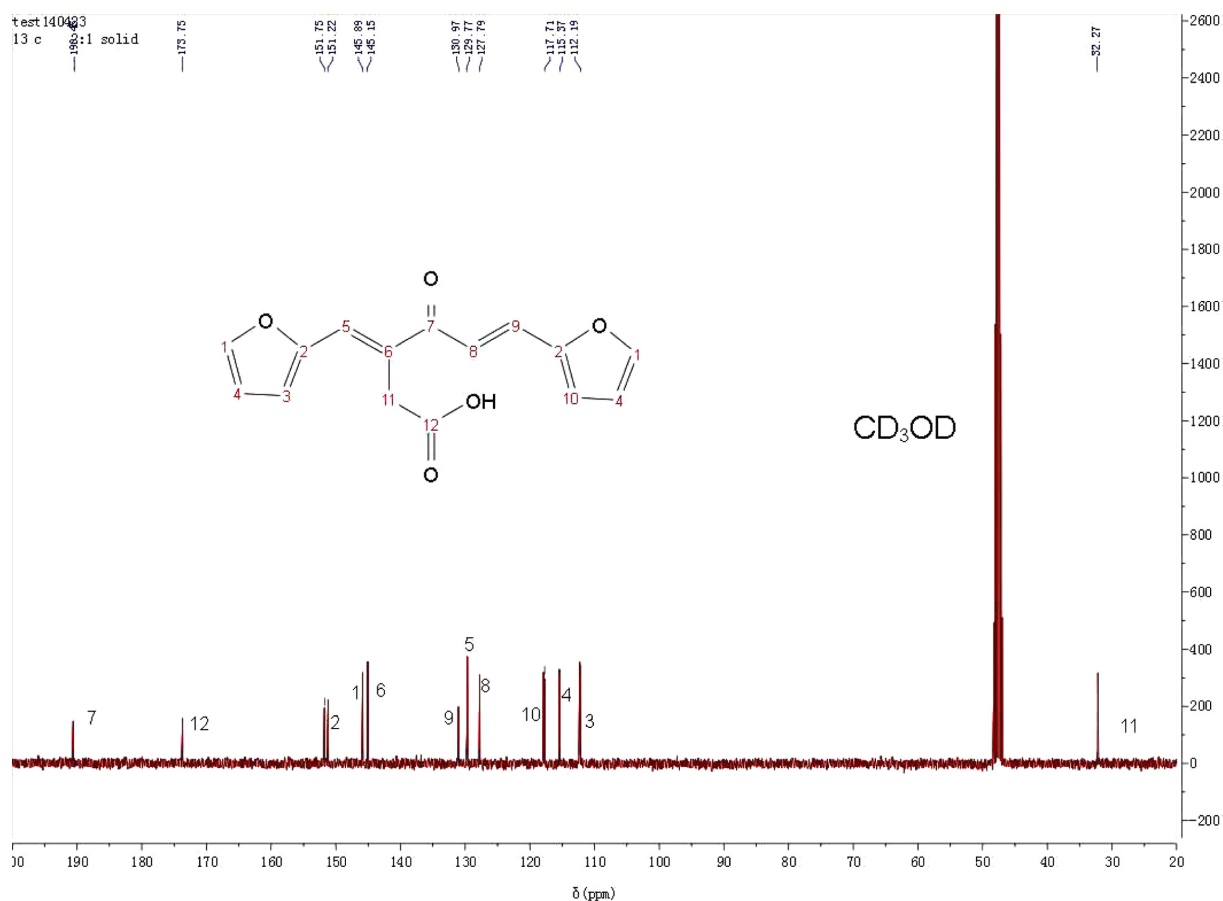
**Fig. 4.** $^{13}$C NMR profile of F$_2$E in CD$_3$OD. Reaction conditions: 323 K, 0.06 mol FA, 0.03 mol EL (-molar ratio of EL/FA 2:1), 0.06 mol KOH, 50 ml H$_2$O.
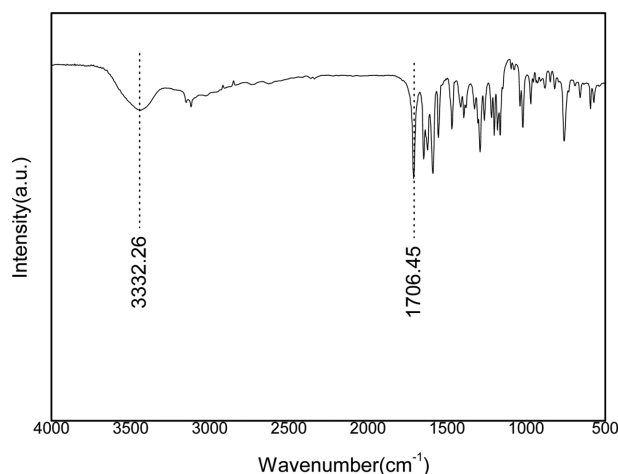


