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A mild synthetic strategy for removing acetic acid from fast pyrolysis-derived bio-oils utilizing Friedel–Crafts acylation reactions†

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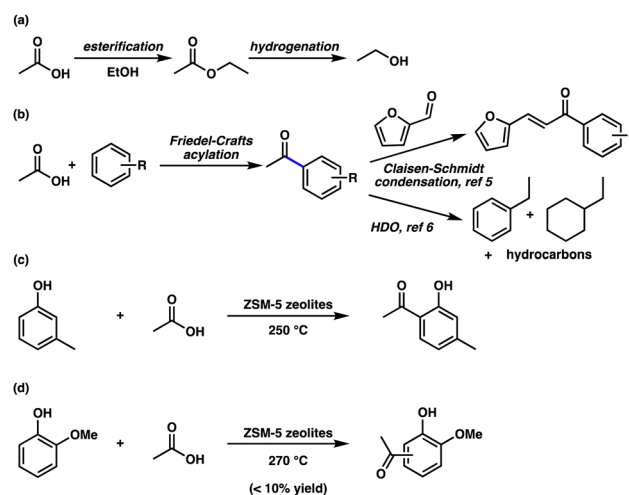
Fast pyrolysis-derived bio-oils contain numerous oxygenated components, including acetic acid and formic acid. However, these acids present in fast pyrolysis-derived bio-oils are responsible for the instability and corrosiveness of the oils. Although these acids have been removed from fast pyrolysis-derived bio-oils by esterification with alcohols to form acetates, these acetates could not be transformed to compounds with a suitable number of carbon atoms required to be used as fuels. In this work, Friedel–Crafts acylation reactions were conducted to remove acetic acid to form acetophenones, which possess more than eight carbons and could be converted to valuable components of fuels.

Bio-oils produced by the fast pyrolysis of biomass have been considered potential substitutes for conventional fuels. However, direct utilization of crude fast pyrolysis-derived bio-oils is limited because they contain high quantities of water (15–30 wt%) and oxygen (30–40 wt%) from oxygenated species (*e.g.*, acids, aldehydes, alcohols, and sugars).¹ The high degree of oxygenated species in crude fast pyrolysis-derived bio-oils results in chemical instability, corrosiveness, and low heating values. Thus, upgrading processes are required for bio-oils obtained from fast pyrolysis to be used as fuels.

The extreme instability and corrosiveness of bio-oils obtained from fast pyrolysis have been attributed to the pH levels of 2–3 resulting from the significant amount of carboxylic acids, mainly acetic acid and formic acid. The acidity of fast

pyrolysis-derived bio-oils leads to the corrosion of construction materials (*e.g.*, carbon steel and aluminum) and sealing materials. In addition, secondary condensation or polymerization of reactive components, such as aldehydes, ketones, and phenols, in the presence of acids changes the physicochemical properties of fast pyrolysis-derived bio-oils.^{2,3}

Thus, significant efforts have been made to develop strategies for the esterification of acids with alcohols, which can also be applicable from fast pyrolysis-derived bio-oils, to lower the acidity and improve the stability of fast pyrolysis-derived bio-oils (Scheme 1a).^{1,4} However, esterification of acids and subsequent hydrogenation produce alcohols, which do not contain the required number of carbon atoms to be used as components for replacing conventional fuels. Here, a mild and



Scheme 1 (a) Removal of acetic acid from fast pyrolysis-derived bio-oils by esterification and subsequent hydrogenation. (b) A strategy for removing acetic acid from fast pyrolysis-derived bio-oils by Friedel–Crafts acylation reactions. (c) Friedel–Crafts acylation reaction between *m*-cresol and acetic acid at 250 °C. (d) Friedel–Crafts acylation reaction between guaiacol and acetic acid at 270 °C.

