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Journal Name

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## Efficient Synthesis of Biofuel Precursor with Long Carbon Chains from Fructose†

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Long carbon biofuel precursors were efficiently synthesized by Aldol condensation of furans (furfural, 5-ethoxymethylfurfural, 5-hydroxymethylfural) and its derivatives (levulinic acid, ethyl levulinate) which were co-produced by fructose transformation in ethanol with using acidic metal salt catalysts. High yields of furans and derivatives were obtained and the mole ratios of them were ingeniously adjusted. The effect of reaction time, temperature and water content on the mole ratios of furans and its derivatives were investigated in detail. Condensation reaction was conducted directly when the mole ratio of furans and its derivatives was located in the range of 1 to 2. The results showed that as high as 91.6 % of total mole yield of furans and its derivatives could be obtained after fructose alcoholysis at 413 K for 2.0 h with using  $\text{Fe}_2(\text{SO}_4)_3$  catalyst. After that, Aldol condensation of produced furans and derivatives with the mole ratio of 1.9 and 1.1 were directly conducted using NaOH as the catalyst and 91.2 % and 89.1 % yields of precursors were gained respectively. This technical route indicates a simple and feasible method to produce renewable long carbon biofuel from biomass.

### Introduction

Compositional changes to the atmosphere are embodied in the disequilibrium of our environment due to anthropogenic emissions.<sup>1</sup> Moreover, some conventional long carbon fuels are derived from the sharply depleting fossil fuel. Therefore, it is urgent to exploit a new route for producing fuel from renewable biomass to substitute those originated from fossil fuels. Although short chain hydrocarbon fuels could be achieved from various platform chemicals derived from biomass directly, the formation of long carbon biofuels further need C-C coupling between key platform chemicals over acid/base catalysts.<sup>2-4</sup> Meanwhile, the involved oxygen atoms of precursors should be removed from condensed compounds by hydrodeoxygenation when used as transportation fuels.<sup>5-7</sup>

In recent years, the routes to long chain biofuels by using biomass include two methods. One is that conversion of biomass to syngas and then using Fischer Tropsch synthesis.<sup>8</sup> But the structure of these synthesized products are almost confined with straight chains. Another one is that conversion of biomass to platform chemicals (furans and derivatives) and then condensation by C-C coupling.<sup>9</sup>

Furfural (FA) and 5-hydroxymethylfural (5-HMF) are the most important furan compounds,<sup>10, 11</sup> and they can be derived into 5-methylfurfural (5-MF), 2-methylfuran (2-MF), levulinic acid (LA) and angelica lactone (AL). In fact, all of these compounds could be selected as feedstock to prolong carbon chains by C-C couplings. Fu and her team reported that the fuel precursors with  $\text{C}_{10}$ - $\text{C}_{14}$  could be easily obtained through direct self-coupling of FA and 5-MF under mild conditions in water.<sup>12</sup> After hydrodeoxygenation, straight or branched  $\text{C}_8$ - $\text{C}_{14}$  alkanes of diesel ranged fuels were obtained in moderate to high yield. Corma also reported that high-quality diesel fuel could be achieved by 2-MF and 6-butylundecane condensation followed by hydrodeoxygenation, obtaining an overall yield of 87 %.<sup>13</sup> Nearest investigation found that C-C bond could be formed between AL through free radical reaction at mild conditions without using noble catalyst and solvent, which gave the carbon chain prolonged products with 10 or 15 carbons with complete conversion and 100 % selectivity.<sup>14</sup>

Actually, cross condensation was the most common style in the carbon chain prolonging reaction. FA and 2-MF could be condensed efficiently over sulfonic acid catalyst under solvent-free conditions.<sup>15</sup>  $\text{C}_8$  and  $\text{C}_{13}$  alkane precursors could be achieved through furfural and acetone by Aldol condensation over base catalyst in aqueous system, and the selectivities of n-alkanes were higher than 50 % through hydrodeoxygenation.<sup>16</sup> 2-MF with acetone and butanal could also be investigated over a series of solid acid catalysts, and evidently higher carbon yields to diesel were obtained when hydroxyalkylation/alkylation product of 2-MF with butanal were used as the feedstock.<sup>17</sup>

