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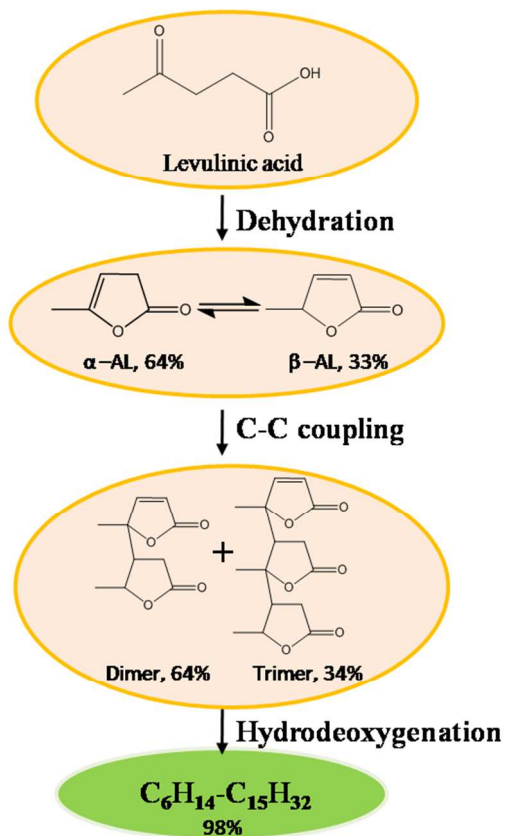
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C-C can be formed between biomass derived angelica lactones through free radical reaction at mild conditions without using solvent

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ARTICLE TYPE

## Formation of C-C Bonds for the Bio-alkanes Production at Mild Conditions

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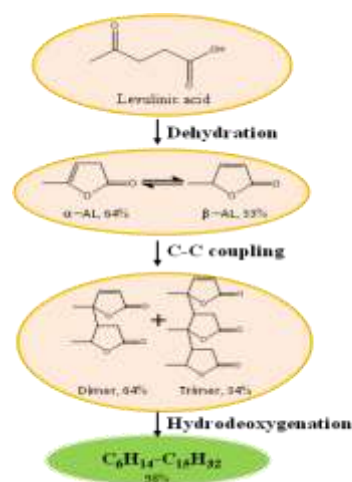
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It is of indispensable importance to form C-C bond between biomass derived compounds for the production of bio-alkanes from biomass. In this study, it was found that C-C can be formed between angelica lactones, a key intermediate derived from biomass through free radical reaction at mild conditions without using noble catalyst and solvent, which gave the carbon chain prolonged di/trimers with 10 or 15 carbons with complete conversion and 100% selectivity. The di/trimers produced serves as a novel feedstock for the carbon backbone of bio-alkanes. Hydrogenation of di/trimers produced C6-C13 hydrocarbons suitable for transportation fuels.

Biomass is regarded as a possible renewable resource for the fuels and chemicals. Current approaches for the conversion of biomass feedstocks into liquid fuels involve gasification to syngas followed by Fischer-Tropsch synthesis, thermal liquefaction and fermentation.<sup>1</sup> These approaches have one or more drawbacks including low fuel properties of products, low conversion, low heat value, long treatment time or high processing cost. Recently, acid hydrolysis to give sugars followed by aqueous-phase processing (APP) to liquid fuel attracted much interest.<sup>2-7</sup> The APP process can convert biomass-derived sugars into liquid fuels with an energy recovery as high as 96% and is believed to be a promising route for industry-scale technology.<sup>8</sup> However, the process needs sugars as the raw materials, the production of sugars is costly and sugars tend to produce dehydration products like hydroxymethylfurfural or humins in the presence of water and acid catalyst, thus decreases the yield of objective products.<sup>9-11</sup>

Furthermore, typical gasoline and diesel fuels are hydrocarbons with 6 to 13 carbons in length, while the major monomer building blocks of biomass are carbohydrates which have 5 or 6 carbons. In order to meet the required fuel specifications, new C-C bond has to be constructed between sugar, cellulose or hemicellulose derived furan compounds. Ketonization and aldol condensation are found to be effective for the purpose. However, ketonization has to be carried out at 623K and 5.7 MPa with Pd or Pt as the catalysts,<sup>12</sup> while aldol condensation needs a ketone as a reactant and low yield is always existed in this reaction.<sup>3, 13</sup>



**Scheme 1.** Reaction pathways for C-C formation between angelica lactone (AL) and the conversion of biomass into bio-alkanes.

