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Formation of C–C bonds for the production of bio-alkanes under mild conditions†

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It is of crucial importance to form C–C bonds between biomass-derived compounds for the production of bio-alkanes from biomass. In this study, it was found that C–C bonds can be formed between angelica lactones, key intermediates derived from biomass, through free radical reactions under mild conditions without using a noble catalyst or solvent, which gave elongated carbon chains of di/trimers with 10 or 15 carbons, with complete conversion and 100% selectivity. The di/trimers produced serve as a novel feedstock for the carbon backbones of bio-alkanes. Hydrogenation of the di/trimers produced C6–C13 hydrocarbons suitable for use as transportation fuels.

Biomass is regarded as a possible renewable resource for fuels and chemicals. Current approaches for the conversion of biomass feedstocks into liquid fuels involve their gasification to syngas followed by Fischer–Tropsch synthesis, thermal liquefaction and fermentation.[1] These approaches have one or more drawbacks, including the poor fuel properties of the products, low conversion efficiencies, low heating values, long treatment times or high processing costs. Recently, acid hydrolysis to give sugars followed by aqueous-phase processing (APP) to yield liquid fuel has attracted much interest.[2–7] 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.[8] However, the process needs sugars as the raw materials and the production of sugars is costly, and sugars tend to produce dehydration products like hydroxylmethylfurfural or humins in the presence of water and an acid catalyst, thus decreasing the yield of the target products.[9–11]

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

In this respect, it is desirable to develop an efficient process that can convert widespread biomass without extensive pretreatment to liquid alkanes, similar to those that have been used for many years from petroleum resources,[14–16] and to design an effective C–C bond formation reaction between biomass-derived compounds under mild conditions. Herein, we introduce an integrated process that converts commonly available biomass into gasoline range alkanes.[17] The strategies of this process are to form elongated-carbon-chain oxygenated intermediates from functional chemicals produced from biomass, and then to remove the oxygens of the intermediates by hydrodeoxygenation to produce gasoline range liquid alkanes/aromatics. As shown in Scheme 1, levulinic acid derived from biomass is dehydrated to angelica lactones (ALs), then the ALs undergo a C–C bond formation reaction to produce C10 or C15 lactones,[18] and these lactones are finally deoxygenated to produce C6–C15 branched-chain alkanes as liquid fuels. In this process, a free radical reaction was employed under mild reaction conditions in the C–C bond formation step to give a high yield. Neither water nor 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. Furthermore, AL, which has a double bond and lactone structure produced by the dehydration of levulinic acid catalyzed by a solid acid catalyst, can be used as a new platform chemical derived from commonly available biomass.[19–21]

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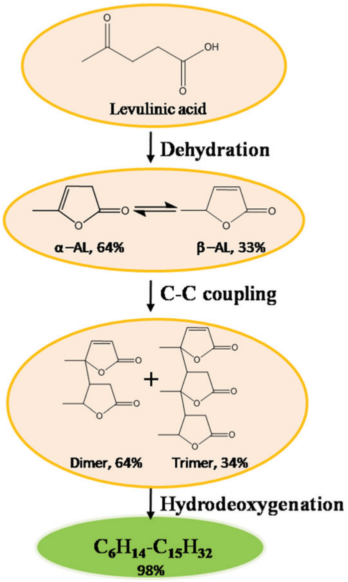


Scheme 1 Reaction pathways for C–C bond formation between angelica lactones (ALs) and the conversion of biomass into bio-alkanes.

