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Communication

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Continuous Micro-flow Synthesis of Fuel Precursors from Platform Molecules Catalyzed by 1,5,7-Triazabicyclo[4.4.0]dec-5-ene

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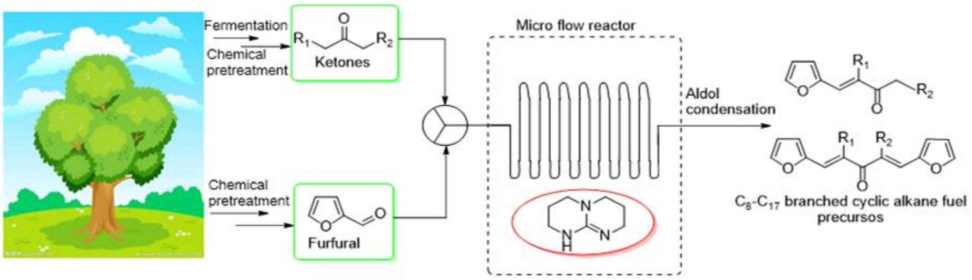
TOC:


Fermentation
Chemical pretreatment
Ketones
R1
R2
O
Chemical pretreatment
Furfural
Micro flow reactor
Aldol condensation
N
N
H
C8-C17 branched cyclic alkane fuel precursos

ABSTRACT

The first continuous flow synthesis of C_8-C_{16} alkane fuel precursors from bio-based platform molecules is reported, TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene) was found to be a recyclable and highly efficient organic base catalyst for the aldol condensation of furfural with carbonyl compounds, and the selectivity of mono- or difuryl product can be easily regulated by adjusting the molar ratio of substrates. By means of flow technique, a shorter reaction time, satisfactory output, and continuous preparation are achieved under the present procedure, representing a significant advance over the corresponding batch reaction condition.

KEYWORDS: Renewable hydrocarbon fuels; Lignocellulose biomass; C_8-C_{16} alkane; Aldol condensation; Flow technique; Bio-based platform molecules.

INTRODUCTION

With the consumption of fossil resources and growing environmental problems, the development pathways for the utilization of biomass feedstocks into renewable fuels is attractive.[1-3] In this context, lignocellulosic biomass can be substituted for fossil resources as it is an abundant, renewable and carbon-neutral resource.[4-7] Generally, lignocellulose biomass conversed into liquid hydrocarbon fuels has two major strategies: one is to treatment of integral lignocellulose conversed to scalable stocks such as syngas or bio-oil by fast pyrolysis,[8,9] gasification and liquefaction[10,11] followed by Fischer-Tropsch synthesis.[12-14] Another refers to depolymerization of lignocellulose to produce platform compounds such as furan-based compounds. (furfural, 2-methyfuran or hydroxymethylfurfural, *etc.*) Catalytic transformation of these platform compounds through hydrogenation and oxygen removal process along with carbon chain elongation reactions is another important approach to convert lignocellulosic biomass into liquid fuels.[15,16] To meet the carbon number for the corresponding fuel range, such as jet and diesel fuels, various reactant have been applied as building blocks for the growth of carbon chain, for example, acetone,[17-21] mesityl oxide,[22] hydroxyacetone,[23,24] methyl isobutyl ketone,[25] and butanal[26-28]. This route is meaningfully while these feedstock is originated from lignocellulose. Recently, we reported acetoin was used as a C_4 bio-based synthons for the synthesis of jet fuel range hydrocarbon fuels.[29] However, for the production of fuels, compared to the other bulk feedstock, the production output of acetoin is relatively small, such as furfural, which has been fabricated on an industrial scale (280,000 t/a) by hydrolysis of hemicellulose part in lignocellulose.[30]

Inspired by the pioneering research of Huber and Dumesic group,[17-20] furfural is known to undergo base-catalyzed aldol condensation reactions with carbonyl compounds to fuel precursors mono- or difuryl components. Mineral base and solid base were the traditional catalysts for this reaction. However, compared with the reaction with acetone, these catalysts showed poor catalytic performance for the reaction with long chain aliphatic carbonyl compounds. Recently, we reported using DBU as a catalyst for the aldol reaction of furan aldehyde with long chain carbonyl compounds.[31] However, this method still has some shortcomings: (i) high dosage of catalyst (> 30 mol%) had to be used to obtain double condensation difuryl components; (ii) long reaction time is required to achieve a reasonable condensation yield; (iii) difficult to separate this homogeneous catalyst from the reaction mixture. Thus, the development of a high reactivity and readily recyclable catalyst is highly desirable.