In this respect, it is desired to develop an efficient process that can convert wide spreading biomass without extensive pre-treatment to liquid alkanes similar to those being used for many years from petroleum resources<sup>14-16</sup> and to design an effective C-C formation reaction between biomass derived compounds under mild conditions. Herein, we introduce an integrated process that converts commonly available biomass into gasoline ranged alkanes.<sup>17</sup> Strategies of this process are to form carbon-chain-prolonged oxygenated intermediates from functional chemicals produced from biomass, and then to remove the oxygen of intermediates by hydrodeoxygenation to produce gasoline-ranged liquid alkanes/aromatics. As show in Scheme 1, levulinic acid derived from biomass is dehydrated to angelica lactones (ALs), then ALs underwent C-C formation reaction to produce C10 or C15 lactones,<sup>18</sup> these lactones are finally deoxygenated to produce C6-C15 branched-chain alkanes as liquid fuels. In this process, free radical reaction was employed at mild reaction condition in the C-C formation step in high yield. No water or any other solvents are used in the process. Therefore, the reaction avoids the shortcoming of energy consumption during the removal of excessive water/solvents or heating up of the reaction mixture commonly employed in APP processes. Furthermore, AL, which has a double bond and lactone structure produced by dehydration of levulinic acid catalyzed by a solid acid catalyst,

can be used as a new platform chemical derived from commonly available biomass.<sup>19-21</sup>

## Experimental

### Catalyst Preparation

HCl, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaOH, H-ZSM5 and SiO<sub>2</sub> (60 mesh) were purchased from J&K Scientific Ltd., Beijing. 10 % Pt/C and NiCrFe (2:2:1) catalysts were prepared similar to that reported before<sup>22, 23</sup>.

### Hydrolysis

All materials used before hydrolysis were dried in an oven at 393 K overnight. Specified amount of material for hydrolysis, distilled water and acid solution were added to a 5 ml high pressure reactor made by Inconel-625 and sealed. The reactor was quickly immersed into the oil bath preheated at designed temperature and kept for a set time interval. After the time interval, the reactor was moved to water bath to quench the reaction. Lignin enriched solid was removed by passing through a 0.2 μm nylon membrane filter. Levulinic acid and formic acid were analyzed by Waters Acquity UPLC system equipped with Acquity UPLC HSS-T3 column and UV-vis detector at wave lengths of 215 and 268 nm. The carrier solvent was 97 % KH<sub>2</sub>PO<sub>4</sub> aqueous solution (0.01 mol/l and pH value adjusted to be 2.7 by H<sub>3</sub>PO<sub>4</sub>) and 3% acetonitrile at a flow rate of 0.1 ml/min and oven temperature was set to be 313 K. Yields of levulinic acid and formic acid were calculated with external method and reported as a percent of theoretical yield from C<sub>6</sub>H<sub>12</sub>O<sub>5</sub> unit in cellulose according to Figure S1.

### Dehydration

100 g levulinic acid was loaded in a 500 ml distillation flask and heated to designed temperature by an oil bath, and then the catalyst was charged into the flask. The outlet of the flask was connected with a vacuum pump set at 0.01 MPa. The produced angelica lactones passed through a glass column with cooling water reflux and collected by a collector at the end of the column. Products from dehydration reaction were washed with 3-4 times of distilled water to remove remained acid catalyst and levulinic acid. The composition of the final products was analyzed by Waters Acquity UPLC system equipped with Acquity UPLC HSS-T3 column (100 mm×2.1 mm, 1.8 μm), and UV-vis detector at a wave length of 215 nm, yields of ALs were determined by external method. The carrier solvent was 50 % deionized water and 50 % acetonitrile at a flow rate of 0.1 ml/min and oven temperature was set to be 313 K.