Experimental

Catalyst preparation

HCl, H_2SO_4, H_3PO_4, K_2CO_3, Na_2CO_3, NaOH, H-ZSM5 and SiO_2 (60 mesh) were purchased from J&K Scientific Ltd, Beijing. 10% Pt/C and NiCrFe (2 : 2 : 1) catalysts were prepared in ways similar to those reported before.[22,23]

Hydrolysis

All materials used were dried in an oven at 393 K overnight before hydrolysis. Specified amounts of the materials 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 in an oil bath preheated to the designated temperature and kept there for a set time interval. After the time interval, the reactor was moved to a water bath to quench the reaction. A lignin-enriched solid was removed by passing the contents through a 0.2 μm nylon membrane filter. Levulinic acid and formic acid were analyzed by a Waters Acquity UPLC system equipped with an Acquity UPLC HSS-T3 column and UV-vis detector at wavelengths of 215 and 268 nm. The carrier solvent was 97% KH_2PO_4 aqueous solution (0.01 mol l^{-1} and pH value adjusted to be 2.7 by H_3PO_4) and 3% acetonitrile at a flow rate of 0.1 ml min^{-1} and the oven temperature was set to 313 K. The yields of levulinic acid and formic acid were calculated by an external method and reported as a percentage of the theoretical yield from the $C_6H_{12}O_5$ unit in cellulose according to Fig. S1.†

Dehydration

100 g levulinic acid was loaded in a 500 ml distillation flask and heated to the designated temperature by an oil bath, and then the flask was charged with the catalyst. The outlet of the flask was connected to a vacuum pump set at 0.01 MPa. The produced angelica lactones passed through a glass column with cooling water reflux and were collected by a collector at the end of the column. Products from the dehydration reaction were washed 3–4 times with distilled water to remove the remaining acid catalyst and levulinic acid. The composition of the final products was analyzed by a Waters Acquity UPLC system equipped with an Acquity UPLC HSS-T3 column (100 mm × 2.1 mm, 1.8 μm) and UV-vis detector at a wavelength of 215 nm, yields of the ALs were determined by an external method. The carrier solvent was 50% deionized water and 50% acetonitrile at a flow rate of 0.1 ml min^{-1} and the oven temperature was set to 313 K.

C–C bond formation

Catalysts used for the di/trimerization of angelica lactone were crushed in an agate mortar and dried in an oven at 373 K overnight. 100 g angelica lactone was loaded in a 500 ml flask and heated to the designated temperature by an oil bath. The reaction temperature of the reactant was measured by a mercury thermometer. When the temperature reached the designated temperature, crushed catalyst was put into the flask. After each reaction, the elemental compositions of the obtained products were analyzed by a Vario EL cube element analyzer (Elementa Co., Germany). The molecular weight distributions of the final products were analyzed by gel permeation chromatography (GPC) with an Agilent LC-1200 system under the following conditions: column, Shodex GF 321-HQ; flow rate, 1.0 ml min^{-1}; carrier solvent, acetonitrile; detector, refractive index detector (RID); and temperature, 313 K. The composition of the products was analyzed by an ultra performance liquid chromatography-mass spectrometer (UPLC-MS, micrOTOF-QII) and the yields were calculated using the area normalization method. The effluent from the LC column was directed into an electrospray ionization (ESI) probe. The 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 the desolvation gas (650 l h^{-1}) and drying gas (4 l min^{-1}). P57 was confirmed in selected ion recording (SIR) mode. $[M + Na]^+ = 901.6$ ion for P57 was selected as the detecting ion. Mass spectra were obtained using a dwell time of 0.1 s in SIR and a scan rate of 5000 Da s^{-1}. ^{1}H NMR spectra were recorded using a JNM-ECS400 NMR spectrometer operating at 300 MHz in $(CD_3)_2SO$. ^{13}C NMR spectra were recorded on the same instrument at an operating frequency of 75 MHz.