**Fig. 5.** FT-IR spectra of F$_2$E. Reaction conditions: 323 K, 0.06 mol FA, 0.03 mol EL (molar ratio of EL/FA 2:1), 0.06 mol KOH, 50 ml H$_2$O.
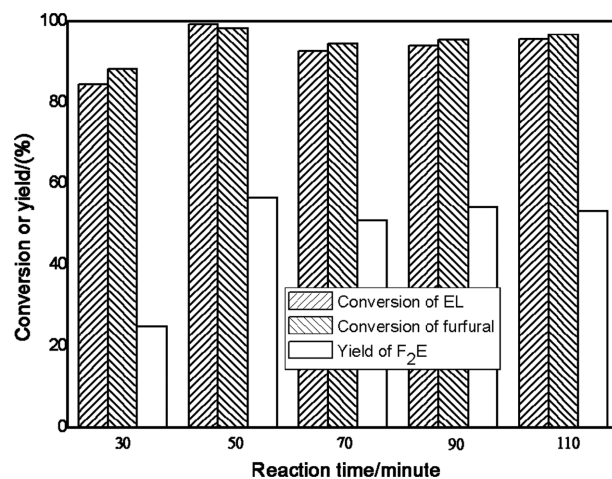


**Fig. 6.** Effect of reaction time on condensation of EL and FA over KOH catalyst. Reaction conditions: 323 K, 0.06 mol FA, 0.03 mol EL (molar ratio of EL/FA 2:1), 0.06 mol KOH, 50 ml H$_2$O.

tion solution was light brown when temperature was 303 K, but with increasing the temperature the solution color deepened to dark brown when the temperature rose to 323 K and above. Obviously, this condensation could take place with gaining high target product yield at the mild temperature of 323 K.

Considering the insolubility of some intermediates in water hav-

ing a negative impact on the targeted product, we further investigated the influence of solvent on this process and the results are given in Fig. 8. When using water as the solvent, the conversion of FA and EL was nearly complete and the F$_2$E yield presented as 56%. As 20% ethanol was mixed with water, both conversions were changed a little, but the target product was slightly reduced to 50%.
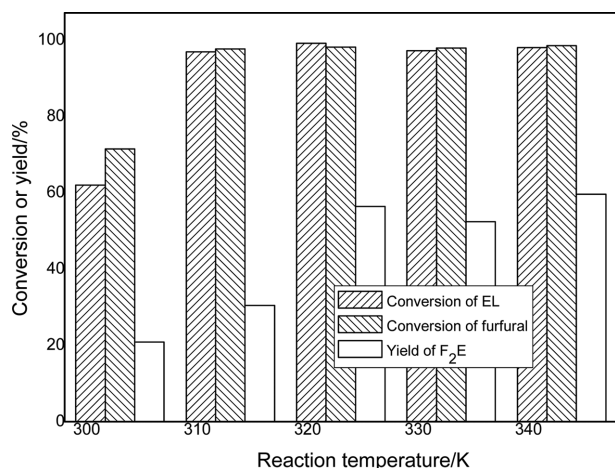
Fig. 7. Effect of reaction temperature on condensation of EL and FA over KOH catalyst. Reaction conditions: 50 min, 0.06 mol FA, 0.03 mol EL (-molar ratio of EL/FA 2:1), 3.36 g KOH, 50 ml $H_2O$.
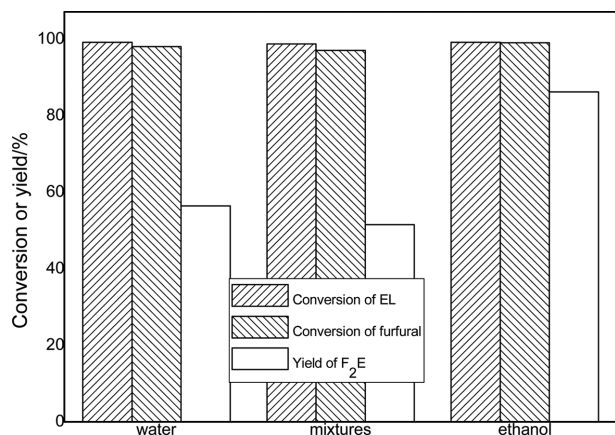


