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Title: Making JP-10 Superfuel Affordable with Lignocellulosic Platform Component

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Making JP-10 Superfuel Affordable with Lignocellulosic Platform Component

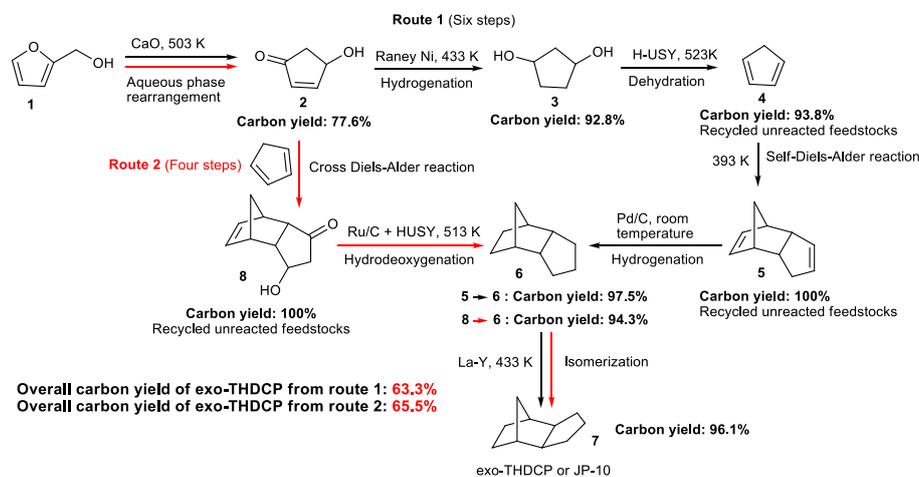
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Dedicated to the 70th anniversary of Dalian Institute of Chemical Physics, Chinese Academy of Sciences

Abstract: The synthesis of renewable jet fuel with lignocellulosic platform components has drawn a lot of attention in recent years. So far, most of work was concentrated on the production of conventional jet fuels. JP-10 is an advanced jet fuel which is obtained from fossil energy nowadays. Due to its excellent properties, JP-10 has been widely used in military aircraft. However, the high price and low availability limit its application in civil aviation. Here, we reported a new strategy for the synthesis of bio-JP-10 fuel with furfuryl alcohol which has been produced in industrial scale with agricultural and forestry residues. Under the optimized conditions, high overall carbon yields (~65%) of bio-JP-10 fuel were achieved. A preliminary economic analysis indicates that the price of bio-JP-10 fuel can be greatly decreased from ~7,091 US\$/ton (by fossil route) to less than 5,600 US\$/ton using our new strategy. This work makes the practical application of bio-JP-10 fuel in sight.

With the increase of social concern about renewable energy and CO₂ reduction, the utilization of biomass as an alternative feedstock for fuels^[1] and chemicals^[2] has drawn tremendous attention. Lignocellulose is the cheapest and the most abundant biomass. Jet fuel is one of the three important transportation fuels. During the past decade, many routes have been developed for the synthesis of bio-jet fuel with lignocellulosic platform components.^[3] However, most of the literature work was concentrated on the production of conventional jet fuels. JP-10 fuel (*i.e.* *exo*-tetrahydrodicyclopentadiene) is a single component advanced jet fuel

which has been considered as a superfuel for military jets, missiles, and supersonic combustion ramjets.^[4] Compared with conventional jet fuels, JP-10 fuel has many attractive properties (such as high-energy density, good thermal stability, low freezing point, *etc.*). For example, the higher density of JP-10 fuel makes it have a higher volumetric heat (39.6 MJ/L) than those of conventional jet fuels (~34.8 MJ/L). In practical application, it can increase the flight range and/or payload of aircraft without changing the volume of oil tank. This is advantageous for long-distance flight because it can save the travel time and decrease the CO₂ emission during the taking off and landing of airplanes.^[5] Nowadays, the JP-10 fuel is produced with cyclopentadiene which was obtained at low yields from coal tar (10–20 g/ton) or by the steam cracking of naphtha (~14 kg/ton).^[6] Moreover, the high price (~7,091 US\$/ton) of JP-10 fuel also limited its application in civil aviation.^[7] Therefore, it is highly desirable to develop some technologies for the synthesis of bio-JP-10 fuel with more available feedstocks.



Scheme 1. Strategy for the synthesis of bio-JP-10 fuel with furfuryl alcohol.

Furfuryl alcohol is a bulk chemical which has been produced in industrial scale with agricultural and forestry residues. Herein, we developed a new strategy for the synthesis of bio-JP-10 fuel with furfuryl alcohol (Scheme 1). To explore the possibility for its future application, we also conducted a preliminary economic analysis to this strategy.