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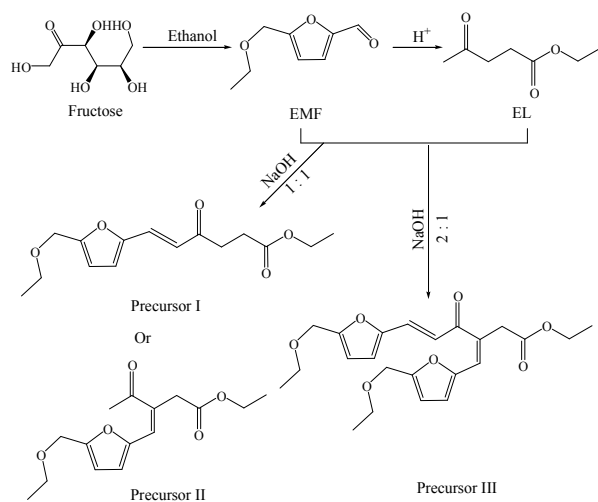
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† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x

Although long chain hydrocarbons (C<sub>8</sub>-C<sub>15</sub>) could be achieved from those feedstock and condensation routes mentioned above, the feedstock adopted in present investigations were still only depended on model chemicals (those chemicals like acetone could not be obtained from biomass easily with high yields) and the main work was focused on hydrodeoxygenation by choosing catalysts. The directions on how to efficiently use biomass and achieve precursors with high yield are neglected largely. Therefore, it was high time to find new substrates and use simple synthesis route to obtain precursors with long carbon chains for biofuel production economically.

Fructose is an important carbohydrate in the conversion of biomass to furan chemicals and its derivatives. Much more investigations about furan compounds and levulinate esters production from fructose have been reported in recent years. The highest 5-ethoxymethylfurfural (EMF) yield of 71.2 % was obtained directly from fructose through a one-pot reaction over AlCl<sub>3</sub>.<sup>18</sup> By controlling reaction conditions, high 5-HMF and EL yields of up to 89 % and 86 % were achieved from fructose, respectively.<sup>19</sup>

Herein, we used fructose as raw material to produce furan compounds (FA, 5-HMF and EMF) and its derivatives (LA and EL) by one-pot conversion. According to the mechanism of Aldol condensation, there are two carbon active sites in furans derivatives formed under alkaline conditions at most. Therefore, only one or two aldehyde carbons of furans could be interlinked with active carbons by C-C coupling.<sup>20, 21</sup> In this paper, furans and derivatives mixture with proper mole ratios from fructose decomposition directly were then used as the feedstock to gain long-chained precursors by Aldol condensation. When the mole ratio of furans with derivatives located in 1 to 2, green Adol condensation would be carried out with completing conversion of furans and derivatives. Due to the majority components of alcoholysis products were EMF and EL (Fig. S1), the main condensation scenario was proposed in Fig. 1. Meanwhile, tiny amounts of FA and 5-HMF could also be condensed with LA and EL respectively over base catalyst. Finally, carbohydrate fuel precursors with different carbon chains were achieved by condensation.



**Fig. 1** Proposed main reaction routes from fructose to long carbon fuel precursors.

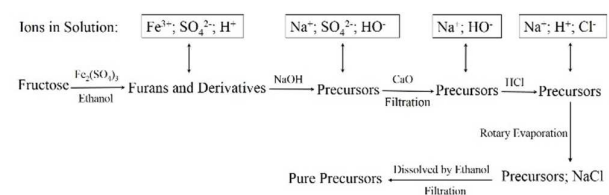
## Experimental section

### Materials

Fructose (purity > 99 %) was purchased from MYM Biological Technology Company Limited; H<sub>2</sub>SO<sub>4</sub>, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, ZnSO<sub>4</sub>, NaH<sub>2</sub>PO<sub>4</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (purity > 99 %) were all bought from Damao chemical reagents company, China; C<sub>2</sub>H<sub>5</sub>OH (purity > 99 %) and NaOH (purity > 96 %) were bought from Guangdong Guanghua Sci-Tech Co. Ltd. China.