Fig. 8. Effect of solvent on condensation of EL and FA over KOH catalyst. Reaction conditions: 50 min, 0.06 mol FA, 0.03 mol EL (molar ratio of EL/FA 2:1), 0.06 mol KOH, 50 ml solvent for each reaction, mixtures=water/ethanol (volume ratio 4:1).

However, as the reaction proceeded in ethanol, despite the conversions of feedstock being similar the yield of $F_2E$ was significantly increased to 90%. The higher $F_2E$ yield by using ethanol as the solvent is possibly due to the enhanced solubility of oily intermediates, which promotes transformation of such kind of intermediates to the dimer $F_2E$.

Aldol condensation of FA and EL is a typical base catalyzed process (Fig. 9). During this processing, OH⁻ released by base catalyst first attacks the α-H atom of EL to form $H_2O$ and the corresponding carbanion. Then the formed carbanion attacks the carbonyl group of FA molecule by coupling C-C bond, obtaining the relative carbanion intermediate. This intermediate captures H atom in $H_2O$ to form FE-OH and releases OH⁻. FE-OH then dehydrated to the monomeric FE product by forming the more stable, conjugated C=O and C=C bonds [25-28]. The targeted product $F_2E$ can be obtained after the monomer reacts with another FA using another α-H of EL by a similar procedure. During the condensation process, EL was hydrolyzed to
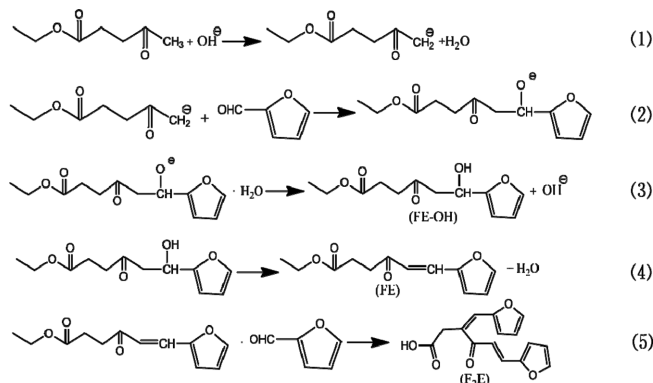


Fig. 9. Proposed mechanism for aldol condensation of FA and EL.

levulinic acid by removing the ester group, as indicated by the analyses of ¹³C NMR and FT-IR mentioned above.

### 3-2. Low temperature hydrogenation of $F_2E$

To improve the hydrodeoxygenation reaction at high temperature, pre-hydrogenation at low temperature for saturating the C=C and C=O bonds of $F_2E$ is necessary because the direct hydrodeoxygenation of pristine precursor at high temperature is prone to coking due to the active C=C and C=O bonds in the precursor [29,30]. The product of low temperature hydrogenation reaction is dark brown (Fig. 1). LC-MS result showed that the molecular ion peak of the hydrogenated product at 413 K presented 285 at 1.285 min (Fig. S3), which indicates that the molecular weigh of H-$F_2E$ is $C_{15}H_{24}O_5$ plus one hydrogen atom. The wide wavenumber of FT-IR centered at 1710 cm⁻¹ showed the existence of carboxylic acid and ketone (Fig. 10). Meanwhile, the absorbencies corresponding to the unsaturated C=C bonds and furan groups disappeared, accompanied with the significantly enhanced peaks relative to the vibration of C-H bonds at 2800~3000 cm⁻¹, as comparing to the pristine $F_2E$ (Fig. 5). This indicates that the unsaturated C=C bonds of $F_2E$ were hydrogenated to form more C-H bonds. We further used ¹³C NMR technology to analyze the structure of H-$F_2E$ (Fig. 11). The peaks at 28, 31, 37, 67, 76
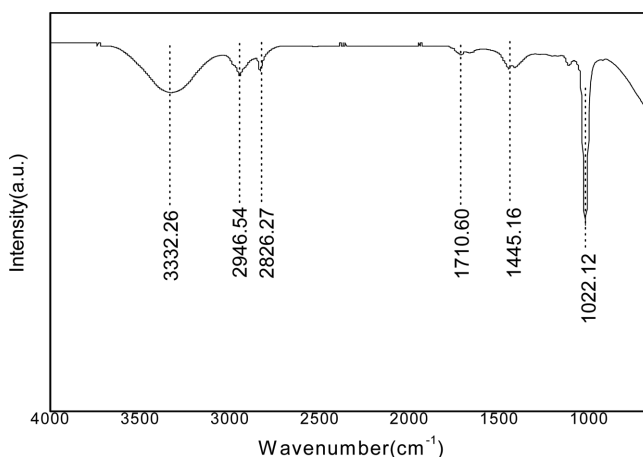


