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Efficient preparation of hybrid biofuels from biomass-derived 5-(acetoxymethyl)furfural and petroleum-derived aromatic hydrocarbons†

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Fuel candidates containing both petroleum-derived and biomass-derived molecules in their structural motifs ensure both feedstocks are used optimally and coherently. This work reports a straightforward and efficient preparation of 5-(arylmethyl)furfurals (AMFFs), 2-(arylmethyl)furans (AMFs), and 2-(arylmethyl)-5-methylfurans (AMMFs) as hybrid biofuels (or fuel oxygenates) starting from carbohydrate-derived 5-(acetoxymethyl)furfural (AcMF) and petroleum-derived aromatic hydrocarbons. The AMFFs were prepared by Friedel–Crafts reaction between AcMF and aromatic hydrocarbons (*e.g.*, BTX, mesitylene) by employing anhydrous $ZnCl_2$ as the catalyst. AMFs were prepared by decarbonylation of AMFFs over the $Pd(OAc)_2$ catalyst under solvent-free conditions. In contrast, AMMFs were produced by hydrogenating AMFFs in methanol using gaseous hydrogen and the 10% Pd/C catalyst. The catalytic transformations were optimized on various parameters, and all the biofuel candidates were obtained in good to excellent isolated yields (>80%) under moderate conditions.

Introduction

The hydrocarbon-based liquid fuels will likely continue to be used in the transportation sector in the foreseeable future, especially in aviation and other difficult-to-electrify sectors.[1] The past two decades have seen coordinated research for finding a sustainable carbon-based feedstock alternative to petroleum for producing liquid transportation fuels. In this regard, biomass has the commercial potential to replace petroleum, at least partially, for producing liquid transportation fuels with the desired societal, economic, and environmental incentives.[2] Several catalytic strategies have been developed over the past three decades for synthesizing hydrocarbon-based drop-in liquid fuels and oxygenated fuel additives from cellulosic biomass that promise to reduce dependence on fossilized carbon.[2] The commercial relevance of producing specific biofuels heavily relies on the availability, cost, and type of the biomass feedstock employed.[3] Coprocessing biomass and petroleum-derived components could ensure feedstock flexibility, moderate the cost of the targeted fuel candidates, and avoid overdependence on either biomass or petroleum feedstock.[2,4,5] Moreover, incorporating petroleum-derived hydrocarbons in biomass-derived oxygenated intermediates increases the energy density in the resultant hybrid fuels and improves fuel properties (*e.g.*, stability).[6,7] Acid-catalyzed hydrolysis and dehydration of abundant hexose sugars (*e.g.*, glucose, sucrose) and polymeric carbohydrates (*e.g.*, starch, cellulose) lead to 5-(hydroxymethyl)furfural (HMF).[8] HMF has been exploited as a renewable chemical platform for producing hydrocarbon-based liquid fuels and fuel oxygenates.[9–11] HMF has been reacted with petroleum-derived aromatic compounds (*e.g.*, mesitylene) by Friedel–Crafts reaction (FCR) to form 5-(mesitylmethyl)furfural (MMFF), a potential fuel oxygenate and hybrid diesel fuel precursor.[12–15] Even though aromatic hydrocarbons are typically obtained from petroleum, they can also be produced selectively from carbohydrates *via* furanic intermediates.[16,17] Aromatic hydrocarbons can be sourced renewably from other biomass fractions, such as by depolymerizing and deoxygenating lignin or deoxygenating the bio-oil produced by pyrolyzing biomass.[18,19] Even though good yields of MMFF (~80%) have been reported in the literature using suitable catalysts, the challenge lies in the scalable, high-yielding, and economical production of HMF. Even after decades of research, HMF production is yet to reach commercialization, primarily due to its inherent hydrophilicity and poor stability (*e.g.*, thermal, storage, hydrolytic).[20]

In this regard, the hydrophobic, stabler analogs of HMF have shown promise to substitute HMF in its derivative chemistry.[21] The esters of HMF, such as 5-(acetoxymethyl)furfural (AcMF), have received particular attention since they are hydrophobic, significantly more stable than HMF, contain only C, H, and O

