Green Chemistry

PAPER

View Article Online
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Cite this: *Green Chem.*, 2019, **21**, 6326

Catalyst-free synthesis of biodiesel precursors from biomass-based furfuryl alcohols in the presence of H_2O and air†

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Received 10th September 2019,
Accepted 19th October 2019

DOI: 10.1039/c9gc03179k

rsc.li/greenchem

Production of biodiesel from biomass resources usually requires elongation of carbon numbers from typical C_5 and C_6 platform molecules through C–C coupling reactions, which were catalyzed by acid, base or metal catalysts traditionally. Herein, a catalyst-free method was developed to produce bis(furan-2-yl)methane derivatives (BFMs) from furfuryl alcohol derivatives (FAs) in the presence of H_2O and air without any other additional catalysts. An 81% yield of bis(5-methylfuran-2-yl)methane (BMFM) can be obtained from 5-methylfurfuryl alcohol (5-MFA) and a 59% total yield of C_{11} biodiesel was obtained from 5-methylfurfural (5-MF). In addition, a H_2O and air mediated free radical decarboxylation mechanism was proposed based on the detailed mechanistic studies. This strategy offers a green, low-cost and environmentally friendly approach to synthesize biodiesel precursors from biomass based platform molecules.

Introduction

Transportation fuels and chemicals are mainly resourced from non-renewable fossil resources, such as crude oil, coal and natural gas, which may be unavailable in the future due to their unsustainability.[1–3] Therefore, it is urgent to explore sustainable resources as replacements. As a low-cost, abundant and renewable resource, biomass is an ideal alternative to fossil resources, which has received widespread attention in recent years.[4–6] Many furan derivatives can be efficiently obtained from cellulose and hemicellulose,[7] the major components of biomass, such as 5-hydroxymethylfuran (5-HMF),[8,9] furfural,[10–12] and 5-methylfurfural (5-MF),[13–17] which are platform molecules for the production of other value-added chemicals to be used in the polymer, agricultural, and pharmaceutical industries.[18–20]

One of the most important applications of the furan derivatives is as a rich carbon source for the production of biofuels *via* further hydrodeoxygenation reaction. Direct hydrodeoxygenation of furan derivatives can only provide C_5–C_6 biogasoline candidates.[21–25] Biodiesel production from biomass is another important research area. Biodiesel, a common fuel with a high heat value, containing long linear, branched, and cyclic C_9–C_{20} alkanes, can be produced from the furan derivatives by the carbon chain elongation reaction.[26] Lately, varieties of methods have been developed to elongate the carbon chains of furan derivatives to prepare biodiesel precursors, such as aldol condensation,[27–32] hydroxyalkylation/alkylation[26,33–37] and C–C coupling.[38] For example, the Ouyang group[28] used a basic ionic liquid as a base catalyst for aldol condensation of furfural with acetoin, and 78% yield of the condensation product was obtained (Scheme 1a). Pioneering studies by Corma,[33,39] Zhang,[35,36] and Rode[37] have achieved excellent results with high dimer product yields by reacting aryl or alkyl aldehyde compounds with 2-methylfuran using an acid catalyst (Scheme 1b). Recently, a new method to increase the chain length was reported by the Wang group,[38] which can coproduce biodiesel precursors and H_2 from lignocellulose-derived 2-methylfuran and 2,5-dimethylfuran *via* acceptorless dehydrogenative C–C coupling driven by visible light over a Ru-doped $ZnIn_2S_4$ catalyst (Scheme 1c). However, most of these methods use acid, base or noble metals as the catalyst, which leads to the corrosion and pollution problems and thus high production cost.

Here, we developed an efficient catalyst-free method to synthesize bis(furan-2-yl)methane derivatives (BFMs) as biodiesel precursors from furfuryl alcohol derivatives (FAs), which can be obtained in large quantities from biomass-lignocellulose[40]

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9gc03179k

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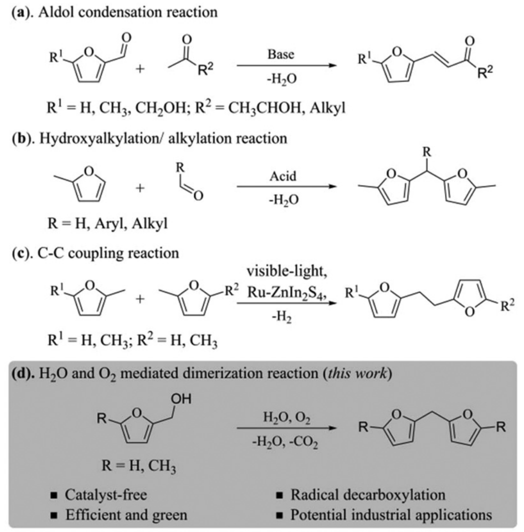


Scheme 1 Biodiesel precursors from biomass-based derivatives.