Fig. 10. FT-IR spectra of H-$F_2E$. Reaction conditions: 413 K, 0.5 g of 5% Pd/C catalyst, 0.02 mol $F_2E$ and 50 ml methanol, 3 Mpa $H_2$.
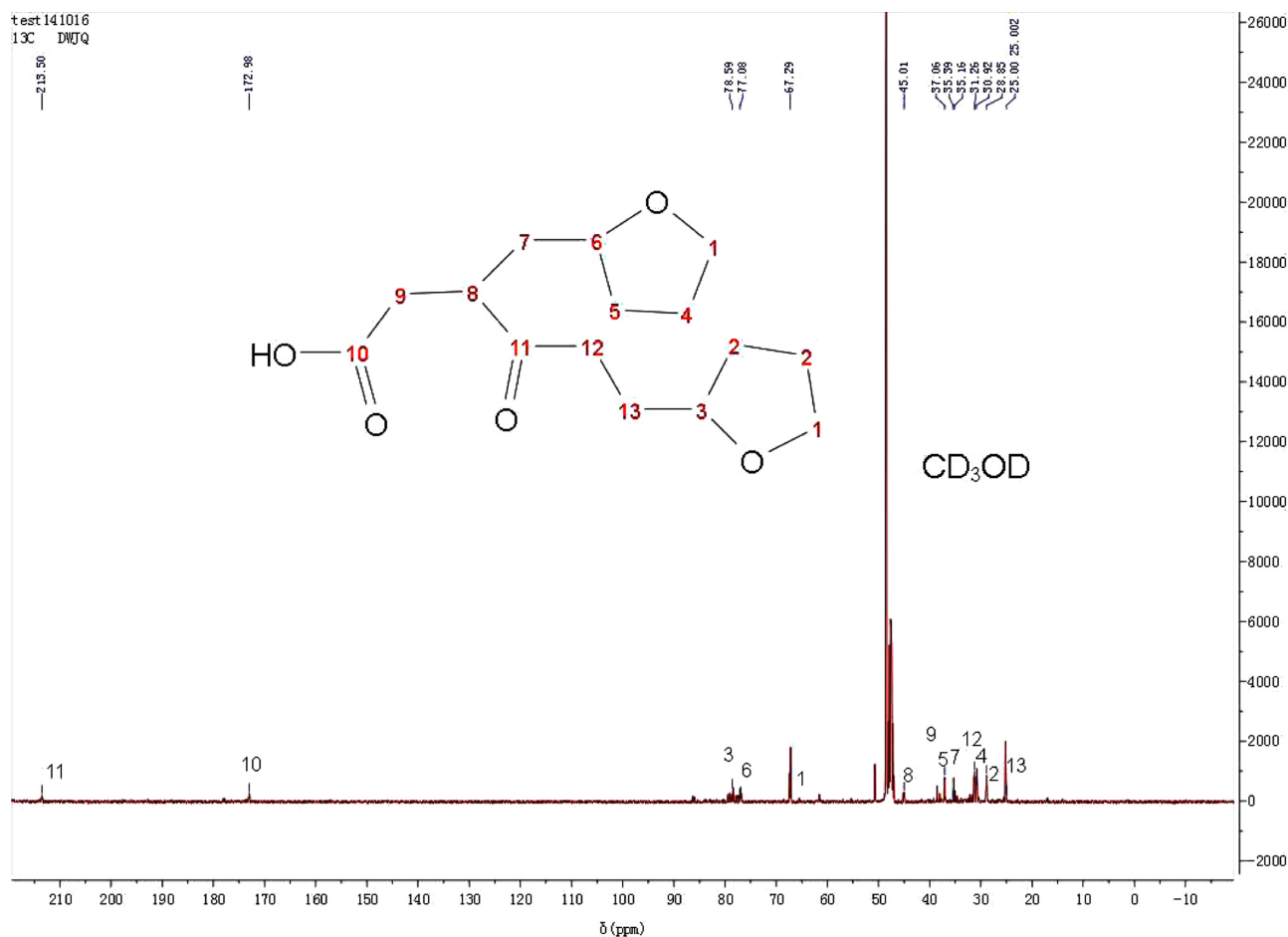
**Fig. 11.** $^{13}$C NMR analysis of H-F$_2$E in CD$_3$OD. Reaction conditions: 413 K, 0.5 g of 5% Pd/C catalyst, 0.02 mol F$_2$E and 50 ml methanol, 3 Mpa H$_2$.