First of all, we synthesized bio-JP-10 fuel with furfuryl alcohol by the route 1 in Scheme 1. This process contains six steps: aqueous phase rearrangement of furfuryl alcohol (1) to 4-hydroxy-cyclopent-2-enone (2), hydrogenation of 2 to 1,3-cyclopentanediol (3), dehydration of 3 to cyclopentadiene (4), self-Diels-Alder reaction of 4 to dicyclopentadiene (5), hydrogenation of 5 to endo-tetrahydro-dicyclopentadiene (6), and isomerization of 6 to exo-tetrahydro-dicyclopentadiene (*i.e.*

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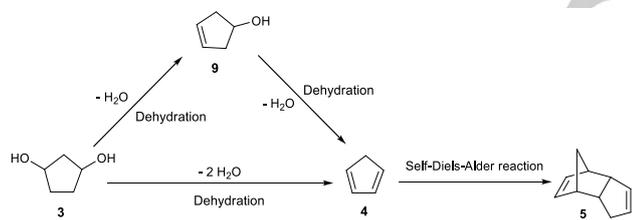
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bio-JP-10 fuel or 7).

The first two steps were carried out by the methods which have been reported in our previous work.^[8] Under the optimized reaction conditions, high carbon yields of **2** (77.6%) and **3** (92.8%) were achieved over the commercially available CaO and Raney Ni catalysts, respectively (see supporting information). The dehydration of **3** was carried out over solid acid catalysts using a fixed-bed reactor. According to our analysis, **4**, **5** and cyclopent-3-enol (*i.e.* **9**) were identified as the products from this reaction. The reaction pathways for the generation of **4**, **5** and **9** from the dehydration of **3** were proposed in Scheme 2. From the results illustrated in Table 1, it was found that H-USY, H-ZSM-5 and H- β zeolites exhibited higher activity than that of amorphous SiO₂-Al₂O₃. Based on the NH₃-TPD and NH₃ chemisorption results illustrated in Figure 1 and Table 2, this phenomenon can be explained by the stronger acidity of zeolite catalysts than that of SiO₂-Al₂O₃. Over H-USY, 58.4% carbon yield of **4** was achieved under the investigated conditions. After being separated with **4** by distillation, the partially dehydrated product (*i.e.* **9**) and residual **3** was used again as the feedstock for the second dehydration. Under the same reaction conditions, high carbon yield of **4** (94.9%) was obtained (Table 1). This means 93.8% carbon yield of **4** can be achieved by the dehydration of **3** over H-USY zeolite (the calculation method was shown in Figure S1 note). The stability of H-USY in the dehydration of **3** was evaluated as well. During the 24 h continuous test, the carbon yield of **4** over H-USY decreased from 58.4% to 40.9% (Supplementary Figure S1), which may be explained by the carbon deposition generated during the reaction.



Scheme 2. Reaction pathways for the generation of different products from the dehydration of **3**.

Table 1. Carbon yields of **4**, **5** and **9** from the dehydration of **3** over solid acid catalysts.^[a]

Catalyst	Conversion of 3 [%]	Carbon yield [%]			Carbon balance [%]
		4	5	9	
SiO ₂ -Al ₂ O ₃	26.0	4.6	0	4.0	82.6
H-USY	92.4	58.4	0.7	20.2	86.9
H- β	99.9	53.1	0	41.6	94.8
H-ZSM-5	99.0	57.6	0	35.3	93.9
H-USY ^[b]	97.6	94.9	0.2	1.2	98.7

[a] Reaction condition: 523 K, 0.1 MPa; 2.5 wt% **3** in tetrahydrofuran (THF) flow rate: 0.04 mL/min, N₂ flow rate: 120 mL/min, 0.15 g catalyst was used in each test. [b] The partially dehydrated product (*i.e.* **9**) and residual **3** were recycled and used again as feedstock for the second dehydration.