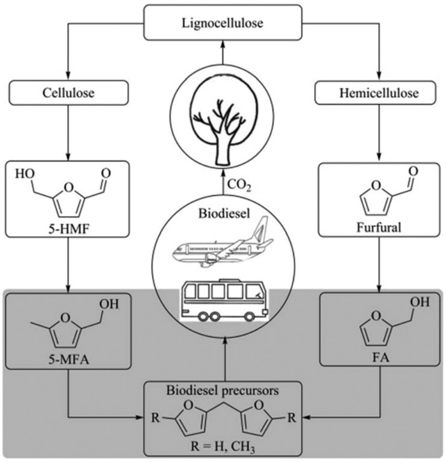
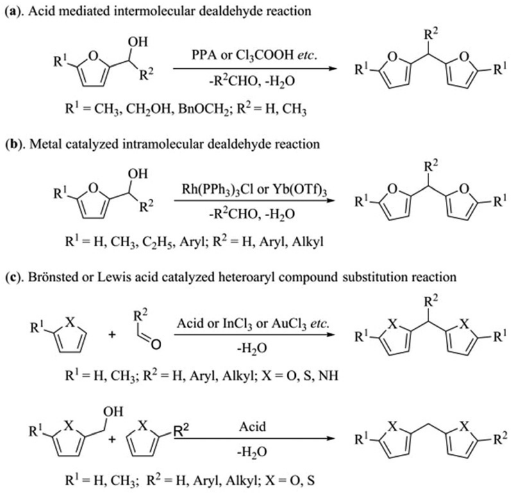


Fig. 1 Pathway for preparing biodiesel precursors from lignocellulose.

(Fig. 1). The reaction conditions are mild and green without additional catalysts or reagents. Only H_2O and air were proved to be necessary in this process (Scheme 1d). In addition, a radical decarboxylation mechanism was proposed by further mechanistic study.

Besides being used as biodiesel precursors, BFMs can be directly used as a valuable odorant and monomer for the preparation of sensors for ion-selective chromatography,[41] a dielectric material by furan/imide Diels–Alder polymers,[42] and a useful intermediate in organic synthesis.[43,44] There are several methods reported for the production of BFMs. BFMs can be obtained by the self-condensation of FAs followed by elimination of an aldehyde catalyzed by an acid.[45–49] For example, the Balaban group[45] reported that high-yield (80–82%) BFMs were produced from FAs with polyphosphoric acid (PPA) in aqueous acetone (Scheme 2a). The Dzhemilev group[41] found that furfuryl alcohol (FA) can provide an 80% yield of bis(furan-2-yl)methane (BFM) with the corresponding amount of formaldehyde over the $Rh(PPh_3)_3Cl$ catalyst. Ramasastry and co-workers[50] developed a method for the self-condensation of FAs followed by elimination of an aldehyde to generate BFMs by using the $Yb(OTf)_3$ catalyst (Scheme 2b). Other bis(heterocyclyl)methane derivatives (BHCMs) were synthesized by the hydroxyalkylation/alkylation of heteroaryl compounds with aldehydes or ketones over Lewis or Brønsted acids, or by the electrophilic substitution between heteroaryl methanol derivatives and another heteroaryl compound with an acid catalyst[51] (Scheme 2c). Thus, our attempt to use only H_2O and air is a big advancement to the current methods for the production of BFMs.



Scheme 2 Synthesis of BHCMs from heteroaryl compounds.

Experimental section

Materials

Unless otherwise noted, all reactants or reagents were obtained from commercial suppliers and used as received without further treatment. 5-Methylfurfuryl alcohol was obtained from Energy Chemical (Shanghai, China), 9-Dingchem (Shanghai, China), and Ark (Chicago, USA). 2-Methylfuran, 5-methylfurancarboxylic acid, furfuryl alcohol, 2-furanoic acid $NaBH_4$, Pd/C (5.0 wt%), undecane, 1,2-dichloroethane, toluene and ethyl acetate were obtained from Aladdin (Shanghai, China). Isopropylmagnesium chloride, 5-methylfurfural, $SOCl_2$, CD_3OD, DMSO-D_6, $CDCl_3$ and D_2O were obtained from Inno-Chem (99.9%, Beijing, China). H-beta zeolite was obtained from Nankai University Catalyst Co., Ltd. Cyclohexane was obtained from Inno-Chem (99.5%, Beijing, China), Xilong Scientific (Shantou, China), and Tokyo Chemical Industry (Shanghai, China). Milli-Q H_2O was used in the experiments. The CHEM^{N}NS-10-C276 high pressure stainless steel reactor, temperature controller and IKA magnetic stirring apparatus were obtained from Anhui Kemi Machinery Technology Co., Ltd.