and 78 ppm were assigned to the carbon atoms of terahydrofuran ring, showing that the C=C bonds in furan rings of F$_2$E was hydrogenated to the saturated C-C bonds. The conjugated C=C bonds of F$_2$E were also hydrogenated by the observation peaks at 24, 31, 35, 44 ppm. Obviously, the C=C bonds of F$_2$E could be easily hydrogenated by using Pd/C catalyst under mild reaction conditions, remaining ketone and carboxylic groups in H-F$_2$E.

We used $^{13}$C NMR technology to analyze the product structure obtained by different hydrogenation temperature (Fig. 12). C=C bonds in the straight chain were hydrogenated completely and C=C bonds of furan ring were hydrogenated partly at 383 K. When the temperature was above 413 K, the C=C bonds of furan ring were completely hydrogenated (Fig. 13), while C=O bonds still were not hydrogenated, indicating that C=C bonds hydrogenation was easier than C=O bonds hydrogenation. This result was consistent with the previous report by Ryan [31].

Fig. S5 shows the XRD pattern of Pd/C catalysts. It can be seen that the catalyst exhibited a broad peak in the range of 15°~30°, which belongs to the amorphous carbon. No diffractions relative to Pd were observed, indicating high dispersion of Pd particles on amorphous carbon surface. Textural properties of Pd/C catalyst are shown in Fig. S6 and Table S1. The nitrogen adsorption desorption isotherm curves belonged to a typical IV style. The Pd/C catalyst possessed high surface area, large mesoporous volume and size as well as the high dispersion of Pd particles, showing the suitable performance for F$_2$E hydrogenation to H-F$_2$E by saturation of C=C bonds. This hydrogenation pre-stabilization is necessary to improve efficiency for subsequent hydrodeoxygenation at high temperature because of removal of active unsaturated group in F$_2$E [17, 32].