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atoms in their moiety, and have several emerging applications.[22,23] Acetic acid required for producing AcMF is biorenewable, inexpensive, thermally stable, and non-toxic. AcMF can be produced conveniently from carbohydrates, HMF, and various hydrophobic analogs of HMF.[24–27]

We have recently reported a solvent-free, scalable, and high-yielding preparation of AcMF from sugars and polymeric carbohydrates using a catalyst system comprising of AcOH and $ZnCl_2$.[28] Interestingly, AcMF has been used as the starting material for synthesizing hybrid biofuels (*e.g.*, MMFF) by FCR using tin-exchanged montmorillonite as a heterogeneous catalyst.[25] Removing reactive oxygen-containing functionalities in biofuels increases the energy density and improves the potential fuel candidates' stability (*e.g.*, storage, thermal). For example, even though furfural and HMF are not used as fuel oxygenates, their partially hydrogenated furanic derivatives, such as 2-methylfuran and 2,5-dimethylfuran, have shown promise as fuel additives.[29] Furanic ethers, such as 5-(ethoxymethyl)furfural has also been proposed as a fuel oxygenate.[30] In this regard, MMFFs and their derivatives enjoy more flexibility in their molecular structure and physicochemical properties. Moreover, the incorporation of aromatic hydrocarbons and furaldehydes in 5-(arylmethyl)furfurals (AMFFs) help to valorize various components of biomass together for improved sustainability. As mentioned above, it is desirable to eliminate the reactive aldehyde group in AMFFs to produce fuel additives with improved stability and higher energy density. The preparation of 2-(mesitylmethyl)furan (MMF), a promising hybrid fuel, has been reported by the Pd/C catalyzed decarbonylation of MMFF.[31] Therefore, the catalytic decarbonylation of AMFFs could be a convenient route to synthesizing 2-(arylmethyl) furans (AMFs) as potential biofuels (Scheme 1). However, the decarbonylation route has never been studied systematically for such hybrid biofuels. Interestingly, various 2-(arylmethyl)-5-methylfurans (AMMFs) have been hydrodeoxygenated into branched cycloalkanes for potential applications as jet fuel using a combination of Pd/C and HZSM-5 catalysts.[32] Alternatively, the aldehyde group in MMFF could be catalytically reduced into a methyl group forming 2-(mesitylmethyl)-5-methylfuran (MMMF), which has never been reported in the literature. Catalytic decarbonylation and catalytic hydrogenation fall under stoichiometric reagentless organic transformations and have excellent green metrics.[33] AMFs and AMMFs have significantly higher C/O and H/O ratios than AMFFs and contain no reactive aldehyde functionality. This work reports the convenient and high-yielding preparation of AMFFs by FCR between AcMF and aromatic hydrocarbons using $ZnCl_2$ as a non-toxic, inexpensive, and readily available catalyst. AMFFs were catalytically decarbonylated into AMFs using palladium(II) acetate as the catalyst under solvent-free conditions. AMFFs were also catalytically hydrogenated in a methanolic solution over a 10% Pd/C catalyst to form AMMFs. The processes were optimized on various reaction parameters, such as temperature, catalyst loading, solvent, and duration, and all the hybrid biofuels were obtained in good to excellent isolated yields. Moreover, the recyclability of the catalysts was investigated.

Experimental section

Materials

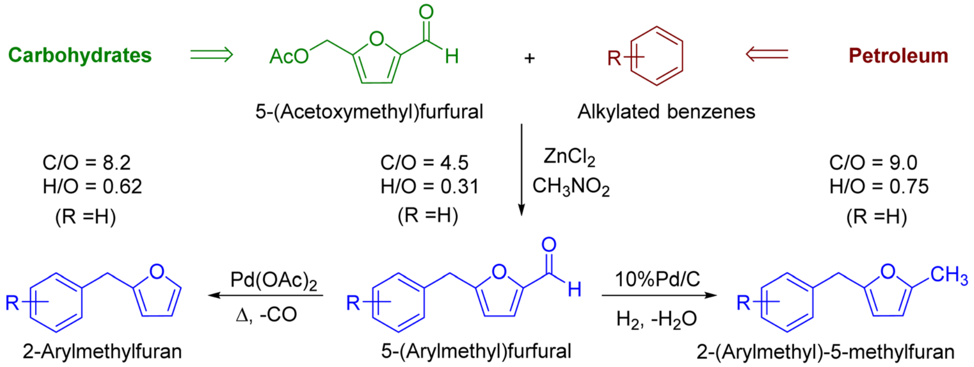
Petroleum ether (60–80 °C, 99%), ethyl acetate (99%), and methanol (99%) were purchased from Loba Chemie Pvt. Ltd. Benzene (99%), toluene (99%), *o*-xylene (99%), *m*-xylene (99%), *p*-xylene (99%), isopropylbenzene (99%), ethylbenzene (99%), mesitylene (99%), zinc chloride (anhydrous, 95%), nitromethane (99%), molecular sieve (4 Å), and silica gel (60–120 mesh) were procured from Spectrochem. Palladium(II) acetate (98%), 10% Pd/C, and Amberlyst-15 were procured from Sigma-Aldrich. 5-(Acetoxymethyl)furfural (AcMF) was prepared from fructose following a literature process.[28] The solvents were dried over activated molecular sieves for 24 h before use. All the chemicals were used as received without further purification.