Experimental procedure

All experiments were performed in a Schlenk tube or a high pressure reactor with a magnetic stirrer. Typically, reactants (5-methylfurfuryl alcohol, 5-methylfurancarboxylic acid, furfuryl alcohol *etc.*) and solvents were added in the vessel, and then the reaction was performed at the desired reaction temperature under an air atmosphere (or filled with N_2, O_2, or their mixtures). Upon completion of the reaction, the reaction mixture was cooled down to room temperature, and the reaction mixture was analyzed by GC, GC-MS, UPLC and other necessary analytical methods. Standard solutions were used to obtain the calibration curves, and the concentrations of the compounds were calculated by the external standard method.

Analysis of the reaction mixture

The reaction mixture was collected and filtered through a 0.22 μm syringe filter. The organic phase was analyzed by GC-MS (Thermo Scientific TRACE 1310) using a chromatographic column (HP-5 capillary column: 30 m × 320 μm × 0.25 μm) and GC (Agilent 7820A gas) using a chromatographic column (HP-5 capillary column: 30 m × 320 μm × 0.25 μm). The aqueous phase was measured by UPLC (Waters, Acquity H-class) using an organic acid column (Alltech OA1000-organic acid column: 6.5 mm ID × 300 mm). The gas phase was analyzed with a top air phase model (PANNA-A91PLUS). The trace metals were measured with a Thermo Scientific 7000 series inductively coupled plasma-atomic emission spectrometer (ICP-AES). Free radical adduct product was detected by ultra performance liquid chromatography quadrupole time-of-flight mass spectrometry (UPLC-X500RQTOF), using an ACQUITY UPLC@BEH C18 1.7 μm (2.1 mm × 50 mm) column. The EPR data were obtained using a Bruker A300 spectrometer (Bruker, Germany). NMR spectra of the compounds were recorded on Bruker Advance III (400 MHz) spectrometers with tetramethylsilane as an internal standard. 5-MFA conversion and BMFM yield were calculated using the following formulae:

$$\text{5-MFA conversion} = \frac{\text{Moles of initial 5-MFA} - \text{Moles of final 5-MFA}}{\text{Moles of initial 5-MFA}} \times 100\%$$

$$\text{BMFM yield} = \frac{\text{Moles of final BMFM}}{\frac{\text{Moles of initial 5-MFA}}{2}} \times 100\%$$

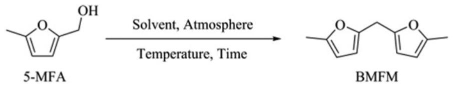
Calculation formula for reaction conversion and yield

Results and discussion

Catalyst-free process development

Initially, we envisioned to develop a catalytic process to produce bis(5-methylfuran-2-yl)methane (BMFM) as a biodiesel precursor by oxidative coupling of 5-methylfurfuryl alcohol (5-MFA), which can be easily obtained from biomass-based 5-methylfurfual (5-MF)[13–17] (Scheme S-1†). To our surprise, it was found that this process can be achieved without additional metals or acid catalysts. After extensive screening, 79% GC yield (74% isolated yield) of BMFM was obtained from 5-MFA (0.2 mmol) in a biphasic reaction system with H_2O (1.0 mL) and cyclohexane (1.0 mL) under an air atmosphere in a sealed tube at 100 °C for 2 h (Table 1, entry 1). The effects of deviations to the standard reaction conditions are listed in

Table 1 Exploration and optimization of the reaction conditions[a]



Entry	Solvent (mL) H_2O/cyclohexane	Atmosphere	Temp. (°C)	Time (h)	Conv.[b] (%)	Yield[b] (%)
1	1.0/1.0	Air	100	2	90	79(74)[c]
2	0.0/1.0	Air	100	2	26	0
3	0.018/1.0	Air	100	2	35	6
4	0.5/1.0	Air	100	2	94	71
5	2.0/1.0	Air	100	2	85	70
6	1.0/0.0	Air	100	2	95	49
7	1.0/1.0[d]	Air	100	2	80	60
8	1.0/1.0[e]	Air	100	2	85	69
9	1.0/1.0[f]	Air	100	2	84	44
10	1.0/1.0	N_2	100	2	21	4
11	1.0/1.0	O_2	100	2	94	43
12	1.0/1.0	Air	25	2	74	0
13	1.0/1.0	Air	60	2	85	36
14	1.0/1.0	Air	140	2	94	78
15	1.0/1.0	Air	100	1	90	68
16	1.0/1.0	Air	100	6	91	76
17[g]	1.0/1.0	Air	100	2	91	78
18[h]	50.0/50.0	Air	100	2	96	(81)[c]