## 4. Conclusions

A new jet fuel precursor of branched and oxygenated C$_{15}$ structure was successfully prepared by aldol condensation of fully renewable biomass-derived FA and EL. KOH was proposed as an efficient base catalyst for obtaining the C$_{15}$ precursor with yield of 56% at mild reaction condition. For stabilizing this kind of precursor by saturating the C=C and C=O bonds in molecule, the hydrogenation pretreatment was implemented with Pd/C catalyst at mild reaction condition. This stabilization pretreatment of precursor is highly desirable for improving the efficiency of the sequential hydrodeoxygenation to branched hydrocarbon fuel at harsh reaction conditions. This technology provided the potential for producing lignocellulosic biomass derived jet fuel by a simple route with less steps, considering
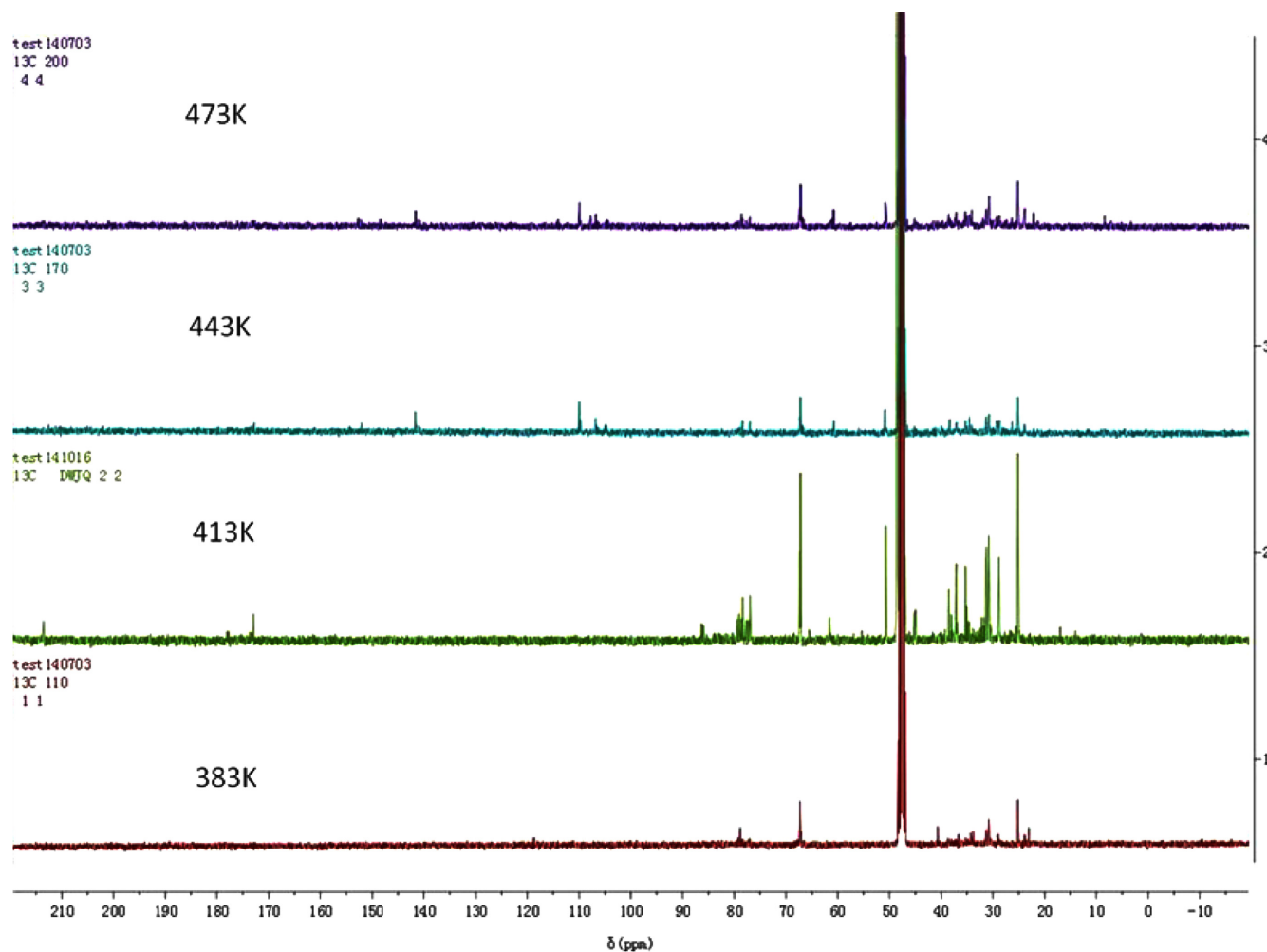
**Fig. 12.** $^{13}$C NMR analysis of H-F$_2$E in CD$_3$OD with different temperature. Reaction conditions: 0.5 g of 5% Pd/C catalyst, 0.02 mol F$_2$E and 50 ml methanol, 3 Mpa H$_2$, 6 h.
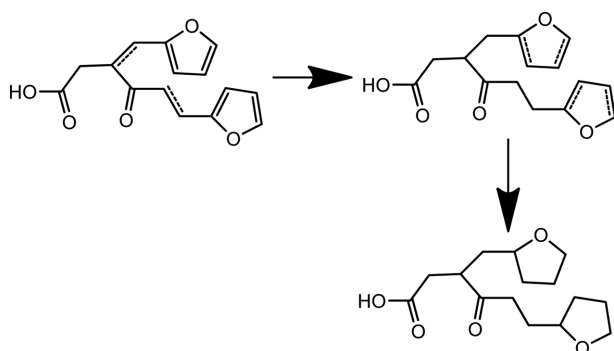


**Fig. 13. Main step of H-F$_2$E formation from low temperature hydrogenation.**

the easy gain of FA and EL, which are directly produced by biomass hydrolysis and sugars dehydration.

## Associated Content

**Supporting information:** Simulated $^{13}$C NMR spectra of F$_2$E and H-F$_2$E; TGA of F$_2$E; LC-MS analysis of H-F$_2$E; textural properties and XRD pattern of Pd/C catalyst.

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