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

Hydrodeoxygenation

The dimers and trimers of angelica lactones were washed with distilled water to remove the remaining catalyst. After the removal of the 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 are listed in Table S3.† Gas products were analyzed by gas chromatography (GC) on a Shimadzu GC2014 instrument equipped with a TCD detector and an HP-PLOT Q capillary column (Agilent, 30 m × 0.53 mm, 40.00 μm) to quantify low molecular weight alkanes, CO and CO_2 by an external method. Qualitative analysis of the liquid products was performed by an Agilent 6890 GC equipped with an HP-5 capillary column (Agilent, 30 m × 0.53 mm, 40.00 μm) and an Agilent 5973 mass selective detector (MSD, Agilent Technologies). The liquid products were quantitatively analyzed by the same GC used for the gas products, with an HP-5 capillary column (Agilent, 30 m × 0.53 mm, 40.00 μm) and the yields were calculated using the 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* the 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.[8] The production of levulinic acid from various sources has been extensively studied,[24,25] thus some results obtained by using cellulose, cotton, fructose, glucose, cornstalk and starch powder are summarized and provided in the ESI (Table S2†).

Dehydration of levulinic acid

The dehydration of levulinic acid results in the production of α-AL, which is further isomerized to produce β-AL in the presence of an acid catalyst at a high temperature. In order to obtain a 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 of levulinic acid and AL by vacuum distillation. We carried out the dehydration reaction of levulinic acid by employing 3 wt% H_3PO_4 as a catalyst under 0.01 MPa and the results are shown in Table 1. Up to 58% yield was obtained in the case of using H_3PO_4 as a catalyst at 448 K. Such a low yield possibly existed because 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% H_3PO_4, H_3PO_4/SiO_2, H-ZSM5/SiO_2 as catalysts. The reactions were carried out in a 500 ml distillation flask and heated to the designated temperature by an oil bath, and then the flask was charged with the catalyst. The outlet of the flask was connected to a vacuum pump set at 0.01 MPa. The produced ALs passed through a glass column with cooling water reflux and were collected by a collector at the end of the column

			Yield [mol%]		
Entry	Catalyst	*T* [K]	α-AL	β-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	H-ZSM5/SiO_2	423	5	3	8
10	H-ZSM5/SiO_2	443	2	2	4
11	H-ZSM5/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 a lower temperature. H_3PO_4 as the homogeneous liquid catalyst may provide good contact with the reactant, but its boiling point is also low, and it may evaporate under negative pressure and condense together with the products. We further added H-ZSM5 as a solid catalyst[19,26] to replace H_3PO_4 for the reaction. However, levulinic acid was also evaporated without reacting at 423 K and 0.01 MPa, with the employment of fine particles of H-ZSM5. 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 the α and β configurations, and that more β-AL was produced at higher temperatures.

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 needed for fuel quality requirements. 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 bond formation has allowed chemists to assemble complex molecular frameworks.[27–31] Besides, Dumesic *et al.*[7,32] found the connection between molecules can be achieved by an aldol condensation reaction between HMF[33–35] or furfural and acetone, while Corma *et al.*[36–38] introduced a method to increase the number of carbon atoms by hydroxyalkylation and alkylation.

In this study, we found that C–C bonds were rapidly formed between AL molecules, without using expensive noble catalysts,

Table 2 AL conversion, isomerization and yield to dimers, trimers and tetramers catalyzed by K_2CO_3, Na_2CO_3, $NaHCO_3$, $Ca(OH)_2$ and NaOH at various temperatures

		Yield [wt%]				
Entry	Catalyst/*T* [K]/time [min]	α-AL	β-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