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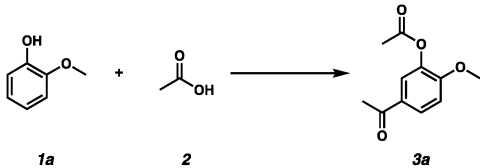
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efficient synthetic strategy to convert acetic acid into valuable components containing more than eight carbons, which could be used as substitutes for conventional oils, was developed (Scheme 1b). Insertion of the acetyl group from acetic acid on aromatic components in fast pyrolysis bio-oils by Friedel–Crafts acylation reactions provided acetophenones. The resulting acetophenones from Friedel–Crafts acylation reactions can be converted into valuable components using further upgrading techniques^{5,6} An array of *C*-acetylated products were prepared from both phenolic and non-phenolic compounds. Although similar strategies have been investigated recently, these reactions require high temperatures, and only the *m*-cresol or guaiacol substrate, with which poor yields of *C*-acetylated products were observed, was examined.^{7–9}

We began our Friedel–Crafts acylation reaction studies with guaiacol as a bio-oil model compound because various methoxyphenol substrates constitute almost 20% of the bio-oil mixture.¹⁰ Initially, we attempted the Friedel–Crafts acylation reaction using commercially available and inexpensive P₂O₅ (Table 1, entries 1–7).¹¹ An investigation of different solvents revealed that the neat conditions were optimal (Table 1, entries 1–3). We discovered that *O*-acylation proceeded as well as the Friedel–Crafts acylation reaction to generate **3a**. The use of 1.0 equivalent of P₂O₅ provided the desired product in 54% yield (Table 1, entry 4). Acetylated compound **3a** was obtained at 140 °C in 61% yield, although a slightly diminished yield was obtained at 150 °C (Table 1, entries 5 and 6). The use of 2.0 equivalents of P₂O₅ produced product **3a** in 61% yield (Table 1, entry 7). However, the use of graphene oxide (GO) for activating both acetic acid and aryl groups¹² or Lewis acidic Nb₂O₅^{13,14} instead of P₂O₅ led to lower yields (Table 1, entries 8–16).

Table 1 Optimization of the Friedel–Crafts acylation reaction between phenolic components of the fast pyrolysis-derived bio-oils and acetic acid



Entry	Conditions	Solvent	Time (h)	<i>T</i> (°C)	AcOH (equiv.)	Yield ^a (%)
1	P ₂ O ₅ (0.5 equiv.)	DCE	12	120	2.0	0
2	P ₂ O ₅ (0.5 equiv.)	DMF	12	120	2.0	0
3	P ₂ O ₅ (0.5 equiv.)	Neat	12	120	15	43
4	P ₂ O ₅ (1.0 equiv.)	Neat	12	120	15	54
5	P ₂ O ₅ (1.0 equiv.)	Neat	12	140	15	61
6	P ₂ O ₅ (1.0 equiv.)	Neat	12	150	10	58
7	P ₂ O ₅ (2.0 equiv.)	Neat	12	140	10	61
8	GO (100 wt%)	Neat	12	120	10	30
9	GO (100 wt%)	CH ₃ NO ₂	12	120	10	0
10	GO (100 wt%)	CHCl ₃	12	120	10	Trace
11	GO (100 wt%)	1,4-Dioxane	12	120	10	0
12	GO (100 wt%)	Triethylene glycol	12	120	10	0
13	GO (100 wt%)	IPA	12	120	10	25
14	Nb ₂ O ₅ (1.0 equiv.)	Neat	12	120	10	0
15	Nb ₂ O ₅ (1.0 equiv.)	MeNO ₂	12	120	10	25
16	Nb ₂ O ₅ (1.0 equiv.)	DMSO	12	120	10	Trace

^a Yield of isolated product.

With the optimized reaction conditions in hand, we investigated the scope of phenolic substrates found in bio-oils for the Friedel–Crafts acylation transformation (Scheme 2). *ortho*-Alkyl substituted phenols, *o*-cresol **1b**, 2-ethylphenol **1c**, and 2-propylphenol **1d**, produced the corresponding products in moderate yields (Scheme 2, entries 1–3). In addition, alkyl substituents at the *meta* position were tolerated under the reaction conditions (Scheme 2, entries 4 and 5). *para*-Cresol **1g**, 4-ethylphenol **1h**, and 4-propylphenol **1i** generated the desired products in 56%, 40%, and 48% yields, respectively (Scheme 2, entries 6–8). However, 2,6-dimethoxyphenol **1j** provided acetylated product **3j** in a reduced yield (Scheme 2, entry 9). 2-Methoxy-4-methylphenol **1k** and 3,4-dimethylphenol **1l** produced the desired products in 57% and 53% yields, respectively (Scheme 2, entries 10 and 11).