### General reaction procedure

The detail procedures on experiment were shown in Fig. 2. 2.0 g fructose, 0.2 g Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and 50 mL ethanol were putted into slurry bed successively. And then, reaction system was heated to expectant temperature for a certain time. After that, the reaction was halted and cooled down to room temperature by cold water. At this time, the main components of products were furan compounds and ethyl levulinate (Fig. S1). Sodium hydroxide was added into mixed solution directly to induce condensation reaction at 373 K for 4.0 hours. Afterwards, calcium oxide powders were introduced into solution to remove Fe<sup>3+</sup> and SO<sub>4</sub><sup>2-</sup> followed by filter step. After that, the pH value of filtrate was adjusted to 5.0 with chlorine hydride. The final filtrate was concentrated by rotary evaporation and vacuum dried at 323 K overnight. And then, the residual solid was dissolved with ethanol and filtered again to remove sodium chloride. Finally, the pure ethanol solution of precursors was achieved.



**Fig. 2** Schemes on the achievement of pure precursors from fructose.

### Analytic methods

The analysis of alcoholysis products was performed on an Agilent GC-7890A gas chromatograph (HP Innovax capillary column 19091N-133N, 30 m × 250 μm × 0.25 μm) with external standard method. The column temperature was hold at 323 K for 2 minutes and then heated by temperature programming at the rate of 283 Kmin<sup>-1</sup> to 523 K holding for 3 minutes. At the same time, the conversion of substrates before and after condensation were evaluated on the Agilent GC-7890A gas chromatograph either. The conversion of fructose was detected by HPLC (Waters 2695) with a SH1011 column (8.0 × 300 mm, 6 μm particle size, Waters) held at 323 K, using 5mM H<sub>2</sub>SO<sub>4</sub> as the mobile phase (0.5 mLmin<sup>-1</sup>) through external standard method. The composition of precursor was analyzed by elemental analyzer (vario EL III). Because of the

viscosity of condensed product at the mole ratio of 1.1, the substrate was first dissolved by methanol, and then  $^{13}\text{C}$  Chemical shifts were measured by nuclear magnetic resonance scanner (Bruker Advance 400 III) with DMSO solvent (100 MHz). The relevant calculation of conversion, yield of products and mole ratio were as the following formulas:

$$\text{Conversion \%} = \frac{n_0 - n_l}{n_0} \times 100\% \quad (1)$$

$$\text{Mole Yield \%} = \frac{n_l}{n_0} \times 100\% \quad (2)$$

$$\text{Mole Ratio} = \frac{\sum n_i}{\sum n_j} \quad (3)$$

$$\text{Yield of Precursor} = \frac{m_{\text{precursor}}}{\sum m_k} \times 100\% \quad (4)$$

For the conversion calculation,  $n_0$  and  $n_l$  are the initial and final mole content of feedstock before and after reaction. Meanwhile,  $n_0$  in mole yield calculation was the same meaning as in (1),  $n_i$  was the mole content of each product respectively. When the mole ratios of furans and its derivatives was adjusted in the optimize ranges, the ratios were calculated according to (3).  $n_i$  represented the mole content of FA, EMF and 5-HMF, and  $n_j$  represented the mole content of EL and LA, respectively. Finally, the yield of precursor was evaluated basing on the formula (4), in which  $m_k$  was the mass of FA, EMF, 5-HMF, EL and LA.

## Results and discussion

### Effect of different catalysts on fructose alcoholysis

**Table 1** Conversion of fructose into key platform chemicals over different catalysts

Entry	Catalysts	Conversion / %	Mole Yield / %					pH	Mole Ratio
			FA	EMF	5-HMF	EL	LA		
1	$\text{Fe}_2(\text{SO}_4)_3$	100	0.5	49.9	0.9	21.3	1.0	3.5	2.3
2	$\text{Al}_2(\text{SO}_4)_3$	100	0.6	47.6	0.5	19.8	0.6	4.0	2.4
3	$\text{H}_2\text{SO}_4$	100	0.4	5.3	-	53.6	1.0	3.0	0.1
4	$\text{ZnSO}_4$	82.3	0.24	7.8	25.3	1.6	-	5.5	20.6
5	$\text{NaH}_2\text{PO}_4$	8.6	0.36	-	8.2	-	0.5	6.0	16.4

Reaction conditions: 5 % fructose; 413 K; 50 mL ethanol; 1.0 h, 0.2 g catalyst.

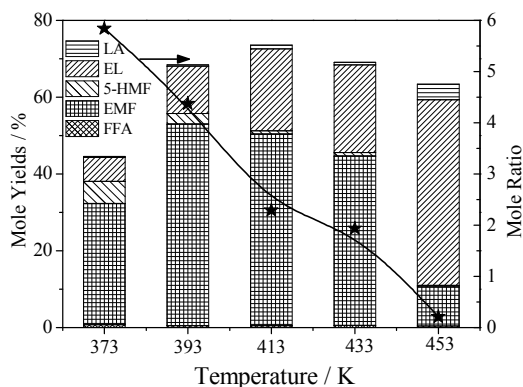
investigation to convert fructose into EMF mixed with EL in ethanol solution.