### C-C formation

Catalysts used for di/trimerization of angelica lactone were crushed by an agate mortar and dried in an oven at 373 K over night. 100 g angelica lactone was loaded in a 500 ml flask and heated to designed temperature by an oil bath. The reaction temperature of the reactant was measured by a mercury

thermometer. When the temperature reaches the designed temperature, crushed catalyst was put into the flask. After each reaction, element composition of the obtained products was analyzed by Vario EL cube element analyzer (Elementa Co., Germany). Molecular weight distribution of final products was analyzed by a gel permeation chromatograph (GPC) with Agilent LC-1200 system under the following conditions: column, Shodex GF 321-HQ; flow rate, 1.0 ml/min; carrier solvent, acetonitrile; detector, refractive index detector (RID); temperature, 313 K. Composition of the products was analyzed by the UPLC-MS (micrOTOF-QII) and the yields were calculated by using area normalization method. The effluent from the LC column was directed into the ESI probe. Mass spectrometer conditions were optimized to obtain maximal sensitivity. The source temperature and the desolvation temperature were maintained at 423 K and 623 K, respectively. The probe voltage (capillary voltage), cone voltage and extractor voltage were fixed at 1.5 kV, 65 V and 2 V, respectively. Nitrogen was used as the source of desolvation gas (650 l/h) and drying gas (4 l/min). P57 was confirmed in selected ion recording (SIR) mode. [M + Na]<sup>+</sup> = 901.6 ion for P57 was selected as detecting ion. Mass spectra were obtained at a dwell time of 0.1 s in SIR and 5000 Da/s of scan rate. <sup>1</sup>H NMR spectra were recorded using a JNM-ECS400 NMR spectrometer operating at 300 MHz in (CD<sub>3</sub>)<sub>2</sub>SO. <sup>13</sup>C NMR spectra were recorded on the same instrument with an operating frequency of 75 MHz.

ESR measurements: ESR measurements were carried out on a JEOL JES FA200 ESR spectrometer at 298 K. Typical spectrometer parameters include: microwave frequency, 9.4 GHz; microwave power, 4 mW; center field, 3374 G; sweep width, 8mT; sweep time, 4 min; and time constant, 30 ms; modulation frequency 100 KHz; modulation amplitude, 0.1 G.

### Hydrodeoxygenation

Dimer and trimer of angelica were washed with distilled water to remove remained catalyst. After removal of catalyst, the products were hydrogenated in a batch type reactor using a 10% Pd/C catalyst at 523, 573 and 648 K for 8-60 h. The amount of catalyst, reaction temperature and time for hydrodeoxygenation reactions were listed in Table S3. Gas products were analyzed by a gas chromatography (GC) with Shimadzu GC2014 equipped with a TCD detector and a HP-PLOT Q capillary column (Agilent, 30 m× 0.53 mm, 40.00μm) to quantify low molecular alkanes, CO and CO<sub>2</sub> with external method. Qualitative analysis of liquid products was analyzed by an Agilent 6890 GC equipped with HP-5 capillary column (Agilent, 30 m× 0.53 mm, 40.00μm) and an Agilent 5973 mass selective detector (MSD, Agilent Technologies). Liquid products were quantitatively analyzed by the same GC with that of gas products with HP-5 capillary column (Agilent, 30 m× 0.53 mm, 40.00μm) and the yields were calculated by using area normalization method.

## Results and discussion

### Preparation of levulinic acid

We studied the process with levulinic acid as the raw material. Levulinic acid can be produced via hydrolysis of saccharides, polysaccharides, cellulose, starch etc. catalyzed by an acid at 100-200 °C with up to 73% yield (mol basis) without comprehensive pre-treatment.<sup>8</sup> The production of levulinic acid from various sources has been extensively studied,<sup>24, 25</sup> thus some results obtained by using cellulose, cotton, fructose, glucose, cornstarch, starch powder are summarized and provided in supporting information (Table S2).