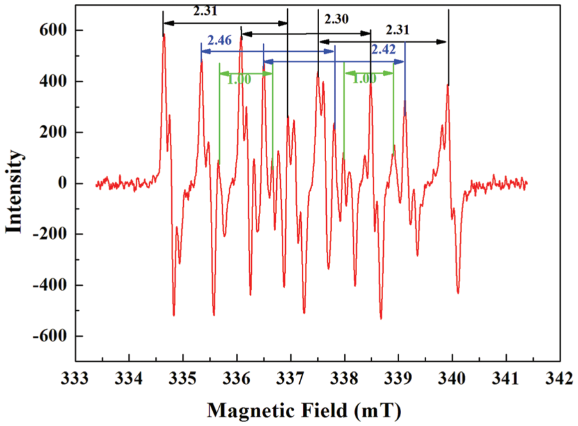
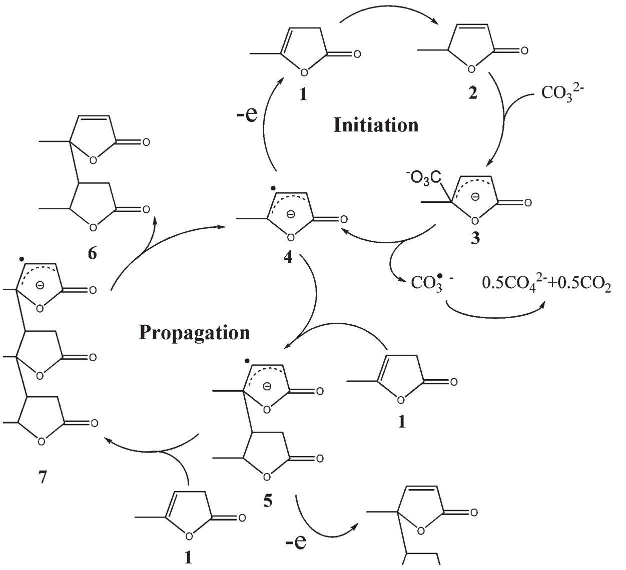


Fig. 1 ESR spectrum of AL in CH_3CN solution with 3 wt% K_2CO_3 at room temperature.



Scheme 2 Proposed free radical mechanism for the C–C bond formation between ALs.

under mild conditions.[39] It is observed that both α- and β-ALs can be converted to a dimer (5-methyl-5-(2-methyl-5-oxo-tetrahydrofuran-3-yl)furan-2(5*H*)-one) or trimer (2,2′-dimethyl-3-(2-methyl-5-oxo-2,5-dihydrofuran-2-yl)tetrahydro-2,3′-bifuran-5,5′(2*H*,2′*H*)-dione) through C–C bond formation in the presence of medium strength alkalis like K_2CO_3 or Na_2CO_3 as catalysts. Firstly, C–C bond formation between the ALs was carried out at 353 K under atmospheric pressure by employing 3% K_2CO_3 as the catalyst. The obtained products at various temperatures are shown in Table 2. We found that the reaction can be completed in a very short time (3.5 min) and a longer reaction time did not significantly affect the composition of the products. At the end of the reaction, a brown, viscous and transparent liquid at room temperature was obtained. The HPLC analysis showed that the ALs were completely converted to dimers and trimers, as well as trace amounts of tetramers. The reaction was exothermic, and resulted in a further increase in temperature, and an induction period was observed before the reaction. When the temperatures employed in the C–C bond formation between the ALs were varied between 353–423 K, the induction periods and obtained dimers and trimers varied with the reaction temperatures. These results can be rationalized, assuming that the C–C bond formation reaction undergoes a free radical pathway.

Although we lack a clear picture of the initiation and propagation of the C–C bond formation between ALs in the presence of a carbonate, we are able to offer some insights into the mechanism. The ESR spectrum of the AL–acetonitrile solution (3 wt%) with K_2CO_3 as a catalyst (3 wt%) and trapped with 100 mM DMPO is shown in Fig. 1. Considering the ESR spectrum and induction period before the C–C bond formation reaction, it is evident that it is a free radical reaction. To the best of our knowledge, the mechanism of the C–C bond formation between ALs has not been reported. From the ESR spectrum, by determining the *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 equal to 2.46 and 2.42 are labelled as $CO_3^{\bullet -}$ and *g* factors equal to 1.00 are labelled as radical **4**. On the basis of the observations described above, we proposed the mechanism shown in Scheme 2. **1** is firstly isomerized to β-AL **2** at the appropriate temperature in the presence of K_2CO_3. CO_3^{2-}, from the ionization of K_2CO_3, gives an electron to **2** to form the radical anion $CO_3^{\bullet -}$ (ref. 40 and 41) and radical anion **3**. **3** undergoes a homolytic cleavage to form $CO_3^{\bullet -}$ and the highly reactive radical anion **4**. The $CO_3^{\bullet -}$

radical further reacts 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 the dimer anion radical **5**, which may react with **1** to form the higher molecular weight radical **7**. Another possibility involving the reaction of **5** is single electron transfer to produce the target product **6**. Similarly, the trimer of AL is also produced in the same manner.