### Effect of temperature on fructose alcoholysis

The reaction was carried out at different temperatures from 373 to 453 K. The results for the conversion of fructose are summarized in Fig. 3. A significant effect of reaction temperature on products distribution had been observed. An increase in the reaction temperature improved the EL yield as a result of decreasing the EMF yield. That is because the improvement of temperature could also promote the

decomposition of EMF to EL. At 373 K, much more 5-HMF and EMF were detected, and this temperature was in favor of 5-HMF etherification to EMF. But the total mole yields of furan compounds and its derivatives was only up to 44.6 %, let alone the adjustment of mole ratios. At 413 K, EMF and EL were observed as the main components of mixed products, and it gave very high total mole yield for furan compounds and its derivatives (73.6 %). Meanwhile, basing on the ideal mole ratios for Adol condensation in Fig 1, the mole ratio of furans and its derivatives under 413 K was about 2.3, which was only one step away from 2 : 1. Therefore, different reaction time were optimized next to achieve this conceive. Fructose is a more efficient and selective substrate than other carbohydrates in the synthesis of furan compounds over acid catalysts.<sup>22</sup> Thus, we adopted several simple mineral acids to convert fructose into furan compounds and its derivatives, and the results are listed in Table 1. According to the results,  $\text{Fe}_2(\text{SO}_4)_3$  had obvious effect on the conversion of fructose into furan compounds and its derivatives. EMF and EL were the main products and the total mole yield was up to 71.2 % after feedstock was complete converted in ethanol. Meanwhile, other furans and its derivatives, for example, FA, 5-HMF and LA were accompanied by alcoholysis with less mole yields. The catalytic behavior of  $\text{Al}_2(\text{SO}_4)_3$  was similar to that of  $\text{Fe}_2(\text{SO}_4)_3$ . Usually, fructose is dehydrated to 5-HMF catalyzed by protons generated from hydrolysis/alcoholysis of  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$ . And then, 5-HMF is decomposed to EL in the presence of ethanol catalyzed by the protons.<sup>23</sup> Although the lowest pH value of  $\text{H}_2\text{SO}_4$  was detected as 3.0 in ethanol, less total mole yields of 63.4 % of furans and the derivatives were achieved. Moreover, majority products in the final mixed system were EL and LA (86.1 %). This result indicated that stronger proton acid could be propitious to dehydration of fructose, forming EL and LA. But humins were inevitable produced under stronger proton acid condition, resulting in less yields of furans and its derivatives. According to the pH value sequence of different catalysts in ethanol solution, weaker proton acids were hard to dehydrate 5-HMF to LA. Meanwhile, undesired humins were difficult to be produced under such reaction conditions. For example, 49.9 % and 47.6 % mole yields of EMF were achieved respectively over  $\text{Fe}_2(\text{SO}_4)_3$  (pH = 3.5) and  $\text{Al}_2(\text{SO}_4)_3$  (pH = 4.0). Lower pH value of  $\text{Fe}_2(\text{SO}_4)_3$  ethanol solution was found comparing with that of  $\text{Al}_2(\text{SO}_4)_3$ , which might enable  $\text{Fe}_2(\text{SO}_4)_3$  to alcoholize more protons to promote the dehydration of fructose to 5-HMF and its subsequent conversion to EL little more efficiently than that of  $\text{Al}_2(\text{SO}_4)_3$ . Therefore,  $\text{Fe}_2(\text{SO}_4)_3$  was adopted in our following

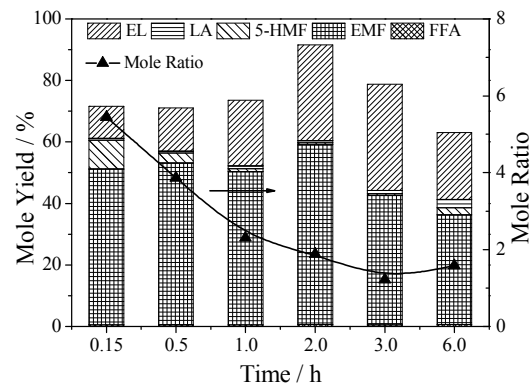
Hence, the optimum temperature was set to 413 K for the highest yield of furan compounds and its derivatives.