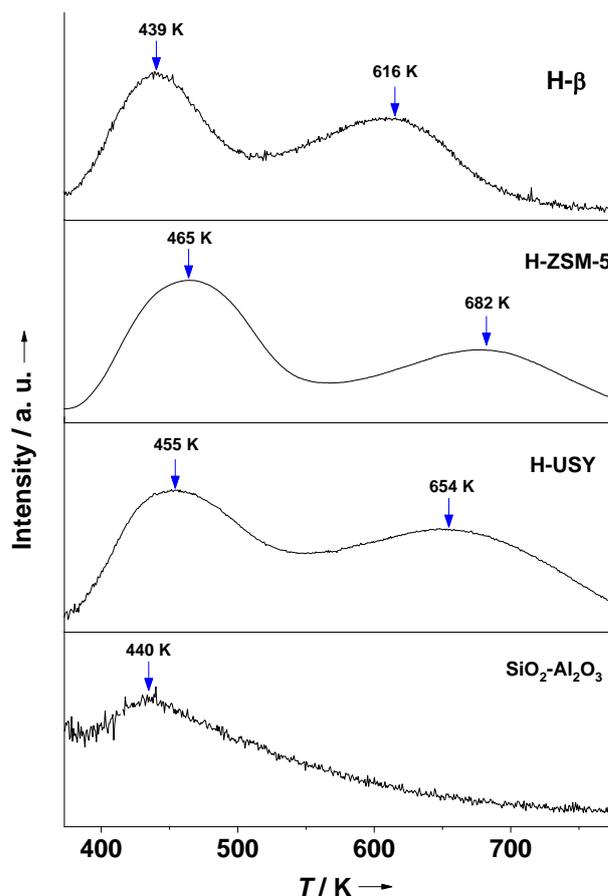


Figure 1. NH₃-TPD profiles of the solid acid catalysts.

Table 2. Acid amounts of solid acid catalysts.

Catalyst	Acid amount [mmol/g] ^[a]	Weak acid amount [mmol/g] ^[b]	Strong acid amount [mmol/g] ^[c]
SiO ₂ -Al ₂ O ₃	0.151	0.151	0.000
H- β	0.391	0.202	0.189
H-ZSM-5	1.089	0.669	0.420
H-USY	1.087	0.534	0.553

[a] Measured by NH₃ chemisorption. [b] Calculated according to the NH₃ desorbed at the temperatures lower than 523 K. [c] Calculated based on the NH₃ desorbed at the temperatures higher than 523 K.

Cyclopentadiene is widely used in the production of a variety of chemicals and fuels.^[4,6] To the best of our knowledge, this is the first report about the synthesis of renewable cyclopentadiene with lignocellulose derived feedstock.

The self-Diels-Alder reaction of **4** to **5** can take place spontaneously. After reacting at 393 K for 2 h, 95.5% of **4** was converted to **5** without using any catalyst (Supplementary Table S1). The residual cyclopentadiene can be easily recycled. Therefore, the theoretical yield of **5** from this reaction can reach 100%. The synthesis of **7** with **5** or **6** has been reported by literature.^[9] The hydrogenation of **5** is a two-step reaction which can occur very easily. First, a C=C bond in **5** is saturated, which

leads to dicyclopentene (**10**, Table S2). Subsequently the **10** is further hydrogenated to **6**. After reacting at room temperature under 4 MPa H₂ for 3 h, a high carbon yield (97.5%) of **6** was obtained (Supplementary Table S2). According to our measurement, **6** has high density (0.894 g/mL). Therefore, it can be potentially used as additive to improve the volumetric heat value of current jet fuels. However, it can't be used as a single component advanced jet fuel due to its high freezing point (350 K).^[10] To overcome this problem, **6** has to be further isomerized to **7** which has much lower freezing point (194 K).^[11] The isomerization reaction was carried out over La-Y zeolite under solvent-free conditions. After reacting at 433 K for 4 h, a high carbon yield (96.1%) of **7** was achieved (Supplementary Table S3). Besides **7**, small amount of adamantane (**11**) was also identified in the products. This is consistent with what has been reported by literature over other catalysts.^[12] Based on the above results, the overall carbon yield of bio-JP-10 fuel from furfuryl alcohol by route 1 was estimated as 63.3%.

As another option (route 2), we first reported the synthesis of bio-JP-10 fuel with furfuryl alcohol and the cyclopentadiene (*i.e.* **4** in Figure 1) which can be derived from either fossil routes or bio-route (*i.e.* route 1). This process contains four steps: aqueous phase rearrangement of **1** to **2**, cross Diels-Alder reaction of **2** with **4** to produce 3-hydroxy-2,3,3a,4,7,7a-hexahydro-1H-4,7-methanoinden-1-one (*i.e.* **8** in Figure 1), hydrodeoxygenation (HDO) of **8** to **6**, and isomerization of **6** to **7**.

