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

Han Byeol Kim,[‡] Pratik Kumar Dutta,[‡] Duck-Hyung Lee[‡] and
Seo-Jung Han[‡]

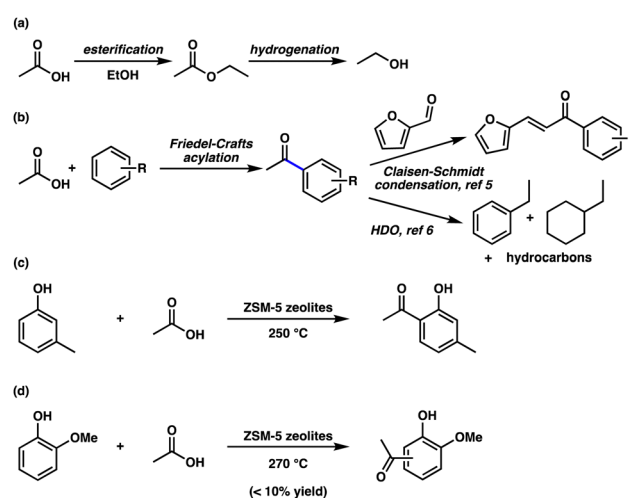
Fast pyrolysis-derived bio-oils contain numerous oxygenated components, including acetic acid and formic acid. However, these acids present in fast pyrolysis-derived bio-oils are responsible for the instability and corrosiveness of the oils. Although these acids have been removed from fast pyrolysis-derived 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.

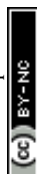
^a Chemical & Biological Integrative Research Center, Korea Institute of Science and Technology, 5 Hwarang-ro 14-gil, Seongbuk-gu, Seoul 02792, Republic of Korea. E-mail: sjhan@kist.re.kr

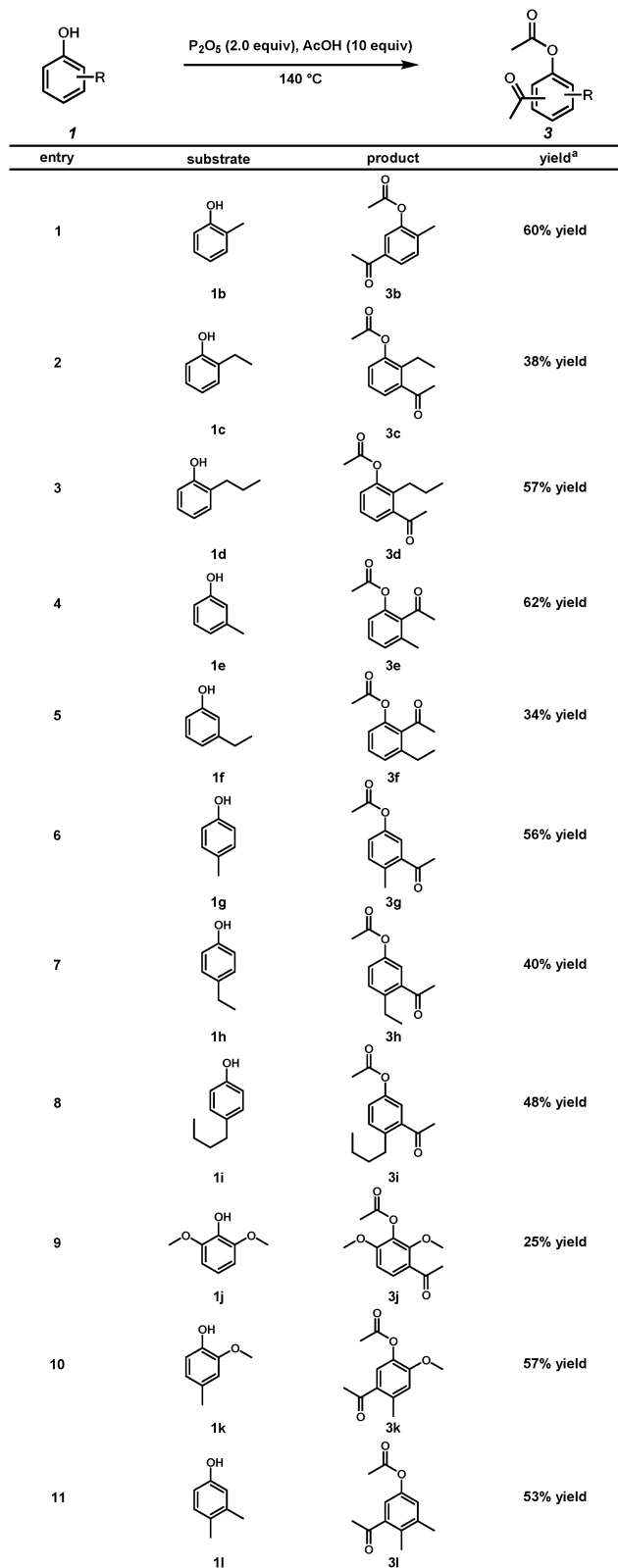
^b Department of Chemistry, Sogang University, 35 Baekbeom Ro, Seoul 04107, Republic of Korea

^c Division of Bio-Medical Science & Technology, KIST School, University of Science and Technology, 5 Hwarang-ro 14-gil, Seongbuk-gu, Seoul 02792, Republic of Korea

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‡ H. B. Kim and P. K. Dutta contributed equally to this work.