On the other hand, the production of fuels through platform molecules route was traditionally conducted in a batch reactor in lab scale experiments. However, for industrial application on large scales, the continuous reaction mode is required to ensure high production intensity in the chemical engineering operation. Recently, process intensification based on flow techniques and microreactors have drawn considerable attention in the fields of chemical synthesis.[32] With the advantage of their high mixing and heat transfer rates, safe operation, and easy modulation, the technologies of microfluidic are rapidly emerging as complements to traditional batch synthesis. Moreover, the potential to run an uninterrupted microreactor sequence, multistage continuous reactions, and easy to enlarge production using continuous flow technology is also beneficial in terms of industrial scale.[33-34] These significant advances in the microreactor technology prompted us to exploit new process to improve the renewable fuels production efficiency.

In a continuation of our efforts for the biomass catalytic conversion,[29,31,35,36] we report herein a continuous flow system for the production of C_8-C_{16} alkane fuel precursors from platform molecules using TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene) as a highly efficient and recyclable organic base catalyst for the aldol condensation (Figure 1).

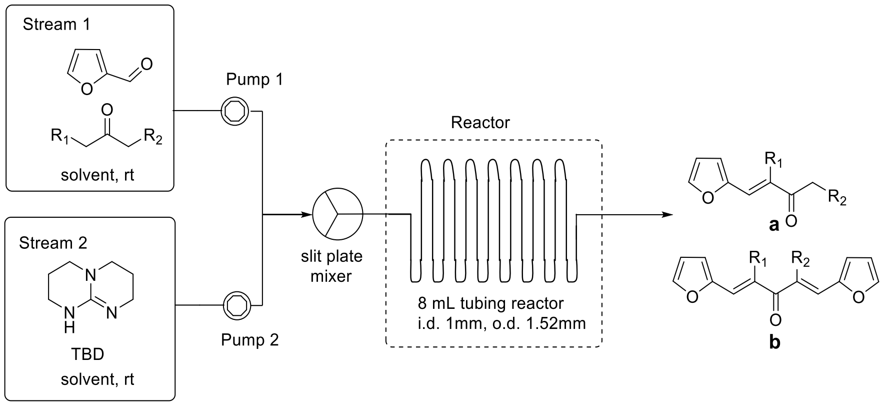


Figure 1. Process diagram for continuous micro-flow synthesis of fuel precursors.

EXPERIMENTAL SECTION

Aldol condensation of 3-pentanone with furfural in batch reactor

Aldol condensation of 3-pentanone with furfural was performed in a 25 mL flask reactor in the presence of amine-based organic catalysts (1-3 mmol). In a typical experiment, furfural (10-25 mmol) and 3-pentanone (10 mmol) were loaded into the reactor and stirred at given temperature under solvent-free conditions for several hours while checking the course of reaction by GC-MS. After reaction, the liquid oil product was diluted and extracted with EtOAc and water, the analytically pure product was obtained after concentrated the organic layer and purified by column chromatography.

Aldol condensation of furfural with ketones under batch condition in Table 3

Aldol condensation of furfural with carbon compounds was performed in a 50 mL flask reactor in the presence of TBD (1 mmol). In a typical experiment, furfural (10-25 mmol) and carbon compounds (10 mmol), solvent (8 mL MeOH/H_2O (1:1) for 3-pentanone, acetone, 2-pentanone, and 2-hexanone, and 16 mL CH_2Cl_2 for cyclopentanone and cyclohexanone) were loaded into the reactor and stirred at given temperature under solvent-free conditions for several hours while checking the course of reaction by GC-MS. After reaction, the reaction solutions was diluted and extracted with EtOAc or water, the aqueous phase was collected and evaporated to recover the catalyst TBD, and the analytically pure product was obtained after concentrated the organic layer and purified by column chromatography.