[a] 0.2 mmol 5-MFA. [b] The conversion and yield were determined by UPLC and GC. [c] Isolated yield in parentheses. [d] 1,2-Dichloroethane. [e] Toluene. [f] Ethyl acetate. [g] The tube was covered with aluminum foil. [h] 40.0 mmol 5-MFA.

Table 1. In the absence of H_2O, no BMFM was detected (Table 1, entry 2). Thus, H_2O is crucial for this transformation. To further study the function of H_2O to be a catalyst or a solvent, five equivalents of H_2O (18 μL) instead of 1.0 mL H_2O were used for the reaction. However, only 6% yield of BMFM was produced (Table 1, entry 3). When the amount of H_2O was increased to 0.5 mL and 2.0 mL, the results were comparable to those obtained under the standard conditions (Table 1, entries 4 and 5), which proves that H_2O is required as an indispensable solvent. With only H_2O as the solvent but not as the organic solvent, the yield of BMFM is 49% (Table 1, entry 6). Thus, the addition of an organic solvent is beneficial for the reaction, probably due to the stabilization of the reaction intermediates.[52] When 1,2-dichloroethane, toluene or ethyl acetate was used instead of cyclohexane, 60%, 69% and 44% yield of BMFM was obtained, respectively (Table 1, entries 7–9), so cyclohexane was selected as the appropriate organic solvent. When N_2 was applied to replace air, only a very small amount of BMFM (4% yield) was detected (Table 1, entry 10). When O_2 was used rather than air in this reaction, the yield of BMFM decreased to 43% (Table 1, entry 11). Therefore, a moderate concentration of O_2 can promote the reaction, which will be discussed in more detail in the mechanistic study section.

The effect of reaction temperature and reaction time was also studied. At 25 °C, no BMFM was detected (Table 1, entry 12). The yield of BMFM increased to 36% at 60 °C, and 78% at 140 °C in 2 h (Table 1, entries 13 and 14). In 1 h, 68% yield of BMFM could be produced, which is slightly lower than that in 2 h (Table 1, entry 15). In addition, the BMFM yield only improved a little as the reaction time was extended to 6 h (Table 1, entry 16). Thus, the conversion of 5-MFA to BMFM is fast in this system.

To study the influence of light, the reaction without light (the tube was covered with aluminum foil) was carried out. The result was similar to that with light, which ruled out a photocatalytic mechanism (Table 1, entry 17).

The reaction was also performed on a large scale. 4.49 g (40.0 mmol) 5-MFA, 50.0 mL cyclohexane, and 50.0 mL H_2O were added into a 500 mL round bottom flask, and then refluxed for 2 h under an air atmosphere. An 81% (16.3 mmol, 2.86 g) BMFM isolated yield was obtained (Table 1, entry 18).

Confirmation of the catalyst-free process

To further verify that this reaction is a catalyst-free process, a series of control experiments were performed. The trace metals were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis on the reaction mixture after the reaction. The concentrations of metal ions in the reaction solution were all below the detection limit of the ICP-AES analysis. Thus, the catalytic effect of trace metal ions can be negligible (Table S-1†). Besides, cyclohexane, H_2O and 5-MFA from different sources (including purified 5-MFA) were used, respectively, to exclude the influence of impurities in the raw materials, and similar results were obtained (Tables S-2 and S-3†). Furthermore, the experiment was repeated with a brand new reactor, a new stirrer and ultrapure H_2O to exclude any other unexpected influences,[53] and a similar result was also obtained. In conclusion, this catalytic system is indeed a catalyst-free process.

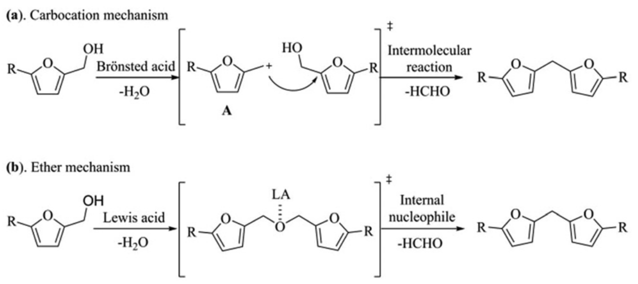
Mechanism investigation experiments

To study the reaction mechanism, the product distribution *vs.* reaction time was performed (Fig. S-1†), which showed that both the conversion and the yield are more than 50% in just 10 min at 100 °C. As a result, the reaction happened too quickly to capture any useful intermediates.