## Dehydration of levulinic acid

Dehydration of levulinic acid results in producing  $\alpha$ -AL, which is further isomerized to produce  $\beta$ -AL in the presence of acid catalyst at a high temperature. In order to obtain high yield of AL and suppress side reactions, AL has to be removed from the reactants once it is produced. The boiling point of AL is about 438-443 K, while the boiling point of levulinic acid is 518 K. The difference in boiling points facilitates the separation between levulinic acid and AL by vacuum distillation. We carried out the dehydration reaction of levulinic acid by employing 3 wt% of  $H_3PO_4$  as catalyst under 0.01 MPa and the results are shown in Table 1. Up to 58% yield was obtained in the case of  $H_3PO_4$  as catalyst at 448 K. Such a low yield was possibly due to the produced AL could not be removed from the reactants immediately. A temperature higher than 458 K led to no reaction due to the rapid evaporation of levulinic acid. The catalytic activity of  $H_2SO_4$  was also studied and it was found that the reactants quickly became dark due to the over-dehydration effect of  $H_2SO_4$  at such a temperature.

**Table 1.** Conversion of levulinic acid into ALs by employing 3 wt% of  $H_3PO_4$ ,  $H_3PO_4/SiO_2$ , HZSM-5/ $SiO_2$  as catalysts. The reactions were carried out in a 500 mL distillation flask and heated to designed temperature by an oil bath, and then the catalyst was charged into the flask. The outlet of the flask was connected with a vacuum pump set at 0.01 MPa. The produced ALs that passed through a glass column with cooling water reflux and collected by a collector at the end of the column.

Entry	Catalyst	T [K]	Yield [mol%]		
			$\alpha$ -AL	$\beta$ -AL	Total
1	$H_3PO_4$	433	19	4	23
2	$H_3PO_4$	433	44	6	49
3	$H_3PO_4$	433	32	8	40
4	$H_3PO_4$	448	49	9	58
5	$H_3PO_4$	458	0	0	0
6	$H_2SO_4$	433	0	0	0
7	None/ $SiO_2$	433	3	1	4
8	$H_3PO_4/SiO_2$	423	50	5	62
9	HZSM-5/ $SiO_2$	423	5	3	8
10	HZSM-5/ $SiO_2$	443	2	2	4
11	HZSM-5/ $SiO_2$	403	64	33	97
12	$H_2SO_4/SiO_2$	423	1	1	2

In order to remove the produced ALs immediately by evaporation, we added  $SiO_2$  (60 mesh) to promote the generation of AL bubbles in the reactant phase. As expected, a higher yield was achieved at lower temperature.  $H_3PO_4$  as the homogenous liquid catalyst may provide a good contacting with reactant, but its boiling point is also low, which may evaporate under negative

pressure and condense together with the products. We further added HZSM-5 as a solid catalyst<sup>19, 26</sup> to replace  $H_3PO_4$  for the reaction. However, levulinic acid was also evaporated without reaction at 423 K and 0.01 MPa with the employment of fine particles of HZSM-5. We carried out the same reaction at 403 K and consequently found that the conversion of levulinic acid was greatly increased and the yield was also increased to 97 mol%. We also noticed that the reaction produced two isomers of AL including  $\alpha$  and  $\beta$  configuration and that more  $\beta$ -AL was produced at higher temperature.

## Formation of C-C bond

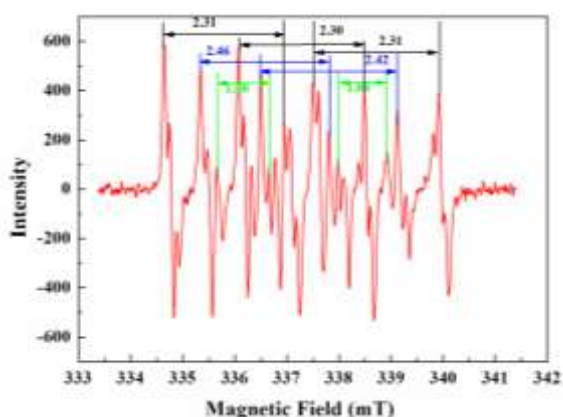
One important issue for the production of alkanes with molecular weights appropriate for gasoline from biomass is to form C-C bonds between molecules to meet the number of carbon atoms for the requirement of fuel qualities. Building a C-C linkage directly from two organic compounds has emerged as an attractive and challenging goal in catalysis. In the past several decades, transition metal-catalyzed C-C formation has allowed chemists to assemble complex molecule frameworks.<sup>27-31</sup> Besides, Dumesic *et al.*<sup>7, 32</sup> found the connection between molecules can be achieved by an aldol condensation reaction between HMF<sup>33-35</sup> or furfural with acetone, while Corma *et al.*<sup>36-38</sup> introduced a method to prolong the number of carbon atoms by hydroxyalkylation and alkylation.