Aldol condensation of furfural with ketones under MFS condition in Table 3

Generally, in the flow system, stream 1 was composed of furfural (100-200 mmol) and ketones (100 mmol) were diluted with solvent to 40 mL. Stream 2 was composed of TBD (10 mmol) was diluted with solvent to 40 mL. Two streams was purged in a given speed into slit plate mixer and at the given temperature passed tubing reactor while checking the reaction progress by using GC-MS. Finally, the product was extracted using EtOAc, the analytically pure product was obtained after concentrated the organic layer and purified by column chromatography, and the aqueous phase was collected and reused. For reaction details see the support information.

RESULTS AND DISCUSSION

Aldol condensation of 3-pentanone with furfural in batch reactor

Initial "in-flask" experiments was first carried out using furfural and 3-pentanone as the model reaction, in our previous work, mineral base and solid base catalysts showed poor activity for this reaction, and double condensation product C_{15} precursor

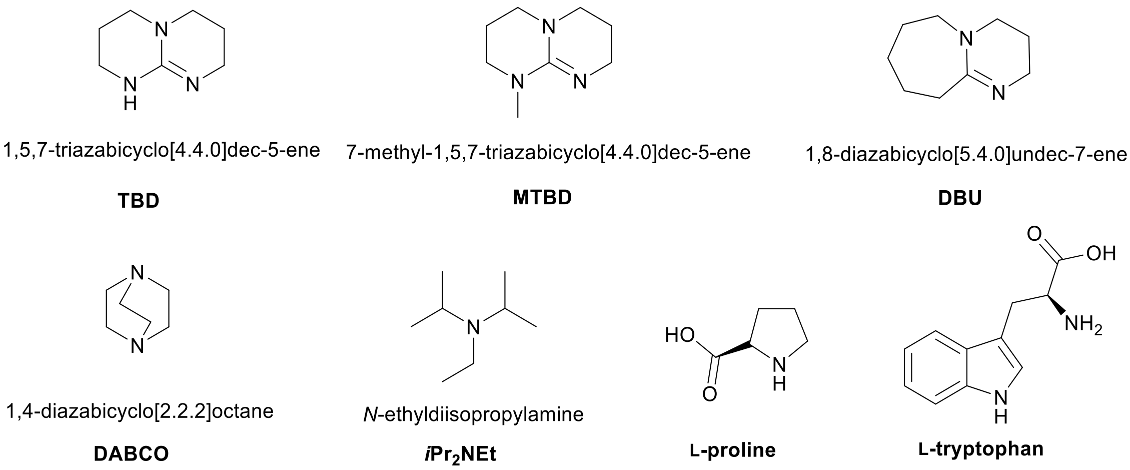
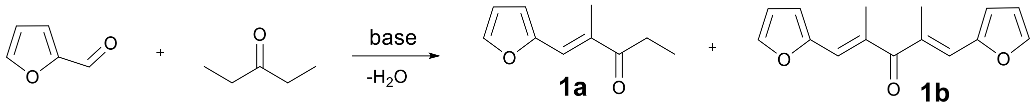


Figure 2. The structures of the catalysts used in this study.

1,5-di(furan-2-yl)-2,4-dimethylpenta-1,4-dien-3-one **1b** cannot be obtained. In order to search for a high activity catalyst, a series of amine-based organic catalysts were tested for this reaction, for example, 1,4-diazabicyclo[2.2.2]octane (DABCO), *i*Pr$_2$NEt, tryptophan and L-proline (see Figure 2). However, all of them were failed to catalyze this reaction. To our delight, from the results of entry 6 in Table 1, we find that under the situation of using 10 mol% TBD as the aldol condensation catalyst, the desired double condensation product **1b** has 93% yield in 2 h.