Instrumentation

The synthesized compounds were characterized by Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and high-resolution mass spectrometry (HRMS) technique. The FTIR spectrum was acquired using the ATR method on a Bruker Alpha II FTIR spectrometer fitted with silicon carbide as an IR source. The purified compounds were dissolved in dichloromethane to make a dilute solution. A drop of the solution was placed on the ATR counter and allowed to evaporate to make a thin film of the compound. Each sample was scanned 24 times with a scan rate of two scans per second and a spectral resolution of 4 cm^{-1}. The synthesized compounds were dissolved in an appropriate deuterated solvent for NMR spectroscopy. The ^{1}H-NMR spectra were acquired in a Bruker NanoBay® instrument operating at 400 & 300 MHz. The ^{13}C-NMR spectra were acquired in the same instrument at the calculated frequency of 100 & 75 MHz. The Bruker Topspin software (version 4.2.0) was used to process raw NMR data. HRMS analyses of the synthesized compounds were collected using the Waters-Xevo G2-XS-QToF instrument. Gas chromatography (GC) analysis was conducted using a LECO Pegasus BT 4D spectrometer with an Rxi-5 ms column (30 m × 0.25 mm × 0.25 μm). High-purity helium gas was used as the carrier gas with a flow rate of 1.40 mL min^{-1}. The injector temperature was fixed at 250 °C, and the split ratio was adjusted to 50 : 1. The column temperature was initially set to 50 °C for 2 minutes, then it was increased up to 300 °C with a rate of 10 °C min^{-1}.

General synthetic procedure for synthesizing AMFFs

AcMF (0.502 g, 2.98 mmol), mesitylene (1.435 g, 4 equiv., 11.94 mmol), anhydrous $ZnCl_2$ (0.250 g, 50 wt%), and nitromethane (5 mL) were added to a 50 mL round-bottomed flask. The reaction mixture was stirred magnetically for 3 h in a preheated (120 °C) oil bath. After the reaction, the reaction mixture was washed with water and saturated sodium bicarbonate solution and then extracted with ethyl acetate (3 × 15 mL). The organic layer was evaporated under reduced pressure and purified using column chromatography (petroleum ether/ethyl acetate, silica gel 60–120) to get 5-(mesitylmethyl) furfural (MMFF, **1f**) as a light-yellow liquid (0.551 g, 81%).



Scheme 1 Synthesis of hybrid biofuels from 5-(acetoxymethyl)furfural and aromatic hydrocarbons.

Under optimized reaction conditions, the same protocol was extended for the synthesis of **1a–1h.**

General synthetic procedure for synthesizing AMFs

A 50 mL round-bottomed flask was charged with MMFF **1f** (0.250 g, 1.10 mmol), molecular sieve 4 Å (0.200 g), and $Pd(OAc)_2$ (0.04 g, 16 mol%). The reaction mixture was magnetically stirred in a pre-heated oil bath at 140 °C for 3.5 h. After the reaction, the reaction mixture was diluted with ethyl acetate and filtered. The residue was washed with ethyl acetate (3 × 10 mL). The filtrate was concentrated under reduced pressure and purified through column chromatography (petroleum ether/ethyl acetate, silica gel 60–120 mesh) to get 2-(mesitylmethyl)furan (MMF, **2f**) as a colorless liquid (0.176 g, 80%). The optimized reaction conditions were extended for the synthesis of **2a–2h.**