**Table 2.** AL conversion, isomerization and yield to dimer, trimer and tetramer catalyzed by  $K_2CO_3$ ,  $Na_2CO_3$ ,  $NaHCO_3$ ,  $Ca(OH)_2$  and NaOH at various temperatures.

Entry	Catalyst/T[K]/Time [min]	Yield [wt%]				
		$\alpha$ -AL	$\beta$ -AL	Di	Tri	Tetr
1	$K_2CO_3/353/0$	90	10	0	0	0
2	$K_2CO_3/353/1$	0	0	0	0	0
3	$K_2CO_3/353/3$	0	0	65	33	2
4	$K_2CO_3/353/5$	0	0	64	34	2
5	$K_2CO_3/353/10$	0	0	64	34	2
6	$K_2CO_3/353/30$	0	0	65	33	2
7	$K_2CO_3/393/30$	0	0	64	31	5
8	$K_2CO_3/433/30$	0	0	63	32	5
9	$Na_2CO_3/353/30$	18	82	0	0	0
10	$Na_2CO_3/353/180$	6	94	0	0	0
11	$Na_2CO_3/413/30$	4	96	0	5	0
12	$Na_2CO_3/433/1$	0	0	71	25	4
13	$NaHCO_3/353/30$	39	61	0	0	0
14	$NaHCO_3/353/180$	11	89	0	0	0
15	$NaHCO_3/413/1$	0	0	73	24	3
16	$Ca(OH)_2/353/30$	67	33	0	0	0
17	$Ca(OH)_2/413/30$	10	90	0	0	0
18	NaOH/353/10	51	49	0	0	0
19	NaOH/353/720	14	86	0	0	0
20	NaOH/413/30	1	99	0	0	0

In this study, we found that C-C bonds were rapidly formed between AL molecules without using expensive noble catalysts under mild conditions.<sup>39</sup> It is observed that both  $\alpha$  and  $\beta$ -ALs can be converted into dimer (5-methyl-5-(2-methyl-5-oxotetrahydrofuran-3-yl)furan-2(5H)-one) or trimer (2,2'-dimethyl-3-(2-methyl-5-oxo-2,5-dihydrofuran-2-yl)tetrahydro-2,3'-bifuran-5,5'(2H,2'H)-dione) through C-C formation in the presence of medium strong alkalis like  $K_2CO_3$  or  $Na_2CO_3$  as

catalysts. Firstly, C-C formation of AL was carried out at 353 K under atmospheric pressure by employing 3%  $K_2CO_3$  as the catalyst. The obtained products at various temperatures were shown in Table 2. We found that the reaction can be completed in very short time (3.5 min) and longer reaction time did not significantly affect composition of products. At the end of the reaction, a viscous and transparent liquid at room temperature in brown colour was obtained. The HPLC analysis showed that AL was completely converted to dimer and trimer as well as trace amount of tetramers. The reaction was exothermic, and further resulted in an increase of temperature, and an induction period is observed before the reaction. When the temperatures employed in the C-C formation of AL can be varied from 353-423 K, the induction period and obtained dimer and trimer varied with reaction temperatures. These results can be rationalized assuming that the C-C formation reaction undergoes a free radical pathway.