Table 1. Results of different catalysts catalyzed the aldol condensation between of furfural and 3-pentanone under solvent-free condition.



Entry	Catalyst	Furfural/ 3-pentanone (molar ratio)	Catalyst loading (mol %)[a]	T (K)	Time (h)	Yield (%)[a] 1a	Yield (%)[a] 1b
1	DABCO	1.0	10	298	12	0	0
2	L-proline	1.0	10	298	12	0	0
3	Tryptophan	1.0	10	298	12	0	0
4	*i*Pr$_2$NEt	1.0	10	298	12	0	0
5	DBU	2.5	30	353	10	8	88
6	TBD	2.5	10	353	2	5	93
7	TBD	2.5	10	298	10	7	90
8	TBD	1.0	10	298	4	94	3
9	TBD	1.0	10	353	1	87	8
10	MTBD	1.0	10	298	20	92	4

[a] 3-pentanone is relative to the limiting reactant.

In our previous work, 30% DBU had to be used to afford 88% yield of **2b** in 10 h (Table 1, entry 5). Furthermore, this reaction can even performed at room temperature, although required a longer reaction time (Table 1, entry 7), which clearly demonstrates its superior catalytic activity. It is noteworthy that the selectivity of mono- or difuryl product could be easily regulated by adjusting the molar ratio of substrates, From the result of entry 8 in Table 1, while the molar ratio of 3-pentanone/furfural is 1, the yield of single condensation product **1a** increases up to

94%, which pointed out the selectivity of double condensation is kinetic control instead of thermodynamic control (Table 1, entry 9). This finding is very helpful because it provides an available tool to change the ultimate desired ingredient of mono- or difuryl product.

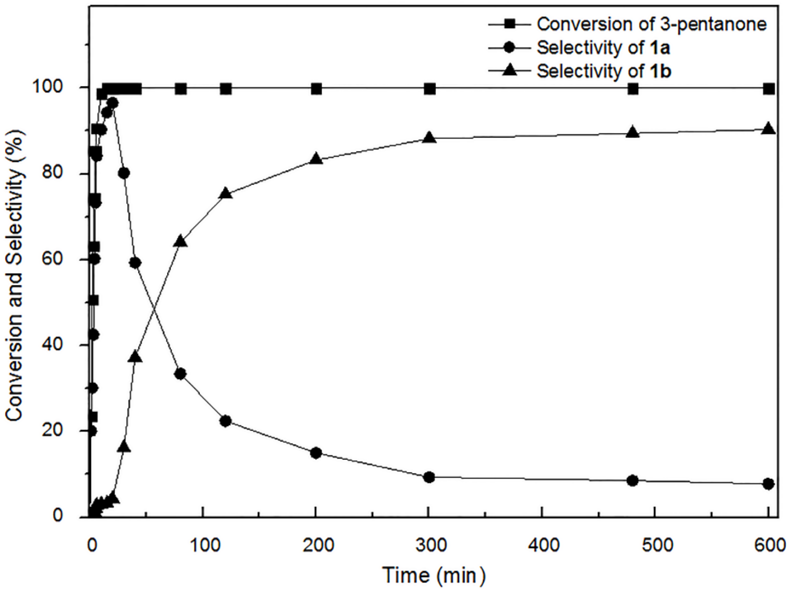
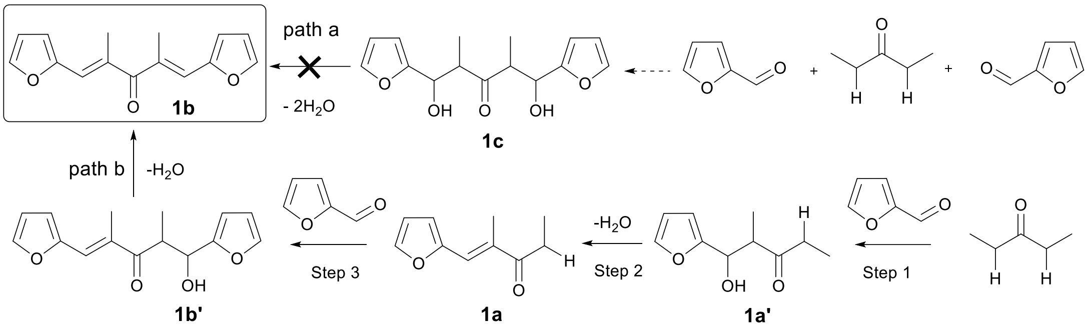