General synthetic procedure for synthesizing AMMFs

MMFF **1f** (0.250 g, 1.10 mmol), 10% Pd/C (0.025 g, 10 wt%), Amberlyst-15 (0.125 g, 50 wt%), and methanol (10 mL) were added to 100 mL two necked round-bottomed flask. Hydrogen gas was purged into the reaction mixture five times using a hydrogen balloon, and the reaction mixture was stirred magnetically at room temperature for 2.5 h. The reaction mixture was centrifuged, decanted, and evaporated under reduced pressure. The reaction mixture was passed through a small plug of silica to get 2-(mesitylmethyl)-5-methylfuran (MMMF, **3f**) as a colorless liquid (0.197 g, 84%). Similar synthetic protocols were followed for the preparation **3a–3h.** The catalyst was recovered by centrifugation of the reaction mixture, followed by decanting. The catalyst was washed with methanol (2 × 10 mL) and dried in an oven for 4 h at 60 °C before subjecting it to the next catalytic cycle. Unfortunately, the catalytic activity decreased drastically on the first recycle, possibly due to the leaching of palladium nanoparticles from the carbon support. The activity remained relatively stable until the fourth recycle, affording around 40% isolated yield of **3f.**

Results and discussion

Initially, the authors concentrated on developing a suitable general catalytic procedure for synthesizing **1a–1h.** The preparation of **1f** has already been attempted from AcMF *via* FCR using Sn^{4+}-exchanged montmorillonite clay as the catalyst.[25] Since we have recently reported the direct preparation of AcMF from sugars and polymeric carbohydrates using a combination of acetic acid and $ZnCl_2$,[28] the efficiency of anhydrous $ZnCl_2$ as a catalyst was explored for preparing **1a**, **1b**, and **1h** from AcMF.[34] The FCR of AcMF with various petroleum-derived arenes were performed.

FCR of AcMF to AMFFs

Initially, the synthesis of **1f** by the FCR between AcMF and mesitylene was optimized. The reaction was carried out in nitromethane as solvent using anhydrous $ZnCl_2$ as the catalyst. The reaction progress was monitored using thin-layer chromatography (TLC), and products were confirmed using NMR (^1H & ^{13}C) and HRMS techniques. When the reaction was carried out at 100 °C and 110 °C, the reaction took 4 h to complete and afforded 77% and 79% yield of **1f** (Fig. 1). Elevating the reaction temperature to 120 °C allowed the reaction to be completed within 3 h and increased the yield of **1f** to 81%. The GC chromatogram of the crude reaction mixture did not show any significant peak except mesitylene, nitromethane, and the product **1f** (ESI, Fig. S73†). Further increase of the reaction

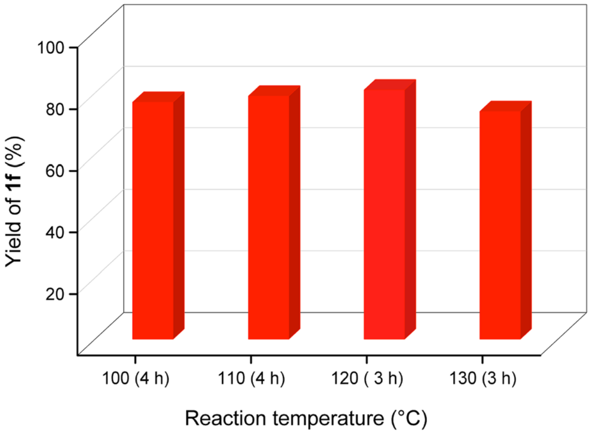


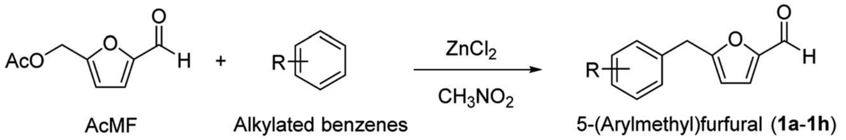
Fig. 1 The effect of reaction temperature on the yield of **1f**. Reaction conditions: AcMF (0.502 g, 2.98 mmol), mesitylene (1.435 g, 4 equiv., 11.94 mmol), $ZnCl_2$ (0.250 g, 50 wt%), and nitromethane (5 mL).