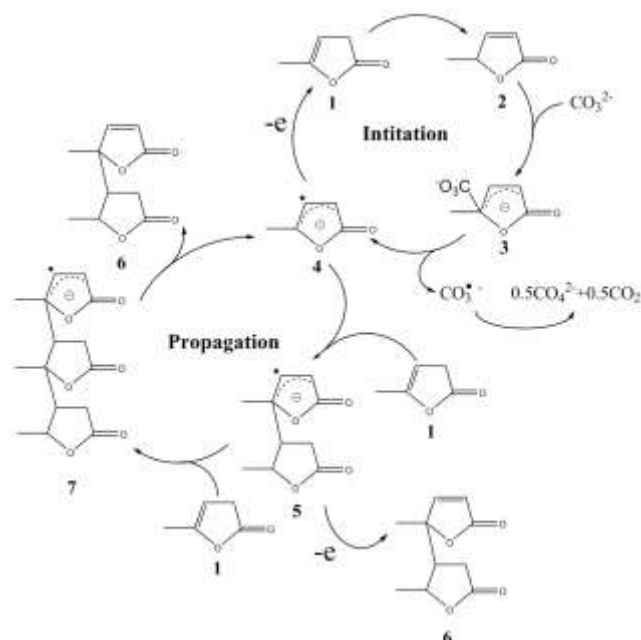


**Fig. 1** ESR spectra of AL in  $CH_3CN$  solution with 3wt%  $K_2CO_3$  at room temperature.

Although we lack a clear picture of initial and propagation of C-C formation between AL in the presence of a carbonate, we are able to offer some insights into the mechanism. The ESR spectrum of AL/acetonitrile solution (3 wt%) with  $K_2CO_3$  as a catalyst (3wt %) and trapped with 100 mM DMPO is shown in Fig. 1. Consider the ESR spectrum and induction period before the C-C formation reaction, it is evident that it is a free radical reaction. To the best of our knowledge, the mechanism of C-C formation between AL has not been reported. From SER spectrum, by determining  $g$  factors, three typical radicals can be labelled.  $g$  factors equal to 2.31 and 2.30 are labelled as radical 3 (scheme 2),  $g$  factors equals to 2.46 and 2.42 are labelled as  $CO_3^{\bullet-}$ ,  $g$  factors equals to 1.00 are labelled as radical 4. On the basis of the observations described above, we proposed a mechanism shown in Scheme 2. 1 is firstly isomerized to  $\beta$ -AL 2 at appropriate temperature with the presence of  $K_2CO_3$ .  $CO_3^{2-}$ , which from the ionization of  $K_2CO_3$ , gives an electron to 2 to form radical anion  $CO_3^{\bullet-}$ <sup>40,41</sup> and radical anion 3. 3 undergoes a homolytic cleavage to form  $CO_3^{\bullet-}$  and high reactive radical anion 4.  $CO_3^{\bullet-}$  radical further terminates to produce  $CO_2$  and  $CO_4^{2-}$ , the produced  $CO_2$  was observed in the experiment and confirmed by GC-MS. Anion radical 4 rapidly reacts with 1 to give dimer

anion radical 5, which may react with 1 to form higher molecular radical 7. Another possibility evolved the reaction of 5 is the single electron transfer to produce the objective product 6. Similarly, trimer of AL is also produced by the same manner.

Effects of different catalysts such as NaOH,  $Ca(OH)_2$ ,  $Na_2CO_3$ ,  $CaCO_3$  and  $NaHCO_3$  on the dimerization/trimerization were also investigated. The reaction catalyzed by 3 wt% NaOH showed significant difference with that catalyzed by  $K_2CO_3$ .  $K_2CO_3$  as a catalyst produced dimer and trimer of AL, while NaOH as catalyst produced isomerized products from  $\alpha$  to  $\beta$  form of AL (Figure S6) and  $Ca(OH)_2$  showed similar behavior with NaOH catalyst. These results suggest that the basicity of the catalyst played an important role in this reaction. In order to illustrate the effect of reaction time on di/trimerization of AL, the changes of  $\alpha$ -AL heated at 353 K for various reaction times without catalyst were studied. As seen from Figure S6, there was almost no change within 1 h but further prolonged reaction time led to the production of some unknown products possibly due to thermal decomposition.