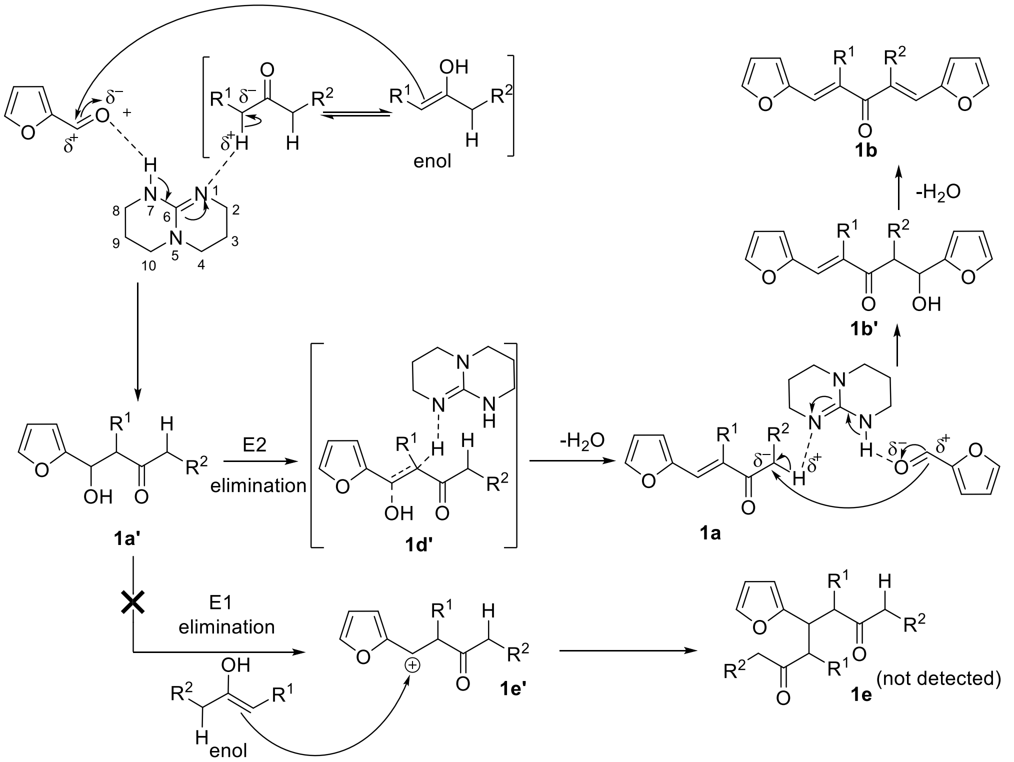
Figure 3. Results of the aldol condensation between of furfural with 3-pentanone catalyzed by TBD. Reaction conditions: furfural (25 mmol) and 3-pentanone (10 mmol) catalyzed by TBD (1 mmol) without solvent at 600 stirring speed under air conditions at room temperature.

To understand the reaction pathway of the **1b** formation, the kinetic curves of the reaction are presented in Figure 3. Following the reaction with time, two main compounds, single condensation product **1a** and double condensation product **1b** were detected during the reaction. As shown in Figure 3, at the initial stage of the reaction, the concentration of **1a** increases up to nearly 100 mol% yield, and then decreases after the first hour of reaction while the yield of **1b** increases, **1b** was practically not formed before all 3-pentanone was converted into **1a**, indicating the pathway of **1b** formation was not through “one-step process” (Scheme 1, path a: one molecule 3-pentanone reacted with two molecule furfural at the same time), a stepwise process (path b) was proposed in this reaction, which comprises four steps: (i) the aldol addition of one molecule 3-pentanone with one molecule furfural to afford **1a'**; (ii) the single aldol condensation product **1a** was produced through dehydration of **1a'**; (iii) the aldol condensation of **1a** with one molecule furfural to afford **1b'**; (iv) dehydration of **1b'** to obtain the desired difuryl product **1b**. As also can be inferred from Figure 3, the generation rate of **1b** was much slower than **1a**, and the dehydration precursors **1a'** and **1b'** was never detected during the reaction, indicating that the step 3 can be considered as the rate-determining step of this reaction.