It was reported that the dimerization of furfuryl alcohol derivatives could go through two different mechanisms.[41,46,50] One is that a carbocation (compound **A**) is formed from a furfuryl alcohol derivative catalyzed by a Brønsted acid, and then the electrophilic substitution between compound **A** and the furfuryl alcohol derivative produces a dimer and an aldehyde (Scheme 3a). Another mechanism is that the furfuryl alcohol derivative undergoes etherification and then intramolecular Friedel–Crafts type reaction catalyzed by a Lewis acid (Scheme 3b), which also generates a molecule of aldehyde.

However, no HCHO was detected in the reaction liquid. We speculated that a gaseous product (CO or CO_2) could be generated. Indeed, CO_2 was detected after the reaction. Furthermore, using HCHO as the reactant, no CO_2 was detected under the same conditions. Therefore, CO_2 is directly produced from the 5-MFA dimerization process (Scheme S-2†). Thus, this reaction does not follow either carbocation or ether mechanism as reported before.

Air has been proved necessary for this reaction in the previous section, which is better than pure O_2. To further study the effect of O_2, the experiments were carried out with different proportions of N_2 and O_2 (Fig. 2). The BMFM yield



Scheme 3 Proposed mechanisms in the literature studies.[41,46,50]

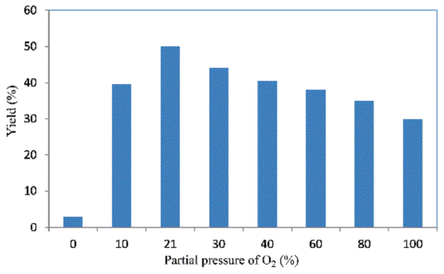
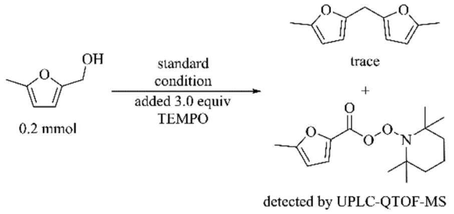


Fig. 2 Effect of O_2 partial pressure on this reaction.



Scheme 4 Free radical trapping experiments.

increased first and then decreased slowly with the increase of O_2 partial pressure, and the highest yield of BMFM was obtained (50%) as the ratio of O_2 and N_2 was around 21%. Low O_2 partial pressure had a negative effect on the BMFM yield, implying that the oxidation reaction happened during this reaction. High O_2 partial pressure may cause overoxidation of 5-MFA, leading to a decreased BMFM yield.

Knowing that this reaction requires O_2 and generates CO_2, it is most probably an oxidative decarboxylation process. As per literature search, decarboxylation under mild conditions usually follows a free radical mechanism,[54,55] so the possibility of a radical mechanism was explored. First, the radical trapping experiments were carried out. When three equivalents of the radical inhibitor 2,2,6,6-tetramethylpiperidinooxy (TEMPO) were added into the reaction under the standard conditions, the yield of BMFM dropped sharply to trace, which indicated that this transformation could undergo a free radical pathway. Besides, an addition product of the free radical intermediate (5-methylfurancarboxylic acid radical, MFCA$^{\bullet}$) and TEMPO was detected by Ultra Performance Liquid Chromatography Quadrupole Time-of-flight Mass Spectrometry (UPLC-QTOF-MS) (Scheme 4 and Fig. S-2†). Therefore, 5-methylfurancarboxylic acid (MFCA) is a possible intermediate, which can be formed by 5-MFA oxidation by O_2. The He group has also reported that benzyl alcohols can be oxidized to aromatic carboxylic acids in bis(methoxypropyl) ether with atmospheric O_2 as the oxidant.[56] In order to further probe the free radical species formed during the reaction, an electron paramagnetic resonance (EPR) study was performed (Fig. 3). Free radical signals were observed in both H_2O and cyclohexane. Therefore, the reaction has been subjected to a free radical process.