**Fig. 3** Effect of reaction temperature on the products distribution and mole ratio. Reaction conditions: 5 % fructose; 50 mL ethanol; 0.2 g  $\text{Fe}_2(\text{SO}_4)_3$ ; 1.0 h.

#### Effect of time on fructose alcoholysis

Basing on the optimization of catalyst and reaction temperature, a typical time profile for the alcoholysis of fructose is depicted in Fig. 4. High fructose conversion of 100 % was achieved only within 0.25 h in ethanol solution over  $\text{Fe}_2(\text{SO}_4)_3$  catalyst. It could be seen that reaction time had little effect on the total mole yields of furans and its derivatives. Moreover, EMF and EL were predominant products when reaction time was prolonged from 0.25 h to 6.0 h. Water could be produced during dehydration of fructose, ethanol to diethyl ether, and EL production by EMF dehydration, but it was proposed to show that tiny amounts of water could not play an essential role in hindering furans further hydrolysis.<sup>24</sup> Thus, the highest total mole yield is achieved after fructose is alcoholized for 2.0 h, and the value could reach 91.6 %. Simultaneously, the value of mole ratio (1.9) in this case was located in 1 to 2, which met the initial objective for synthesis of long carbon chain precursors. Therefore, 2.0 h was the optimal reaction time. However, undesired humins and other byproducts appeared during prolonged alcoholysis process, resulting in the decrease of total mole yield of furans and its derivatives.<sup>25</sup>



**Fig. 4** One-pot alcoholysis of fructose at different time. Reaction conditions: 5 % fructose; 413 K; 50 mL ethanol; 0.2 g  $\text{Fe}_2(\text{SO}_4)_3$ .

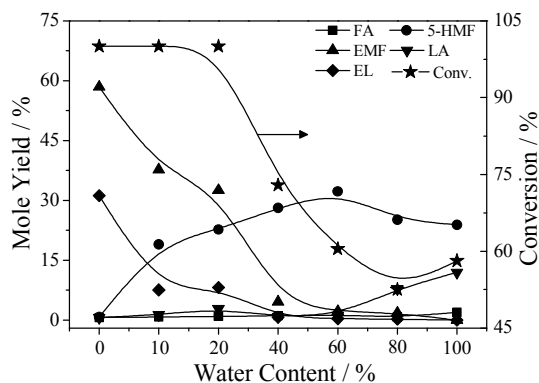
#### Effect of water percentage on fructose alcoholysis

Water is not only a solvent in this system, but also a product for the alcoholysis procedure. Previous investigations had suggested that the presence of enough water would also enhance the rehydration of 5-HMF to LA and formic acid.<sup>26</sup> Thus, the effect of different water content in this system was investigated and the results are shown in Fig. 5.

Obviously, a great deal of furans were detected in ethanol/water system when water content was only 10 %, and this result was in accord with the previous investigation.<sup>24</sup> 5-HMF was esterified fast after dehydration of fructose, resulting in the large amount of EMF. However, esterification was inhibited sharply when water content was up to 40 %, leading to the increase of 5-HMF existence in system. Interestingly, an increase of LA happened only when water content is at a certain percentage (60 %). Moreover, fructose conversion was decreased gradually when water content was increased. According to these results, it indicated a conclusion that water not only shifts the equilibrium to products but also affects the rate of the hydrolysis reaction.

Because of furans and its derivatives disproportionality, the mole ratio was not located in the ideal range (1 - 2) due to plenty of furans existence. However, large amount of LA production after adding 60 % water was beneficial to reduce the value of mole ratio. Although mole ratios could be adjusted by changing the percentage of water, the total mole yields of furan and its derivatives were lower than that of pure ethanol system obviously. Such as the results of alcoholysis in ethanol (91.6 %) and water (37.7 %).





**Fig. 5** Effect of water on the distribution of alcoholysis products variation. Reaction conditions: 5 % fructose; 413 K; 2.0 h; 0.2 g  $\text{Fe}_2(\text{SO}_4)_3$ .