Scheme 1. The reaction pathway of the formation of **1b**.

A plausible catalytic mechanism of TBD is depicted in Scheme 2. N1 in TBD first induced the deprotonation of α-H from 3-pentanone to form enol. This intermediate state acted as a carbonyl donor to attack furfural to produce **1a'**, which then dehydration via E2 elimination to generate the single condensation **1a**. If the dehydration is E1 elimination, the corresponding carbocation **1e'** would serve as nucleophilic receptor to react with enol to afford product **1e**. However, **1e** was not detected during the reaction according to the GC-MS. The regenerated TBD then reacts with **1a** to provide another enol intermediate, which undergoes similar reaction process to produce the difuryl product **1b**. Furthermore, TBD could also activate the furfural to promote the above process due to the H-N7 in TBD increases the positive charge of the homologous carbon atom through hydrogen-bonding synergism. Thus, TBD served as a bi-functional catalyst during the reaction, which not only promotes the deprotonation process (the role of N1 in TBD), but also motivates the furfural by generating hydrogen-bonding synergism (the role of H-N7 in TBD), that can be used to explain why TBD has better catalytic activity than DBU. To confirm this point, the control experiment was conducted under the same reaction conditions using 7-methyl-1,5,7-triazabicyclo [4.4.0] dec-5-ene (MTBD) as a catalyst. The basicity of MTBD (pK_a = 24.97) is similar to TBD (pK_a = 24.70),[37] however, the hydrogen atom in N7 position of MTBD is replaced by methyl group, which means it cannot form the hydrogen-bonding network with furfural. As can be seen from Table 1, entries 8 and 10, a sharply decreased catalytic activity of MTBD was observed compared to the TBD. Thus, the reaction pathway catalyzed by TBD was not merely base-catalyzed condensation, a synergistic catalysis effect was believed to occur during the reaction.



Scheme 2. Tentative mechanism for the aldol condensation of furfural with 3-pentanone catalyzed by TBD.

Aldol condensation of 3-pentanone with furfural in flow system

Based on the results of "in-flask" experiments, "in flow system" experiments were then carried out also using furfural and 3-pentanone for comparison. One of the chief concerns in the fluidic experiment is the formation of solids in the reactor, which could block the slit plate mixer and tubing reactor. Thus, a significant challenge of converting batch conditions into a flow process is the poor solubility of double aldol condensation products in common organic solvents. Hence, we first examined the effects of solvents under the present flow system. As can be seen from Table 2, the property of the solvent plays a significant role in this system, for example, using THF, EtOAc or CH_2Cl_2 as the solvent was not successful for this reaction, which is due to the poor solubility of TBD in EtOAc, and poor solubility of double aldol condensation product in CH_2Cl_2 or THF, respectively. Hence, the solvent used in this reaction should dissolve all of the components of the reaction: substrate, single aldol condensation product, double aldol condensation product, and the catalyst TBD. Among the tested solvents, MeOH meets the above conditions, however, methanol could reacted with furfural catalyzed by TBD to afford the corresponding etherification by-product (Figure S2). After further screening, to our delight, we found a mixed solvent of methanol and water could inhibit this side reaction effectively. In the case of using MeOH-H_2O (v/v = 1/1) as the solvent, the desired double condensation product **1b** was obtained in 87% yield (Table 2, entry 6, Figure S6). It is worth mentioning that the reaction time in flow system was reduced dramatically, which only need 20 min to complete the reaction, and that is diminished about 6-fold compared to the batch system (Table 1, entry 6). Furthermore, under batch synthesis conditions, side reactions such as resinification of furfural, Cannizaro reaction, and Michael addition to the formed enol intermediate may happen during the reaction.[38,39] In order to obtain the double condensation product **1b**, over-dose of furfural (at least 2.5 equiv. to 3-pentanone) has to be used in the reaction. However, these side reactions were effective suppressed under the present flow system, and the dosage of furfural could be decreased to its theoretical ratio (2 equiv.) without loss of yield of **1b** (Table 2, entry 6), which clearly demonstrated the advancement of the present system. Furthermore, similar to the batch reaction, the selectivity of this reaction could be also easily regulated by adjusting the molar ratio of substrates, when the reaction was conducted at the molar ratio of 3-pentanone/furfural is 1, the yield of single condensation product **1a** increases up to 91% (Table 2, entry 7, Figure S6), which means the present flow system did not change the intrinsic kinetics of the reaction. For product separation and recovery of TBD catalyst, the method is very simple and easy. TBD is completely soluble in water, but has poor solubility in EtOAc (Figure S3), which could be beneficial since it provides a convenient method to separate the catalyst and the products. After the reaction, using EtOAc to extract the mixture resulted in the separation between the condensation products and the catalyst TBD.