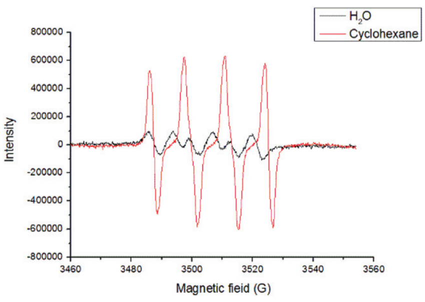
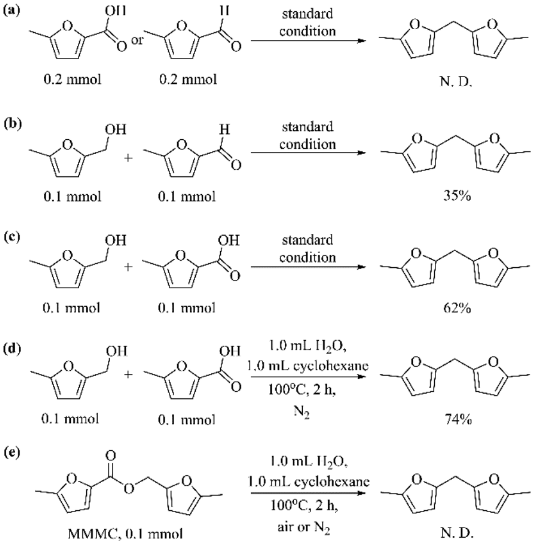


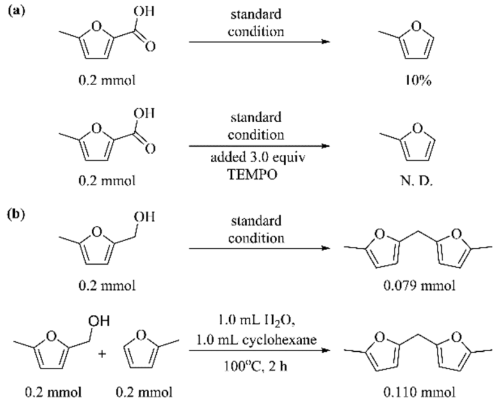
Fig. 3 EPR free radical signal detection experiments.



Scheme 5 Condensation pathway investigation experiments.

To make the condensation pathway clear, experiments with different reactants were carried out (Scheme 5). No BMFM was formed from pure 5-methylfurancarboxylic acid (MFCA) (Scheme 5a), which indicated that BMFM was not produced by the dimerization of MFCA. According to some references,[56–58] the process of converting an alcohol into an acid generally goes through an aldehyde. Thus, 5-methylfurfural (5-MF) as a substrate was also investigated under the standard conditions. No BMFM was detected either (Scheme 5a). Based on these results and considering that air is better than pure O_2, we speculated that it is probably a partial oxidation process that leads to the reaction between a molecule of alcohol and a molecule of acid.[59–61] Consequently, reactions of 5-methylfurfuryl alcohol (5-MFA) with one equivalent of 5-MF or MFCA, respectively, under standard conditions were implemented. With 5-MF, the BMFM was obtained with only 35% yield (Scheme 5b). Repeating the same sequence with MFCA resulted in the formation of 62% BMFM (Scheme 5c). Then the standard conditions were adjusted by using N_2 instead of air considering that the oxidation of alcohol is not needed anymore. A 74% yield of BMFM was obtained with an equal amount of 5-MFA and MFCA, similar to that with 5-MFA alone under the standard conditions (Scheme 5d). According to these results, it is safe to conclude that the process is a partial oxidation reaction and the condensation is between 5-MFA and MFCA. Based on the literature studies,[62,63] the dimerization of 5-MFA and MFCA may undergo esterification and then decarboxylation. However, no BMFM was detected from (5-methylfuran-2-yl)methyl 5-methylfuran-2-carboxylate (MMMC) (Scheme 5e), which excluded the ester pathway. Thus, MFCA probably undergoes decarboxylation first and then dimerization reaction happens between 5-MFA and the decarboxylation product.

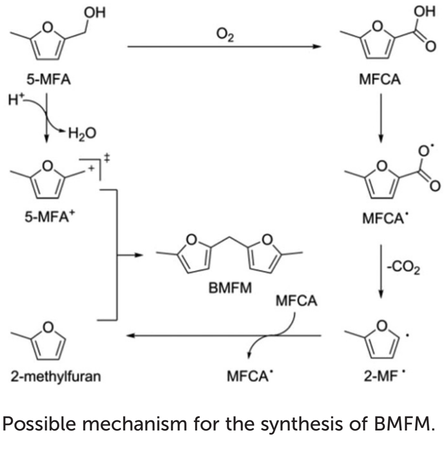
To probe the decarboxylation process of MFCA, MFCA was used as a reactant under the standard conditions, and 10% of



Scheme 6 MFCA decarboxylation and 2-methylfuran intermediate experiments.