### Condensation reactions in ethanol system

According to the mechanism of condensation and previous investigation,<sup>16</sup> NaOH was adopted to catalyze furans and its derivatives to form long carbon chains compounds. Here, we presented the condensation results of furans and its derivatives when mole ratio were 1.9 and 1.1, which were achieved after fructose was alcoholized in pure ethanol for 2.0 and 3.0 h over  $\text{Fe}_2(\text{SO}_4)_3$ . As reported in reference 20, the condensed products at the mole ratio of 1:1 could be further condensed by self-Michael additions, as well as other Aldol-adduct, resulting in furanic-keto acid polymer over strong base catalyst for a long time (48 h)<sup>20</sup>. We thought that the mole ratio had something to do with self-Michael additions, unnecessary long reaction time. That is, not only reaction time but also mole ratio effected the final condensed product components. After that, condensation was conducted in ethanol system directly after fructose was alcoholized completely. In these two systems, the mole yields of FA, 5-HMF, EMF, LA and EL were 0.7 %, 0.3 %, 45.9 %, 0.9 % and 41.9 % when the mole ratio was 1.1, and when the mole

ratio was 1.9, they were 0.6 %, 0.8 %, 58.4 %, 0.6 % and 31.2 % respectively.

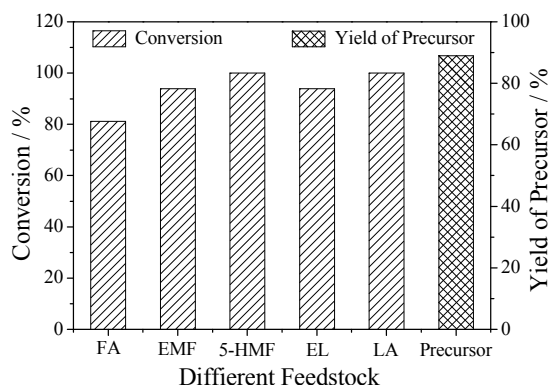
The results after condensation showed that fructose was highly efficient converted into furans mixed with its derivatives. Traces of furans and EL were detected in ethanol system (Fig. 6 and Fig. 7) after reaction. That is to say, the condensation could be more efficiently conducted in alcohol system comparing to previous investigations.<sup>16</sup> High yield values of final precursors were achieved at 89.1 % and 91.2 % when the mole ratio were 1.1 and 1.9. In fact, two main ideal reaction processes were as follows in Fig. 1. Precursor I, precursor II and precursor III were selectively produced respectively by changing the mole ratio of EMF and EL in the same system. Although other furan chemicals and derivatives like FA, 5-HMF and LA are co-produced simultaneously, all of them were also the feedstock of condensation.<sup>12, 16</sup> Moreover, our results suggested that two reaction routes were conducted at the same time in despite of mole ratio was 1.1. Under this condition, the final precursor was mixture, and this conclusion was approved by <sup>13</sup>C NMR. Comparing chemical shifts of synthesized precursors with theoretical precursors (Fig. S2, S3, S4, S5, S6 and S7), it revealed that cross condensation and different feedstock are the effect factors on precursor components.<sup>27</sup> Meanwhile, further condensed products formed by self-Michael additions were not observed. It suggested that shorter condensed time could not induce self-Michael additions. The carbon prolonging style was only the Adol condensation at the mole ratio of 1.1 in shorter reaction time (4.0 h).

However, the condensed routes basing on the mole ratio of 1.9 were composed of Adol condensation and self-Michael additions. The <sup>13</sup>C NMR results showed that mixed precursors were achieved when the mole ratio of furans with derivatives was 1.9 (Fig. S8). Polymer was formed under proper higher mole ratio condition even if shorter reaction time. Therefore, we could conclude that the mole ratio of furans with its derivatives effected the condensation style and controlled the length of carbon chains of precursors.

**Table 2** Element composition analysis of precursors.

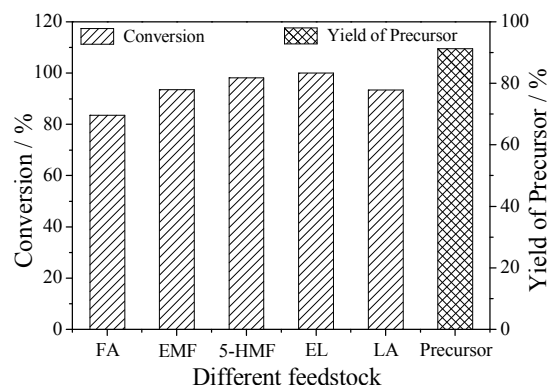
Precursor <sup>a</sup>	Element Content / %			Precursor <sup>b</sup>	Element Content / %		
	C	H	O		C	H	O
Precursor <sup>a</sup>	60.7	6.8	32.3	Precursor <sup>b</sup>	64.6	5.4	30.0

Precursor <sup>a</sup> and Precursor <sup>b</sup> were produced when the mole ratio of furans and its derivatives were 1.1 and 1.9 respectively.