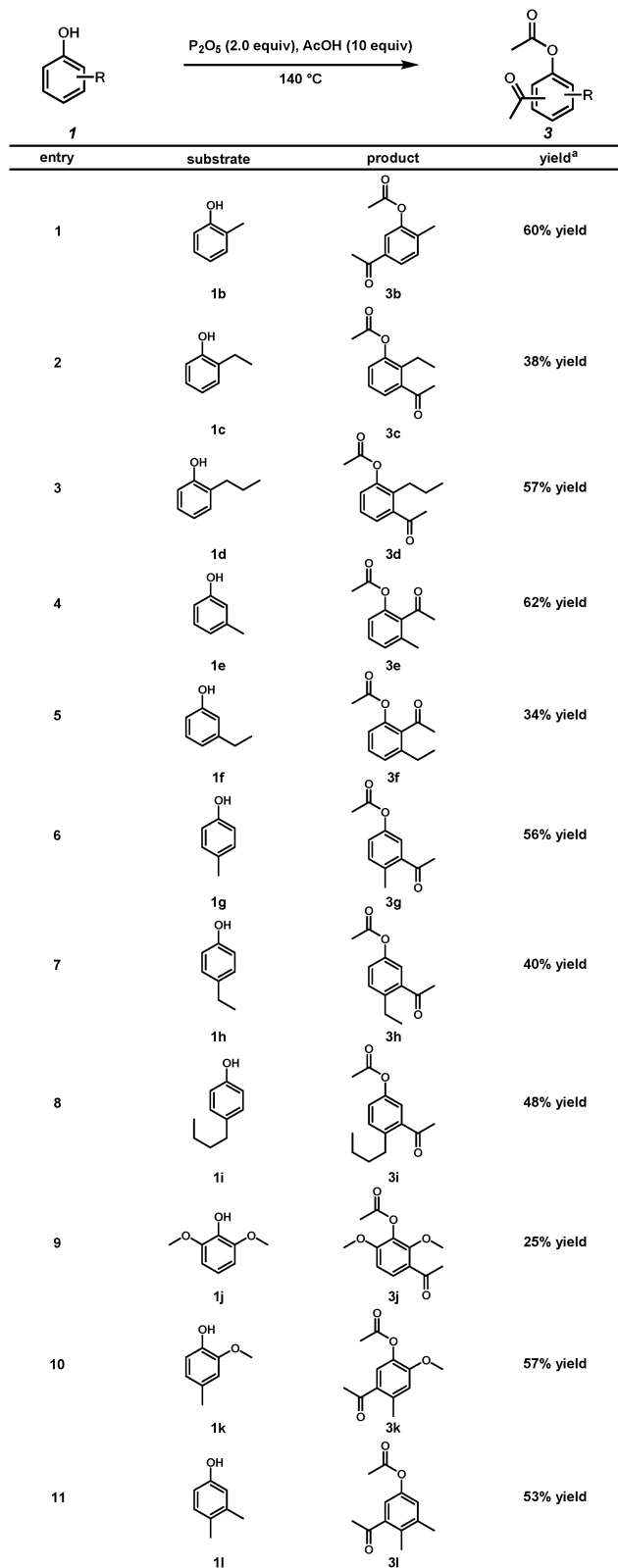
Non-phenolic aromatic components are also commonly found in bio-oils. Therefore, the Friedel–Crafts acylation reaction on non-phenolic aromatic components was optimized using anisole **4a** as a model substrate (Table 2). Initially, we attempted the Friedel–Crafts acylation reaction under optimized conditions for phenolic substrates. However, desired compound **5a** was obtained in a diminished yield (Table 2, entry 1). The use of more equivalents of acetic acid provided **5a** in higher yields (Table 2, entries 2–4). 4-Methoxyacetophenone **5a** was obtained in 70% yield using 20 equivalents of acetic acid (Table 2, entry 4). We discovered that the addition of 1.0 equivalent of P₂O₅ resulted in a lower yield (Table 2, entry 5).

We investigated the substrate scope of non-phenolic components in bio-oils (Scheme 3). 2-Methylanisole **4b** produced acetophenone **5b** in 53% yield (Scheme 3, entry 1). Xylene **4c** was tolerated under the reaction conditions, producing **5c** in a moderate yield (Scheme 3, entry 2). In addition, Friedel–Crafts acylation of indan **4d** and furan **4e** generated **5d** and **5e**, respectively (Scheme 3, entries 3 and 4).