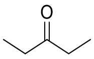
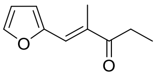
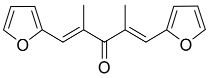
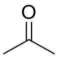
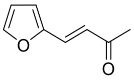
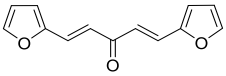
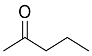
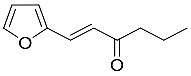
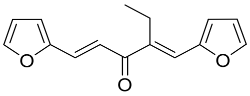
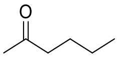
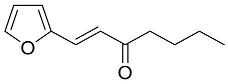
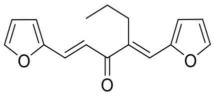
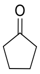
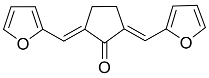
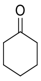
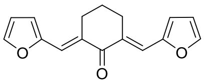
Table 2. Optimization of double aldol condensation of 3-pentanone with furfural catalyzed by TBD under flow system.[a]

Entry	Solvent	Ratio (Furfural: 3-pentanone:TBD)	Flow rate (mL/min) (Stream 1:2)	Time (min)	Yield (%)	
					1a	1**b**
1	THF	6.25M:2.5M:0.25M	0.2:0.2	20	51	34
2	CH_2Cl_2	6.25M:2.5M:0.25M	0.2:0.2	20	31	23
3	EtOAc	6.25M:2.5M:0.25M	0.2:0.2	20	14	7
4	MeOH	6.25M:2.5M:0.25M	0.2:0.2	20	13	78
5	MeOH-H_2O	6.25M:2.5M:0.25M	0.2:0.2	20	7	89
6	MeOH-H_2O	5M:2.5M:0.25M	0.2:0.2	20	5	87
7	MeOH-H_2O	2.5M:2.5M:0.25M	0.2:0.2	20	91	2

[a] Reaction conditions: flow reaction were run in 1.0 mm i.d. PFA (perfluoroalkoxy) tubing reactor, residence time was controlled by adjusting the flow rate at 353K unless specified otherwise.

These interesting results encouraged us to find the best reaction conditions for this system, various parameters of this reaction was then screened, such as material concentration, flow rate and reaction temperature (for more reaction details see Table S1). By retaining the whole of key parameters of this the present flow system, this procedure was applied for the synthesis of various fuel precursors using micro-flow system (MFS in Table 3). The batch synthesis system under similar reaction conditions was also applied for the comparative purposes (Batch in Table 3). As shown in Table 3, compared to the batch condition, the reaction time under the present flow system are declined significantly, which probably due to the high heat and mass transfer efficiency of MFS (Figure S23). Most substrates underwent smooth

Table 3 Synthesis of fuel precursors catalyzed by TBD under Batch or MFS System.