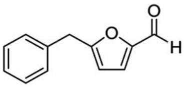
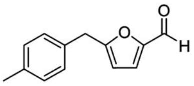
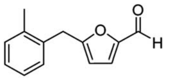
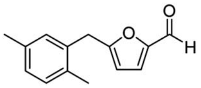
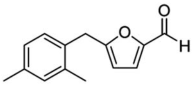
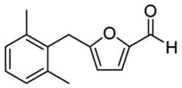
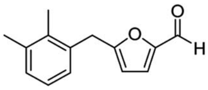
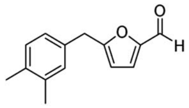
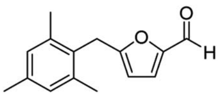
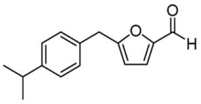
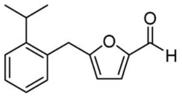
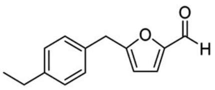
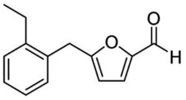
temperature to 130 °C decreased the yield of **1f** to 74%. When the reaction was carried out under similar reaction conditions in excess mesitylene without nitromethane, the conversion of AcMF reached completion in 5 h. However, the isolated yield of **1f** drastically decreased to 38% due to the decomposition of AcMF.

After optimizing the reaction temperature, the effect of the equivalent of arene on the yield of AMFFs was investigated. Using 4 equiv. of mesitylene (compared to AcMF) gave an 81% isolated yield of **1f.** Increasing the amount of mesitylene to 5 equiv. didn't improve the yield of **1f** any further. However, decreasing the amount of mesitylene to 3 equiv. lowered the yield of **1f** to 71%. After the reaction, the unreacted mesitylene was recovered by the column chromatography. It must be pointed out here that chromatography was chosen for product purification to minimize mass loss at the lab-scale reaction. During the process scale-up, fractional distillation can be used to separate the excess reagent and the product. Furthermore, increasing the catalyst loading to 100 wt% did not significantly change the yield (77%). The reaction was performed in a sealed glass pressure reactor to prevent moisture in the reaction mixture and the reaction afforded a 74% yield of **1f.**

After process optimization of **1f**, the reaction conditions were applied for the synthesis of the other derivatives. FCR of AcMF with benzene, *para*-xylene, and mesitylene gave exclusively one structural isomer. In contrast, toluene, *ortho*-xylene, *meta*-xylene, isopropylbenzene, and ethylbenzene gave two structural isomers, and the combined yield of the two isomers is reported (Table 1). FCR of AcMF with benzene was performed at 120 °C for 3 h in a round-bottomed ACE glass pressure vessel, which afforded a 59% isolated yield of **1a**. The moderate yield of **1a** was attributed to the partial charring of the reaction mixture. When the transformation was performed in an open vessel under reflux, a 50% isolated yield of **1a** was obtained. Even though the

Table 1 The synthesis of AMFFs from AcMF using FCR[a]



Entry	Product code	Product(s)	Yield (%)
1	**1a**		59[b]
2	**1b**	 	76[c]
3	**1c**		82
4	**1d**	 	77[c]
5	**1e**	 	76[c]
6	**1f**		81
7	**1g**	 	79[c]
8	**1h**	 	75[c]

[a] Reaction conditions: AcMF (0.502 g, 2.98 mmol), arene (4 equiv., 11.94 mmol), ZnCl$_2$ (0.250 g, 50 wt%), 120 °C, 3 h. [b] A round-bottomed ACE glass pressure vessel was used. [c] Combined yield of *ortho-* and *para-*isomer.

conversion of AcMF was not quantitative, noticeable decomposition was observed.

The structural isomers of **1b**, **1g**, and **1h** (*i.e.*, *ortho*- and *para*-substitution on the monoalkylated arenes) were found to form in nearly equal molar ratio based on the integration value of signals on the ^{1}H-NMR spectra. The combined isolated yield of the two isomers were 76% for **1b**, 79% for **1g**, and 75% for **1h**, respectively (entries 2, 7, & 8, Table 1). For **1d**, the molar ratio of *ortho*- and *para*-isomers was approximately 1 : 3, with a combined yield of 77%. In the case of **1e**, the ratio was nearly 1 : 2 with a 76% isolated yield (entry 5, Table 1). All the synthesized AMFFs were used as substrates for the catalytic decarbonylation and catalytic hydrogenation reactions.