The 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 a significant difference from that catalyzed by K_2CO_3. K_2CO_3 as a catalyst produced dimers and trimers of AL, while NaOH as a catalyst produced isomerized products of AL in its α and β forms (Fig. S6†) and $Ca(OH)_2$ showed similar behavior to that of the 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 the reaction time on the di/trimerization of AL, the changes to α-AL heated at 353 K for various reaction times without a catalyst were studied. As seen from Fig. S6,† there was almost no change within 1 h but more prolonged reaction times led to the production of some unknown products, possibly due to thermal decomposition.

Hydrogenation of di/trimers of AL

The produced dimers and trimers 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 the reaction and extra hydrogen was supplied to maintain the overall pressure. The obtained products separated into two phases when the products were settled and cooled at room temperature. The upper phase was the organic phase, containing liquid alkanes/aromatics and partly hydrodeoxygenated products,[42] and the lower phase was the aqueous phase (mainly composed of water). We first carried out the reaction with 5 g of products from the di/trimerization reaction from AL with H_2 at a pressure of 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 the products and oxygenated compounds constitute 51% of products, and were caused by the incomplete hydrodeoxygenation reaction.[43] We further increased the reaction temperature and time. As shown in Fig. 2B–2D, under suitable conditions, the obtained products were mainly C6–C12 alkanes and/or aromatics with molecular weights appropriate for gasoline.[44,45] Ideally, the liquid organic products from the hydrogenation of the dimers and trimers from AL should be C10 (from dimer) and C15 (from trimer) alkanes and accompanied by H_2O as a by-product. However, most of the products were found to be C8–C10 under the optimum conditions. The gaseous products produced during the hydrogenation were CO/CO_2, methane and *n*-butane as shown in Fig. S8.† This indicates that C–C bond cleavage also took place during hydrogenation.[46] The production of CO_2 in the final products leads to the lower consumption of H_2 for oxygen removal.[47,48] The result also showed that Pd/C is effective for oxygen removal. Other factors that affect the distribution of the molecular weights of the alkanes are the temperature and time,[19,49] a higher temperature and longer reaction time result in higher alkane yields.

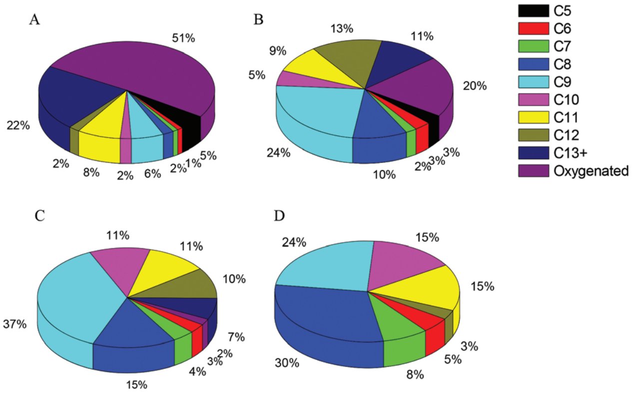


Fig. 2 Product distribution of the organic phase produced in the hydrogenation reaction of the di/trimerization products of the ALs. (A) Hydrodeoxygenation of dimers and trimers produced from ALs at 573 K and 5 MPa H_2 with 10% Pd/C catalyst for 12 h. (B) Hydrodeoxygenation of dimers and trimers produced from ALs at 623 K and 5 MPa H_2 with 10% Pd/C catalyst for 18 h. (C) Hydrodeoxygenation of dimers and trimers produced from ALs at 648 K and 5 MPa H_2 with 10% Pd/C catalyst for 60 h. (D) Dimer and trimer products of the ALs were pre-hydrogenated at 648 K and 5 MPa H_2 with a NiCrFe catalyst for 12 h, and then the liquid products were hydrodeoxygenated under the same conditions with a newly added catalyst.