Entry	Substrate	Product	Method[a]	*T* (K)	Time (min)	Yield (%)
1	 3-pentanone	 1-(furan-2-yl)-2-methylpent-1-en-3-one (**1a**)	MFS	353	20	91
			Batch	353	240	92
2		 1,5-di(furan-2-yl)-2,4-dimethyl-penta-1,4-dien-3-one (**1b**)	MFS	353	20	87
			Batch	353	600	89
3	 Acetone	 1-(furan-2-yl)pent-1-en-3-one (**2a**)	MFS[b]	R.T.	10	86
			Batch[b]	R.T.	120	81
4		 1, 5-di(furan-2-yl)-penta-1,4-dien-3-one (**2b**)	MFS	R.T.	20	92
			Batch	R.T.	480	90
5	 2-pentanone	 1-(furan-2-yl)hex-1-en-3-one (**3a**)	MFS	333	20	90
			Batch	333	240	90
6		 1-(furan-2-yl)-4-(furan-2-yl-methylene)hex-1-en-3-one (**3b**)	MFS	353	40	82
			Batch	353	1400	86
7	 2-hexanone	 1-(furan-2-yl)hept-1-en-3-one (**4a**)	MFS	353	20	90
			Batch	353	240	94
8		 1-(furan-2-yl)-4-(furan-2-yl-methylene)hept-1-en-3-one (**4b**)	MFS	353	40	72
			Batch	353	1400	80
9[c]	 Cyclopentanone	 2,5-bis(furan-2-ylmethylene) cyclopentan-1-one (**5b**)	MFS	R.T.	5	91
			Batch	R.T.	240	92
10[c]	 Cyclohexanone	 2,6-bis(furan-2-ylmethylene) cyclohexan-1-one (**6b**)	MFS	R.T.	5	90
			Batch	R.T.	240	93

[a] For the detailed reaction conditions see support information. [b] Acetone was used as the solvent for both MFS and Batch conditions. [c] CH_2Cl_2 was used as the solvent for this reaction due to the poor solubility of products in $MeOH$-H_2O system.

transformation to afford the corresponding mono- or difuryl products in moderate to excellent yields. For aliphatic straight-chain compounds, the reaction reactivity decreased with the increase of carbon chain length, and the reaction of symmetric carbonyl compound is relatively easy to those asymmetric compounds, and the following order of substrate reactivity was observed: acetone > 3-pentanone > 2-pentanone > 2-hexanone (Figure S24). This phenomen on can be explained by the steric effect, the longer alkyl side chain may prevent the carbonyl donor to attack enol, and hence reduced the reaction efficiency.

Together with the satisfying results with aliphatic straight-chain compounds, the yields of double condensation product produced from the reaction of naphthenone are also quite high (Table 3, entries 9-10). It is well known that cyclic alkanes is another important constituent which are used with the mass percentage of 20-50 wt% in the military and commercial jet fuels.[40,41] Cyclic alkanes usually have higher volumetric heating values and energy density compared with straight alkanes due to their strong ring strain.[42-44] But it also should notice that single condensation products are hard to get under the present flow system even under the condition of using excess naphthenone. Double aldol condensation of naphthenone was the main reaction under such conditions, which probably due to the high reactivity of naphthenone. Similar situation was also occurred under the batch conditions, and that is in accord with previous report.[43]

CONCLUSION

In conclusion, TBD was found to be a highly efficient and recyclable organic base catalyst for the aldol reaction of furfural with carbonyl compounds. With the aid of flow technology, a rapid, efficient and promising route for the continuous synthesis of various alkane fuel precursors is presented. This study provides a new general strategy for the production of fuel precursors using liquid biomass platform compounds. Further studies on the continuous production of renewable fuels by nonseptate combination between flow equipment (for C-C coupling) with fixed bed (for hydrodeoxygenation) are currently underway in our laboratory.

ASSOCIATED CONTENT

Supporting Information

Experimental details including reaction procedures and full spectral characterization of all compounds (^{1}H NMR, ^{13}C NMR, GC-MS). This material is available free of charge via the Internet at ACS Publications website.

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Notes

The authors declare no competing financial interest.

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