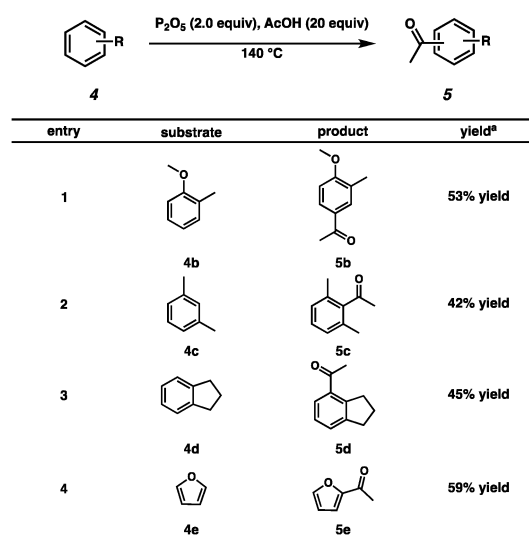


Scheme 2 Friedel–Crafts acylation on phenolic components of fast pyrolysis-derived bio-oils (^aYield of the isolated product).

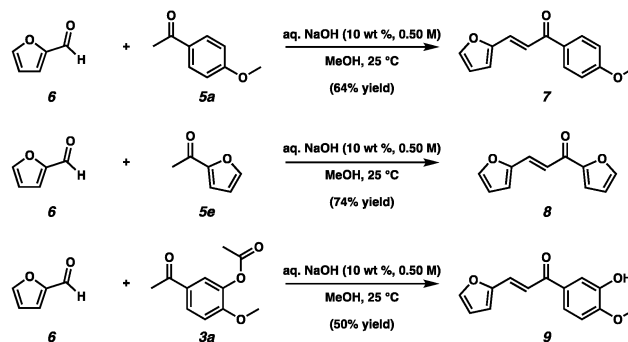
Table 2 Optimization of the Friedel–Crafts acylation reaction between non-phenolic components of the fast pyrolysis-derived bio-oils and acetic acid

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.



Conflicts of interest

There are no conflicts to declare.

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References

- 1 N. Lohitharn and B. H. Shanks, *Catal. Commun.*, 2009, **11**, 96; J. Chen, Q. Cai, L. Lu, F. Leng and S. Wang, *ACS Sustainable Chem. Eng.*, 2017, **5**, 1073.
- 2 C. Liu, H. Wang, A. M. Karin, J. Sun and Y. Wang, *Chem. Soc. Rev.*, 2014, **43**, 7594.
- 3 S. Czernik and A. V. Bridgwater, *Energy Fuels*, 2004, **18**, 590; S. Czernik, D. K. Johnson and S. Black, *Biomass Bioenergy*, 1994, **7**, 187.
- 4 Q. Zhang, L. Zhang, T. Wang, Y. Xu, Q. Zhang, L. Ma, M. He and K. Li, *Energy Procedia*, 2014, **61**, 1033; J.-J. Wang, J. Chang and J. Fan, *Energy Fuels*, 2010, **24**, 3251; Y. Liu, Z. Li, J. J. Leahy and W. Kwapinski, *Energy Fuels*, 2015, **29**, 3691; Y. Xu, L. Zhang, W. Lv, C. Wang, C. Wang, X. Zhang, Q. Zhang and L. Ma, *Catalysts*, 2021, **11**, 818; L. Ciddor, J. A. Bennett, J. A. Hunns, K. Wilson and A. F. Lee, *J. Chem. Technol. Biotechnol.*, 2015, **90**, 780.
- 5 G. Yadav and A. R. Yadav, *RSC Adv.*, 2014, **4**, 63772.
- 6 C. González, P. Marín, F. V. Díez and S. Ordóñez, *Energy Fuels*, 2015, **29**, 8208.
- 7 H. K. Chau, D. E. Resasco, P. Do and S. P. Crossley, *J. Catal.*, 2022, **406**, 48.
- 8 S. Gutiérrez-Rubio, M. Shamzhy, J. Cejka, D. P. Serrano, I. Moreno and J. M. Coronado, *Appl. Catal., B*, 2021, **285**, 119826.
- 9 M. K. Montañez-Valencia, C. L. Padró and M. E. Sad, *Appl. Catal., B*, 2020, **278**, 119317.
- 10 I. B. Adilina, N. Rinaldi, S. P. Simanungkalit, F. Aulia, F. Oemry, G. B. G. Stenning, I. P. Silverwood and S. F. Parker, *J. Phys. Chem. C*, 2019, **123**, 21429.
- 11 (a) A. Zarei, A. R. Hajipour and L. Khazdooz, *Tetrahedron Lett.*, 2008, **49**, 6715; (b) A. R. Hajipour, A. Zarei, L. Khazdooz and A. E. Ruoho, *Synth. Commun.*, 2009, **39**, 2702; (c) A. Sumita, Y. Otani and T. Ohwada, *Org. Biomol. Chem.*, 2017, **15**, 9398; (d) P. E. Eaton, G. R. Carlson and J. T. Lee, *J. Org. Chem.*, 1973, **38**, 4071; (e) D. Zewge, C.-Y. Chen, C. Deer, P. G. Domer and D. L. Hughes, *J. Org. Chem.*, 2007, **72**, 4276.
- 12 F. Hu, M. Patel, F. Luo, C. Flach, R. Mendelsohn, E. Garfunkel, H. He and M. Szostak, *J. Am. Chem. Soc.*, 2015, **137**, 14473.
- 13 M. H. Sarvari and H. Sharghi, *Synthesis*, 2004, 2165; S. M. A. H. Siddiki, N. Rashed, A. Ali, T. Toyao, P. Hirunsit, M. Ehara and K.-i Shimizu, *ChemCatChem*, 2019, **11**, 383.
- 14 M. A. Ali, S. M. A. H. Siddiki, K. Kon and K.-i Shimizu, *ChemCatChem*, 2015, **7**, 2705.