With the scope of the established Friedel–Crafts acylation reactions, we sought to demonstrate the utility of the synthesized acylated products in the synthesis of valuable components containing more than eight carbons, which could be used as substitutes for the conventional oil after further upgrading. Claisen–Schmidt condensation of furfural **6** and acylated products from non-phenolic components of fast pyrolysis-derived bio-oils **5a** and **5e** produced desired products **7** and **8**, respectively in good yields under mild reaction conditions (Scheme 4). In addition, Claisen–Schmidt condensation of furfural **6** and **3a** that was synthesized from phenolic components of fast pyrolysis-derived bio-oils and acetic acid generated **9** in moderate yield (Scheme 4).

In summary, the Friedel–Crafts acylation reaction was utilized to remove acetic acid to upgrade bio-oils. The resulting acetophenones can be converted into more valuable components for fuels. Friedel–Crafts acylation using 2 equivalents of P₂O₅ provided the corresponding acetophenones in moderate to good yields. Both the phenolic and non-phenolic components of the bio-oils were all well tolerated under our reaction conditions. In addition, we found that the products from the Friedel–Crafts acylation reactions can be further upgraded by Claisen–Schmidt condensation under mild reaction conditions.



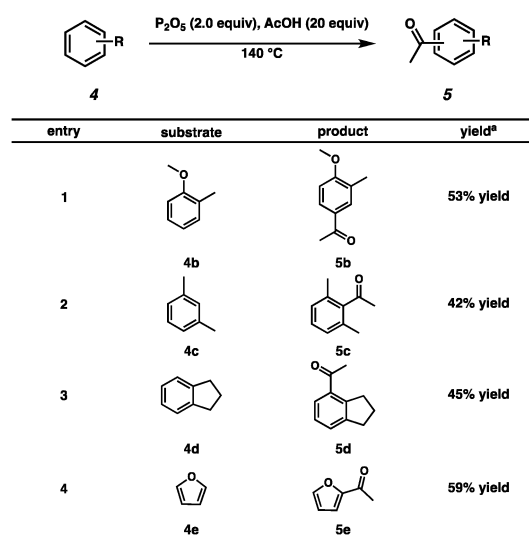


Scheme 2 Friedel–Crafts acylation on phenolic components of fast pyrolysis-derived bio-oils (^aYield of the isolated product).

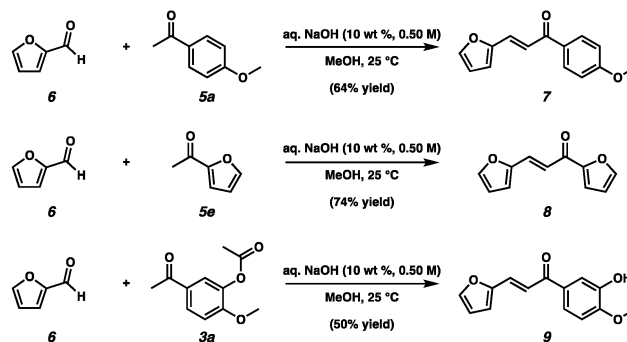
Table 2 Optimization of the Friedel–Crafts acylation reaction between non-phenolic components of the fast pyrolysis-derived bio-oils and acetic acid

Entry	Conditions (equiv.)	Solvent	Time (h)	T (°C)	AcOH (equiv.)	Yield ^a (%)
1	P ₂ O ₅ (2.0)	Neat	12	140	10	31
2	P ₂ O ₅ (2.0)	Neat	12	140	13	36
3	P ₂ O ₅ (2.0)	Neat	12	140	15	40
4	P ₂ O ₅ (2.0)	Neat	12	140	20	70
5	P ₂ O ₅ (1.0)	Neat	12	140	20	38

^a Yield of the isolated product.



Scheme 3 Friedel–Crafts acylation on non-phenolic components of fast pyrolysis-derived bio-oils (^aYield of the isolated product).



Scheme 4 Claisen–Schmidt Condensation between furfural **6** and acetylated compounds from the Friedel–Crafts acylation reactions.