Decarbonylation of AMFFs to AMFs

The decarbonylation of AMFFs was done under solvent-free conditions using conventional heating. The decarbonylation of AMFFs was optimized by using **1f**. Initially, decarbonylation reaction was performed at 110 °C and 120 °C using $Pd(OAc)_2$ (0.17 mmol, 16 mol%), afforded only 30% and 33% yield of **2f** even after 24 h reaction due to incomplete conversion of **1f**. When the reaction temperature was increased to 130 °C, resulted in 50% of **2f** in 18 h (Fig. 2). The increase of reaction temperature to 140 °C gave a maximum 80% yield of **2f** in 3.5 h under similar reaction conditions. Further increase in the reaction temperature to 150 °C diminished the yield of **2f** to 72% due to partial decomposition of the product.

After optimizing the reaction temperature, the effect of catalyst loading was investigated by altering the amount of catalyst. When the catalyst amount was decreased to 8 mol%, the reaction was completed in 10 h and a 57% yield of **2f** was achieved. The result may be attributed to slower kinetics of decarbonylation at lower catalyst loading and thermal decomposition of MMFF during heating for an extended period. Increasing the catalyst loading to 20 mol% did not significantly change the yield of **2f** (Fig. 3). It has been observed that molecular sieves facilitate the reaction by providing more surface area for the catalyst and substrate to react. Under similar conditions, the decarbonylation of **1f** was performed in the absence of molecular sieves and resulted in a 74% isolated yield of **2f.** Furthermore, the molecular sieve amount was varied between 0.10 g and 0.30 g. When the reaction was carried out at 0.10 g, it afforded a 77% yield of **1f.** Increasing the molecular sieve amount to 0.20 g improved the isolated yield of **1f** to 80%. Further increasing the amount of the molecular sieve to 0.30 g afforded only a marginal increase in yield (82%). This shows that the yield gradually improves with increasing amounts of molecular sieves introduced in the reaction mixture. However, during process scale-up, the improvement of yield may be weighed against the cost of using and recycling molecular sieves.

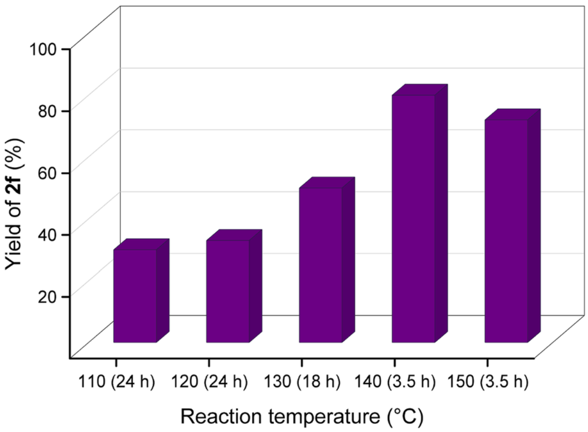


Fig. 2 The effect of reaction temperature on the yield of **2f**. Reaction conditions: MMFF **1f** (0.250 g, 1.10 mmol), $Pd(OAc)_2$ (0.04 g, 16 mol%), and molecular sieve 4 Å (0.200 g).