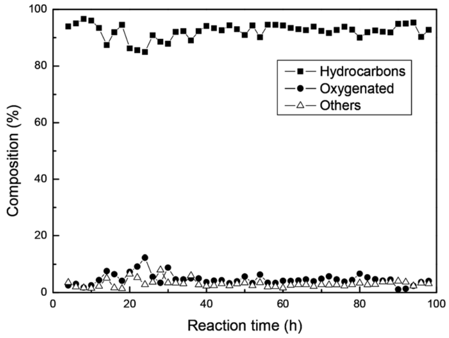


Fig. 3 Product distribution of the hydrogenation reaction of the di/trimerization products of the ALs in a fixed-bed reactor. Reaction conditions: 0.5 g 10% Pd/C catalyst, 573 K, 5 MPa H_2 and a flow rate of 2 ml h^{-1}.

Since the catalyst lifetime is an important factor in the evaluation of the process, we carried out a 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% oxygenated compounds detected in the products, caused by incomplete deoxygenation under these conditions (Fig. 3).

The integrated system for the conversion of biomass into alkanes consists of four reactors in series. Raw materials, liquid acid catalysts and water are fed into the first reactor to carry out the hydrolysis reaction. An aqueous solution containing levulinic acid, formic acid and acid catalysts is filtered to remove the solid residue that mainly consists of lignin and humins. After its separation from formic acid, the catalyst and water, levulinic acid is subjected to the second reactor for the dehydration reaction under vacuum conditions by employing H-ZSM5 as the catalyst. The obtained products from the vacuum dehydration reaction are collected in a sealed container, in which the products separate into two phases; the upper (lighter) phase contains water and the lower (heavier) phase contains AL. The lower phase (AL) is transferred to the third reactor by employing carbonate as a catalyst to produce the AL dimers and trimers. Finally, the AL dimers and trimers are washed with hot distilled water to remove the catalyst, and then fed into the hydrodeoxygenation reactor to produce bio-alkanes for gasoline. It is worth noting that part of the H_2 for hydrogenation can be obtained from the decomposition of formic acid produced in the hydrolysis step,[50–54] which reduces the H_2 consumption and makes economic use of the 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 of the carbon numbers suitable for the requirements of gasoline, from cellulose/hemicelluloses and sugar-containing biomass. The raw materials used for this process can be widely 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 this can be further converted into dimers and trimers with a carbon yield of 100 wt%. After hydrogenation, 92 wt% dimers/trimers of AL are converted into alkanes and remain in the liquid phase. According to the above-mentioned yields, it is possible to convert nearly 65% of the carbon of cellulose or sugars into alkanes and aromatics. In other words, 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_2 (1 C=C bond and 4 oxygens) to produce 1 mol of decane from cellulose. Besides, if H_2 is produced from formic acid, its consumption can be reduced. However, the obtained bio-alkanes are oxygen-free, which results in a calorific value that is 1.8 times higher than that of ethanol. A striking breakthrough is that our process starts from the biomass directly rather than from sugars. Moreover, the formation of the C–C bond in di/trimerization could take place under mild conditions (353 K) with 100% selectivity through free radical reactions, while such reactions usually lead to a diverse spectrum of products. The general conclusion from this study is that alkanes/aromatics can be formed by converting biomass into platform chemicals; increasing the number of carbons and finally hydrogenating the products to remove the oxygen by hydrogenation.

Conclusions

The major monomeric 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 between the biomass-derived molecules. In this study, it was found that C–C bonds can be formed between angelica lactones through free radical reactions under mild conditions without using a noble catalyst or solvent, which gave the elongated carbon chain products with 10 or 15 carbons with complete conversion and 100% selectivity. After hydrogenation, C6–C15 hydrocarbons can be obtained for transportation fuels.

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