2-methylfuran was detected. When three equivalents of TEMPO were added to the reaction under the same conditions, no 2-methylfuran was detected (Scheme 6a). Thus, decarboxylation of MFCA undergoes a radical pathway to form 2-methylfuran. A sulfonic acid anion, which is similar to $MFCA^-$, has been reported to form the corresponding free radical by oxidation with O_2.[64–66] Therefore, MFCA probably forms 5-methylfuran-2-carboxylate ($MFCA^-$) first by ionization in H_2O, which further converts to $MFCA^•$ by oxidation and then goes through decarboxylation to form 2-methylfuran, and the dimerization process could happen between 5-MFA and 2-methylfuran. To confirm this hypothesis, equal amounts of 5-MFA and 2-methylfuran were reacted under the standard conditions, and the detected BMFM yield was higher than that obtained with 5-MFA alone under the same conditions (Scheme 6b). These pieces of evidence indicate that MFCA can form 2-methylfuran by free radical decarboxylation and 2-methylfuran is involved in the dimerization reaction.

Therefore, the reaction mechanism is proposed in Scheme 7 for the catalyst-free conversion of 5-MFA to BMFM. First, 5-MFA is oxidized to MFCA under O_2. MFCA further converts to $MFCA^•$, which splits into CO_2 and 5-methylfuran-2-free radical ($2\text{-}MF^•$) by decarboxylation. Afterwards, $2\text{-}MF^•$ and MFCA reacts to generate $MFCA^•$ and 2-methylfuran. At the same time, $5\text{-}MFA^+$ is generated from 5-MFA by eliminating a molecule of H_2O with H^+ coordination. Finally, $5\text{-}MFA^+$ and 2-methylfuran produce BMFM through electrophilic substitution reaction.



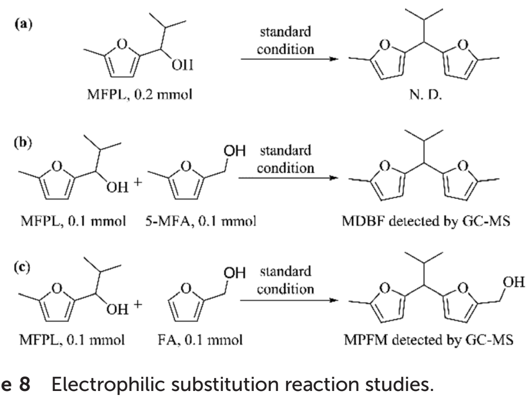
Scheme 7 Possible mechanism for the synthesis of BMFM.

Mechanism verification experiments

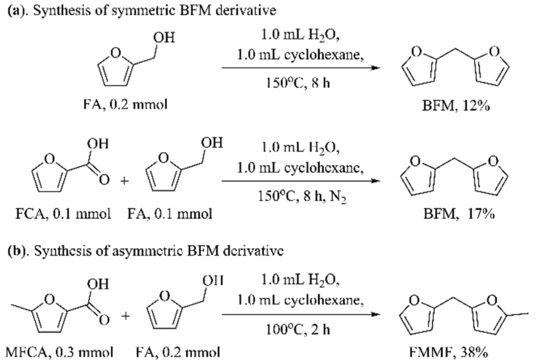
To further confirm the formation of a carbocation, 2-methyl-1-(5-methylfuran-2-yl)propan-1-ol (MFPL) was used as the starting material. No dimer was detected under the standard conditions as expected, since MFPL is unable to form an acid (Scheme 8a). However, when equivalent amount of MFPL and 5-MFA were used as the starting materials, the dimer 5,5′-(2-methylpropane-1,1-diyl)bis(2-methylfuran) (MDBF) was detected as the major product by GC-MS (Scheme 8b). MDBF is formed as the major product instead of BMFM most probably due to the fact that MFPL can form a carbocation more easily. In addition, when FA was used instead of 5-MFA, the dimer product (5-(2-methyl-1-(5-methylfuran-2-yl)propyl)furan-2-yl)methanol (MPFM) was detected (Scheme 8c). It must be that MFPL can form the carbocation ($MFPL^+$) readily, and then $MFPL^+$ attacks the active hydrogen of the furan ring to form the dimerization product by an intermolecular electrophilic substitution reaction.