The cross Diels-Alder reaction of **2** with the **4** that can be obtained in this work (by bio-route) was carried out in a batch reactor at the initial **2/4** molar ratio of 1:1 (see Figure 2). After the reaction was conducted at room temperature and atmospheric pressure for 12 h, 48.7% carbon yield of **8** was achieved in the absence of catalyst. By extending the reaction time to 72 h, 75.0% carbon yield of **8** was reached. Meanwhile, **5** was also obtained in carbon yield of 19.3% (by the self-Diels-Alder reaction of **4**).

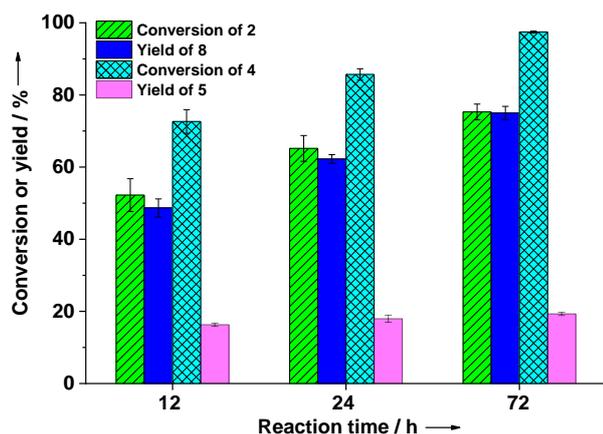
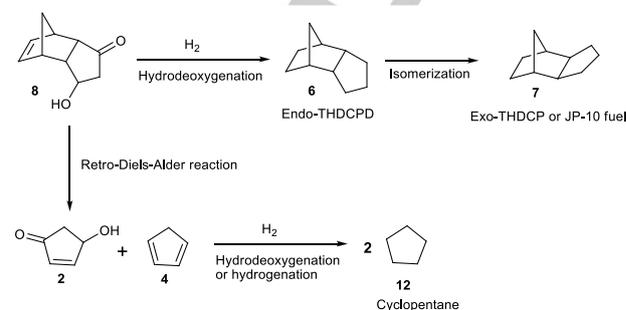


Figure 2. Conversions of substrates and the yields of different products from the reaction of **2** and **4** at room temperature and atmospheric pressure. Reaction condition: 393 K, 0.6 g **2**, 1.0 g or 0.45 g mixture of **4** and **5** (contains 92 wt% of **4** and 8 wt% of **5**) and 0.2 g decalin were used for each test.

When we doubled the amount of **4** in the feedstock, higher carbon yield (85.3%) of **8** was obtained after the reaction was carried out at room temperature for 72 h (Supplementary Table S4 and Figure S2). The cross Diels-Alder reaction of **2** with **4**

can be accelerated by increasing the reaction temperature. For example, ~60% carbon yield of **8** could be achieved after the reaction was carried out at 353 K for 1 h (Supplementary Table S4). By recycling the unreacted **2** in the feedstock, the theoretical yield of **8** can reach 100%.

Table 3. Carbon yields of different compounds from the HDO of **8**.^[a]



Reaction temperature [K]	Conversion of 8 [%]	Carbon yield [%]			Carbon balance [%]
		6	7	12	
473	100	6.2	0.0	0.7	6.9
493	100	12.4	0.0	1.1	13.5
513	100	64.1	8.4	1.8	74.3
513 ^[b]	100	84.8	9.5	1.8	96.1

[a] Reaction condition: 4 MPa H₂, 2 h; 200 mg **8**, 30 mg 5 wt% Ru/C, 50 mg H-USY zeolite (SiO₂/Al₂O₃ molar ratio = 12:1), 28 g cyclohexane, 0.3 g decalin were used in each test. [b] Reaction condition: 4 MPa H₂, 4 h; 200 mg **8**, 30 mg 5 wt% Ru/C, 50 mg H-USY zeolite (SiO₂/Al₂O₃ molar ratio = 12:1), 28 g cyclohexane, 0.3 g decalin were used in each test.

Subsequently, the **8** as obtained was hydrodeoxygenated to **6** under the co-catalysis of Ru/C and H-USY. After reacting at 513 K and 4 MPa H₂ for 4 h, **8** was completely converted and a high total carbon yield (94.3%) of **6** and **7** was achieved (Supplementary Table S5). Under the catalysis of La-Y, **6** can be easily converted to **7** (or bio-JP-10 fuel) in a carbon yield of 96.1% (Entry 4, Supplementary Table S3). Based on the experimental results we obtained in this work, the overall carbon yield of bio-JP-10 fuel by the route 2 was estimated as 65.5%.