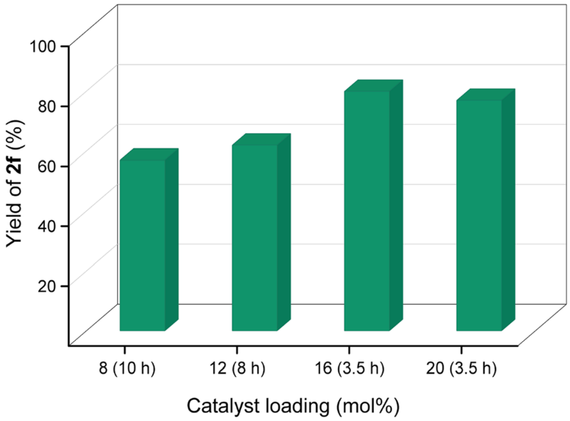


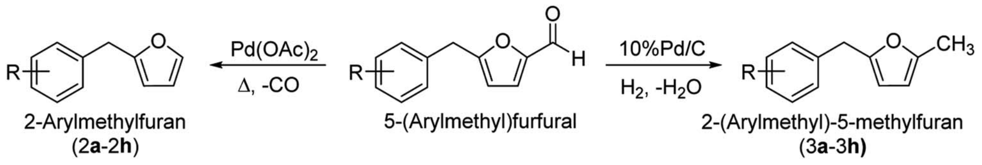
Fig. 3 Effect of catalyst loading on the yield of **2f**. Reaction conditions: MMFF **1f** (0.250 g, 1.10 mmol), molecular sieve 4 Å (0.200 g), 140 °C.

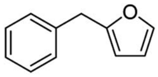
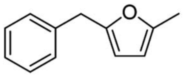
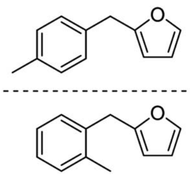
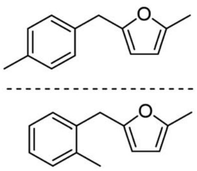
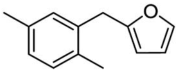
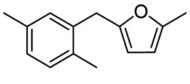
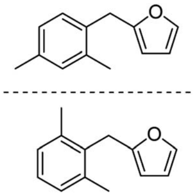
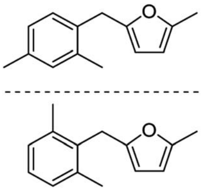
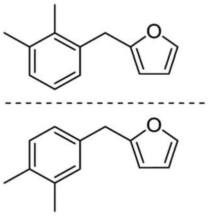
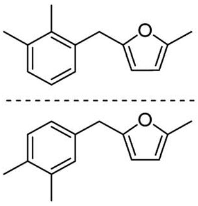
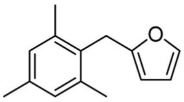
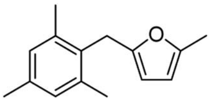
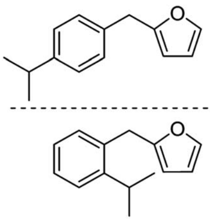
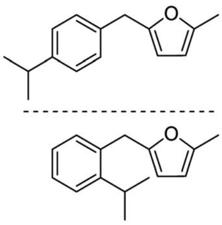
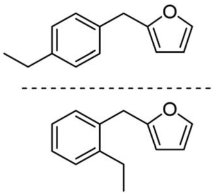
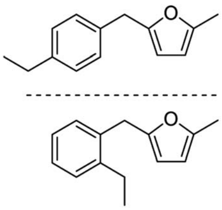
The decarbonylation of **1f** was also performed in the ACE glass pressure reactor using solvents like cyclohexane, isooctane, and heptane, which gave 35%, 25%, and 10% yields, respectively. The substrate **1f** was not fully consumed even after 24 h (monitored by TLC), which could be attributed to the *in situ* generation of CO being trapped in the pressure reactor and poisoning the catalyst by the chemisorption of the active sites. The high-boiling solvents, such as anisole and dodecane, were also screened for the decarbonylation of **1f.** The solvents gave 20% and 32% yields of **2f**, respectively, due to the incomplete conversion of **1f** even after 24 h reaction time. After ensuring the best selectivity and yield for **2f**, the optimized reaction conditions were applied for decarbonylating other AMFFs into AMFs. The decarbonylation of **1a**, **1c**, and **1f** gave 73% yield of **2a**, 80% yield of **2c**, and 80% yield of **2f**, respectively. Both *ortho*- and *para*-structural isomers of **1b**, **1d**, **1e**, **1g**, and **1h** were used for the decarbonylation reaction. The combined yield of the two structural isomers was 76% for **2b**, 78% for **2d**, 76% for **2e**, 77% for **2g**, and 75% for **2h**, respectively (Table 2).