To understand a clearer role of H^+ in the mechanism, the effect of acidity or alkalinity on the reaction was studied. When 0.1 mL CH_3COOH was added to the reaction system, no effect on the reaction result was observed, while no product was obtained after adding 0.1 mL Et_3N (Scheme S-3†). It is possible that the MFCA formed during the reaction provides H^+, which plays a crucial role in the carbocation production. This cannot occur in an alkaline environment.

The effect of H_2O on the reaction was also studied in depth. It was reported that the decarboxylation process of some 2-furancarboxylic acid derivatives also requires H_2O.[67] Therefore, experiments were designed with and without H_2O by using MFCA as the substrate under the otherwise standard conditions. The decarboxylation product 2-methylfuran was detected with 10% yield in the presence of H_2O, and a trace amount of 2-methylfuran was detected in the absence of H_2O (Scheme S-3†). Therefore, besides being a solvent, H_2O also plays a vital role in the decarboxylation process.



Scheme 8 Electrophilic substitution reaction studies.



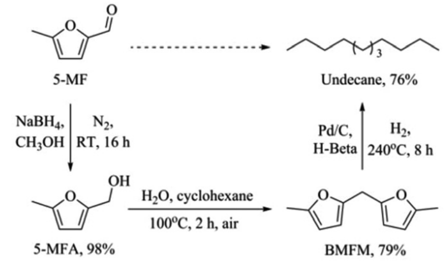
Scheme 9 Substrate scope.

Substrate scope

Besides 5-MFA, furfuryl alcohol (FA) was also used as the starting material. Few BFM was obtained from FA under the standard conditions. By increasing the reaction temperature and prolonging the reaction time (150 °C, 8 h), only 12% of BFM was obtained. We believe the reason for the high reactivity of 5-MFA is that the methyl group at the 5-position can stabilize the free radical and the carbocation intermediate, so that the 5-MFA reactivity is promoted. The instability of FA in a high temperature aqueous solution is another reason for the low BFM yield. FA can react with 2-furanoic acid (FCA) to form BFM in 17% yield under N_2 (Scheme 9a). Additionally, in asymmetric synthesis experiments, a 38% yield of 2-(furan-2-ylmethyl)-5-methylfuran (FMMF) was synthesized *via* FA and MFCA (Scheme 9b).

Production of C_{11} biodiesel from 5-MF

Based on this work, a synthetic route was developed to synthesize C_{11} biodiesel from 5-MF (Scheme S-4†). Different from lipid-based biodiesel (C_{17}–C_{18}, freezing point 22–29 °C), C_{11} biodiesel is a kind of light diesel oil with a −26 °C freezing point, which can be used at low temperature. First, a 98% yield of 5-MFA can be obtained from 5-MF by hydrogenation, then BMFM was synthesized under the standard conditions described above with 79% yield, and finally, a 76% yield of C_{11} biodiesel was synthesized from BMFM *via* hydrodeoxygenation over Pd/C and H-beta zeolite (Scheme 10). A 59% total yield of C_{11} biodiesel was obtained from 5-MF based on this method. This synthetic method is a simple operation under mild conditions, which has great potential for the synthesis of biodiesel.



Scheme 10 Synthesis of C_{11} biodiesel from 5-MF.

Conclusions

In summary, a novel approach was reported to synthesize BFMs as biodiesel precursors from biomass-based furfuryl alcohols in the presence of only H_2O and air without catalysts. Up to 81% yield of bis(5-methylfuran-2-yl)methane (BMFM) can be obtained from 5-methylfurfuryl alcohol (5-MFA) at 100 °C for 2 h in a biphasic system of H_2O and cyclohexane. A free radical decarboxylation mechanism for this reaction was proposed based on control experiments and intermediate trapping exploration. Part of 5-MFA is oxidized to 5-methylfurancarboxylic acid (MFCA) first. Then 2-methylfuran is formed by the radical decarboxylation of MFCA. Finally, the dimerization happens between 5-MFA$^+$ and 2-methylfuran by electrophilic substitution. H_2O is indispensable as a solvent and for the decarboxylation of MFCA. Air is better than O_2 for this partial oxidation reaction. Based on this method, 59% total yield of C_{11} biodiesel was synthesized from 5-MF by hydrogenation, dimerization and hydrodeoxygenation. Overall, this synthetic method has great potential in practical applications for the production of biodiesel precursors, with features such as being catalyst-free, requiring mild conditions and short reaction time, and being environmentally benign. This synthetic method is an important addition in regard to industrial applications for energy development needs.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the funds from financial support of the National Natural Science Foundation of China (Grant No. 21808100), the "Thousand Young Talents" Program of China, and the "Thousand Talents" Entrepreneurship Program of Jiangxi Province.

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