Finally, we also conducted a preliminary economic analysis for the two routes we developed and compared them with the conventional fossil route (Supplementary Figures S4-S5 and Tables S5-S21). The process flow diagram was simulated by Aspen Plus V8.8, assuming the plant capacity is 10 kiloton bio-JP-10 per year and the working time is 8,000 h per year. The energy was supplied by steam at the price of 18 US\$/ton (see Tables S7, S13, S18). The overall carbon yields of bio-JP-10 fuel by the route 1 and route 2 are 63.2% and 64.7%, respectively. These yields are slightly lower than the overall carbon yields shown in Scheme 1, which is due to the loss of the product during the separation process.

According to the current unit price of furfuryl alcohol (~1,500 US\$/ton), the unit production costs for bio-JP-10 fuel produced by route 1 and route 2 were estimated as 5,031 US\$/ton and 5,538 US\$/ton (see Figure 3), respectively. These values are lower than the price of JP-10 fuel (~7,091 US\$/ton) derived from

fossil energies. Therefore, we believe that the production of bio-JP-10 fuel is economically possible. In fact, the situation will be even better with the technological innovation of furfural production. In the recent work of Huber *et al.*,^[13] a cost-effective technology was developed. It was proposed that the furfuryl alcohol unit price can be greatly decreased to ~400 US\$/ton by the utilization of their new process. Based on this information, the future unit production costs for bio-JP-10 fuel by route 1 and route 2 can be decreased to 2,547 US\$/ton and 2,887 US\$/ton, respectively. These prices are about 2-3 times of conventional jet fuel (or the same level as other current bio-jet fuels). However, they are much lower than the current price of JP-10 fuel (~7,091 US\$/ton). Therefore, we believe that the future commercialization of bio-JP-10 fuel is very promising especially taking policy support and exemption of CO₂ emission tax into consideration.

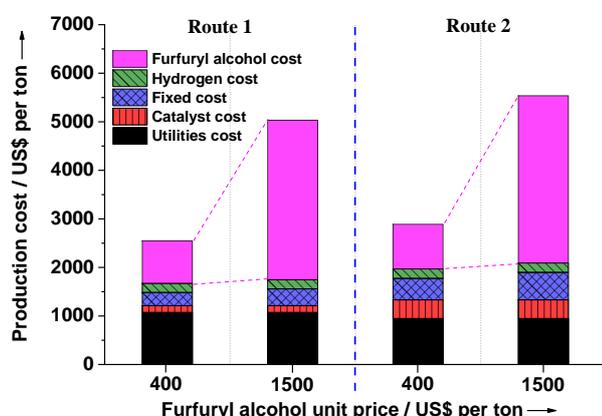


Figure 3. Production costs of bio-JP-10 fuel by route 1 and route 2 at different furfuryl alcohol unit prices. The definitions and calculation methods of different costs were given in Tables S11 and S22.

In summary, we reported two routes for the synthesis of bio-JP-10 fuel with furfuryl alcohol. Both routes have their own features. For example, the last three steps of route 1 are same as what were used in conventional route for the production of JP-10 fuel. Therefore, it is possible to use the conventional facility for the production of bio-JP-10 fuel. Furthermore, the cyclopentadiene produced in route 1 can also be used as a chemical or feedstock for the production of other high-density jet fuels (such as RJ-5, RJ-7, *etc.*). In contrast, route 2 has fewer steps (4 steps vs. 6 steps) than route 1. Moreover, route 2 is economically more flexible. Based on the price of feedstock, we can either choose the cyclopentadiene from fossil resources or use the one from biomass to produce the JP-10 fuel with lower cost. A preliminary analysis indicates that the two routes developed in this work are economically advantageous than the conventional one. This work makes the practical application of bio-JP-10 fuel in sight.

Acknowledgements

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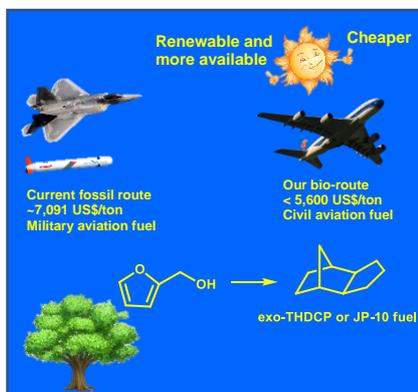
Keywords: Lignocellulose • jet fuel • JP-10 • furfuryl alcohol • cost-effective

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Entry for the Table of Contents

RESEARCH ARTICLE

A new strategy was first reported for the synthesis of bio-JP-10 fuel with furfuryl alcohol which has been produced in industrial scale with agricultural and forestry residues. Compared with the conventional fossil route, the new synthetic strategy has evident advantage at lower cost and higher feedstock availability.



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