**Fig. 6** Conversion of furans and its derivatives, and the yield of precursor after condensation. Reaction conditions: 373 K; 4.0 h; 0.4 g NaOH; Furans and its derivatives are alcoholized from fructose in pure ethanol for 3.0 h over  $\text{Fe}_2(\text{SO}_4)_3$  and the mole ratio was 1.1.

Basing on the results of element analysis of precursors (Table 2), the final Precursor<sup>a</sup> was composed of only C, H, O and the molecular formula was  $\text{C}_{5.1}\text{H}_{6.8}\text{O}_{2.0}$  in short. In fact, theoretical molecular formulas of precursor I, II and III were  $\text{C}_{15}\text{H}_{21}\text{O}_5$ ,  $\text{C}_{15}\text{H}_{21}\text{O}_5$  and  $\text{C}_{23}\text{H}_{30}\text{O}_8$  respectively. In order to compare the components differences of actual with theoretical products, theoretical molecular formulas were changed into  $\text{C}_{6.0}\text{H}_{8.5}\text{O}_{2.0}$ ,  $\text{C}_{6.0}\text{H}_{8.5}\text{O}_{2.0}$  and  $\text{C}_{5.8}\text{H}_{7.5}\text{O}_{2.0}$  according the oxygen content in actual condensed product. This result indicated that much more  $-\text{CH}_2\text{CH}_3$  functional groups in synthesized esters might be dissociated from precursors during condensation, resulting in the decrease of carbon and hydrogen number. The element content results of precursor<sup>b</sup> showed that the molecular formula was  $\text{C}_{5.7}\text{H}_{5.8}\text{O}_{2.0}$  in short. The C relative content in precursor<sup>b</sup> was higher than that in precursor<sup>a</sup> ( $\text{C}_{5.1}\text{H}_{6.8}\text{O}_{2.0}$ ). Meanwhile, the lower H relative content in precursor<sup>b</sup> indicated that polymer was formed by self-Michael additions, resulting in longer carbon chains (Fig. S8).<sup>20</sup> Comparing with theoretical molecular formulas of precursor I, II ( $\text{C}_{6.0}\text{H}_{8.4}\text{O}_{2.0}$ ) and III ( $\text{C}_{5.8}\text{H}_{7.5}\text{O}_{2.0}$ ), it also suggested that some  $-\text{CH}_2\text{CH}_3$  functional groups could be also dissociated from precursors during condensation under strong base condition.



**Fig. 7** Conversion of furans and its derivatives, and the yield of precursor after condensation. Reaction conditions: 373 K; 4.0 h; 0.4 g NaOH; Furans and its derivatives are alcoholized from fructose in pure ethanol for 2.0 h over  $\text{Fe}_2(\text{SO}_4)_3$  and the mole ratio was 1.9.

## Conclusions

Long carbon biofuel precursors were efficiently synthesized by condensation from fructose. Furans and its derivatives could be co-produced at the high yield of 91.6% after fructose alcoholysis. Reaction time, water content and temperature had obvious effect on the yields and mole ratio adjustment of furans and derivatives. Condensation could happen when the mole ratio was adjusted at the range of 1 to 2. Meanwhile,  $-\text{CH}_2\text{CH}_3$  functional groups in ester were dissociated accompanying condensation under strong base condition. Two Adol condensation styles were conducted simultaneously even if the mole ratio was 1.1, resulting in the complex composition of final precursors. However, the condensed route basing on the mole ratio of 1.9 was composed of Adol condensation and self-Michael additions, resulting in polymer formation with different longer carbon chains.

## Acknowledgements

This work was supported by grants from the National High-Tech Research and Development Program (No.2012AA101806); the National Key Basic Research and Development Plan (No. 2012CB215304); the National Natural Science Foundation of China (No.51376185) and the Key Laboratory of Renewable Energy Open Foundation (NO. y407j51001).

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