Hydrogenation of AMFFs to AMMFs

Catalytic hydrogenation of AMFFs to AMMFs was performed at room temperature in methanol under H_2 balloon pressure with 10% Pd/C as the catalyst. The synthetic procedure was

Table 2 The list of catalytically synthesized hybrid biofuels starting from carbohydrate-derived AcMF



Product code[a]	Product(s)	Yield (%)	Product code[b]	Product(s)	Yield (%)
2a		73	**3a**		84
2b		76[c]	**3b**		87[c]
2c		80	**3c**		85
2d		78[c]	**3d**		81[c]
2e		76[c]	**3e**		83[c]
2f		80	**3f**		84
2g		77[c]	**3g**		84[c]
2h		75[c]	**3h**		83[c]

[a] Reaction conditions: AMFF (0.250 g), $Pd(OAc)_2$ (16 mol%), molecular sieve 4 Å (0.200 g), 140 °C, and 3.5 h. [b] Reaction conditions: AMFF (0.250 g), 10% Pd/C (0.025 g, 10 wt%), Amberlyst-15 (0.125 g, 50 wt%), hydrogen balloon pressure, room temperature, and 2.5 h. [c] Combined yield of the *ortho*- and *para*-isomers.

optimized by using **1f**. The reaction progress was monitored by TLC, and products were confirmed using NMR (^{1}H & ^{13}C) and HRMS techniques. When the reaction was performed at room temperature, it took 2.5 h for the quantitative conversion of **1f**. The reaction was optimized by varying the amount of Amberlyst-15 and 10% Pd/C catalyst loading. When the reaction was carried out using 10 wt% and 20 wt% of Amberlyst-15 (compared to the initial weight of **1f**), it afforded 69% and 75% yield of **3f**, respectively. Further increase of Amberlyst-15 to 30 wt% afforded a 79% yield of **3f**. When the reaction was carried out at 5 wt% loading of the 10% Pd/C catalyst, it afforded a 68% yield of **3f**. An increase of catalyst loading to 10 wt% afforded an 84% yield of **3f** at room temperature in 2.5 h. The catalyst loading was further increased to 20 wt%, decreasing the yield to 75% of **3f**. The isolated yield of **3f** with fresh Amberlyst-15 and 10% Pd/C was 84%. Unfortunately, after the first cycle, the yield of **3f** decreased to 48%.

After optimization of **3f**, the reaction conditions were extended for the synthesis of the other derivatives. The catalytic hydrogenation of **1a**, **1c**, and **1f** afforded 84% **3a**, 85% **3c**, and 84% **3f**, respectively. The hydrogenation reaction of both *ortho*- and *para*-isomers of **1b**, **1d**, **1e**, **1g**, and **1h** were performed and afforded 87% yield of **3b**, 81% yield of **3d**, 83% yield of **3e**, 84% yield of **3g**, and 83% yield of **3h**, respectively (Table 2).

Conclusions

A series of furan-based hybrid biofuels have been synthesized, starting from carbohydrate-derived AcMF and petroleum-derived aromatic hydrocarbons. The aromatic hydrocarbons were coupled with AcMF by the FCR in nitromethane solvent catalyzed by anhydrous $ZnCl_2$. Predictably, the heavily alkylated aromatics showed more reactivity towards the FCR with AcMF. Moreover, the reactive aldehyde group in the products was removed by palladium-catalyzed decarbonylation or by palladium-catalyzed catalytic hydrogenation to produce stabler hybrid biofuels with higher C/O ratios. No apparent patterns emerged on the reactivity of the FCR products towards decarbonylation and catalytic hydrogenation reactions. All the products were obtained in satisfactory and comparable isolated yields under similar reaction conditions. The decarbonylation reaction was performed under solvent-free conditions. The catalytic hydrogenation was performed in the liquid state under mild reaction conditions. All the products were isolated in good to excellent yields. Future work will concentrate on scaling up the production of some representative fuel candidates reported in this work and studying their physicochemical and combustion characteristics. The reactivity of these novel compounds will also be studied for their downstream value addition as chemical intermediates.

Author contributions

Abhishek Kumar Yadav designed the experiments, characterized the products, and prepared the ESI.† Navya Subray Bhat worked on the initial development of the project and edited the manuscript. Sonal Kaushik performed some of the experiments, optimized the reaction conditions, and analyzed the products. Asiful H. Seikh was responsible for funding acquisition and editing the manuscript. Saikat Dutta conceptualized the work, supervised, and wrote the original draft.

Conflicts of interest

There are no conflicts to declare.

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