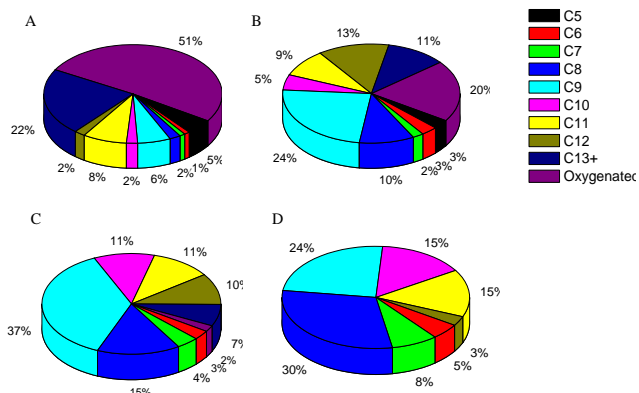


**Scheme 2.** Proposed free radical mechanism for the C-C formation between AL.

## Hydrogenation of di/trimers of AL

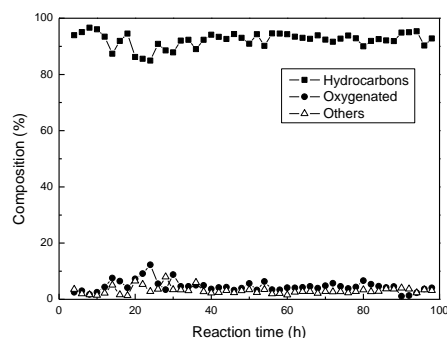
The produced dimer and trimer were hydrodeoxygenated in a 100 mL batch-type reactor at 573-648 K with 10% Pd/C or NiCrFe micro particles as catalysts. Hydrogen was consumed during reaction and extra hydrogen was supplied to maintain the overall pressure. Obtained products separated to two phases when the products were settled and cooled at room temperature, upper phase was organic phase containing liquid alkanes/aromatics and partly hydrodeoxygenated products<sup>42</sup> and lower phase was aqueous phase (mainly composed of water). We first carried out the reaction with 5 g of products from di/trimerization reaction from AL with  $H_2$  pressure at 5 MPa at 623 K in a batch-type reactor and the results are shown in Fig. 2A (selected values from Table S3). Alkanes containing more than 5 carbons constitute

49% of products and oxygenated compounds constitute 51% of products caused by the incomplete hydrodeoxygenation reaction.<sup>43</sup> We further increased the reaction temperature and time. As shown in Fig. 2B, 2C and 2D, under suitable conditions, the obtained products were mainly C6-C12 alkanes and/or aromatics with molecular weights appropriate for gasoline.<sup>44, 45</sup> Ideally, the liquid organic products from hydrogenation of dimer and trimer from AL should be C10 (from dimer) and C15 (from trimer) alkanes and accompanied by H<sub>2</sub>O as a by-product. However, the most products were found to be C8-C10 under the optimum condition. The gaseous products produced during hydrogenation were CO/CO<sub>2</sub>, methane and *n*-butane as shown in Figure S8. This indicates that C-C bond cleavage also took place during hydrogenation.<sup>46</sup> Production of CO<sub>2</sub> in the final products leads to the less consumption of H<sub>2</sub> for oxygen removal.<sup>47, 48</sup> The result also showed that Pd/C is effective for the oxygen removal. Other factors that affect the distribution of alkanes are the temperature and time,<sup>19, 49</sup> higher temperature and longer reaction time results in higher alkane yields.



**Fig. 2** Products distribution of the organic phase produced in the hydrogenation reaction of di/trimerization products from AL. (A) Hydrodeoxygenation of dimer and trimer produced from AL at 573 K and 5 MPa H<sub>2</sub> with 10% Pd/C catalyst for 12 h. (B) Hydrodeoxygenation of dimer and trimer produced from AL at 623 K and 5 MPa H<sub>2</sub> with 10% Pd/C catalyst for 18 h. (C) Hydrodeoxygenation of dimer and trimer produced from AL at 648 K and 5 MPa H<sub>2</sub> with 10% Pd/C catalyst for 60 h. (D) Dimer and trimer products from AL were pre-hydrogenated at 648 K and 5 MPa H<sub>2</sub> with NiCrFe catalyst for 12 h, and then the liquid products were hydrodeoxygenated under the same conditions with newly added catalyst.

Since the catalyst lifetime is an important factor in the evaluation of the process, we carried out the continuous reaction for 100 h with 10% Pd/C as the catalyst. After hydrogenation, the organic phase contained 90-97% hydrocarbons. There were also 3-5% of oxygenated compounds detected in the products caused by incomplete deoxygenation under this condition.



**Fig. 3** Products distribution of the hydrogenation reaction of di/trimerization products from AL in a fixed-bed reactor. Reaction conditions: 0.5 g 10% Pd/C catalyst, 573 K, 5 MPa H<sub>2</sub>, flow rate 2 ml/h.

The integrated system for conversion of biomass into alkanes consists of four reactors in series. Raw materials, liquid acid catalysts and water are fed to the first reactor to carry out hydrolysis reaction. An aqueous solution containing levulinic acid, formic acid and acid catalysts is filtered to remove solid residue that mainly consists of lignin and humins. After separation of formic acid, catalyst and water, levulinic acid is subjected to the second reactor for dehydration reaction under vacuum condition by employing HZSM-5 as the catalyst. The obtained products from vacuum dehydration reaction are collected in a sealed container, in which the products separate into two phases; the upper (lighter) phase contains water and lower (heavier) phase contains AL. The lower phase (AL) is transferred to the third reactor by employing carbonate as catalyst to produce AL dimer and trimer. Finally, AL dimer and trimer are washed with hot distilled water to remove catalyst and then fed into the hydrodeoxygenation reactor to produce bio-alkanes for gasoline. It is worth to note that a part of H<sub>2</sub> for hydrogenation can be obtained from the decomposition of formic acid produced in hydrolysis step,<sup>50-54</sup> which reduces the H<sub>2</sub> consumption and makes economic use of by-product.

The research shows that it is possible to produce alkanes in the range of C6-C13, most of them are C8 and C9 alkanes, which are in the carbon number suitable for the requirement of gasoline from cellulose/hemicelluloses and sugar containing biomass. The raw materials used for this process can be mostly available biomass such as wood, saw dust, rice straw, corn stalk, bagasse, waste paper and so on. Under the optimal reaction conditions, 73 wt% carbon in cellulose/sugar is converted into levulinic acid, the produced levulinic acid can be upgraded to AL with a carbon yield of 97 mol% and which can be further converted into dimer and trimer of a carbon yield of 100wt%. After hydrogenation, 92 wt% of dimer/trimer of AL are converted into alkanes and remain in liquid phase. According to the above-mentioned yields, it is possible to convert nearly 65% carbon of cellulose or sugars into alkanes and aromatics. In another word, the process can produce about 32 kg alkanes from 100 kg cellulose or sugars or about 250 kg wood. This amount is similar to that of ethanol from 100 kg cellulose. Accordingly, the process consumes 5 mol H<sub>2</sub> (1 C=C bond and 4 oxygen) to produce 1 mol of decane from cellulose. Besides, if H<sub>2</sub> is produced from formic acid, its consumption can be reduced. However, the obtained bio-alkanes are oxygen-free, which results in the calorific value is 1.8 times higher than

ethanol. A striking breakthrough is that our process starts from the biomass directly rather than from sugars. Moreover, the formation of C-C bond in di/trimerization could take place at mild condition (353 K) with 100 % selectivity through free radical reactions, while such reactions usually lead to diverse spectrum of products. The general conclusion from this study is that alkanes/aromatics can be formed by converting biomass into platform chemicals; prolonging the number of carbon and finally hydrogenating the products to remove oxygen by hydrogenation.

## Conclusions

The major monomer building blocks of biomass are carbohydrates typically containing 5 or 6 carbons. Petroleum derived gasoline and diesel fuels are hydrocarbons having 6 to 15 carbons. Therefore, to produce gasoline and diesel fuel from biomass, there must be a C-C bond formation from the biomass-derived molecules. In this study, it was found that C-C can be formed between angelica lactones 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. After hydrogenation, C6-C15 hydrocarbons for fuels can be obtained for transportation fuel.

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## Notes and references

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