Continuous flow esterifications harnessing vibrational-coupled thin film fluidics

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Supplementary information

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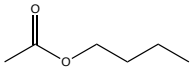
Experimental Procedure

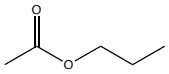
Unless otherwise indicated, all reagents were commercially available and used directly from the supplier without further purification. ^{1}H and ^{13}C NMR were recorded at 20.6 °C using $CDCl_3$ (7.27 ppm) unless otherwise indicated. Chemical shift values are expressed in parts per million (ppm) and *J*-values in Hertz (Hz). Splitting patterns are indicated at s: singlet, d: doublet, t: triplet, q: quartet, quin: quintet, sex: sextet, sept: septet or combination br s: broad singlet or m: multiplet. FT-IR were recorded using a Perkin Elmer FTIR monitor. GC-MS were recorded on a Varian CP-3800 gas chromatography unit coupled with a 2200 Saturn MS detection unit. Injection occurred at 25 °C and increased at a rate of 10 °C /min until 300 °C was achieved. A reverse phase column (30 M X 25 µM X 0.25 mM) was used, and mass spectrometry data was analysed with NIST 05 molecular recognition software.

[1] *n*-Butyl acetate



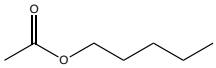
IR νmax (cm^{-1}); 2962, 2937, 2876, 1740, 1466, 1366, 1229, 1065, 1031, 951; ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.01 (t, *J* = 7.0 Hz, 2 H, CH_2), δ 1.99 (s, 3 H, CH_3), δ 1.53 (quin, *J* = 7.0 Hz, 2 H, CH_2), δ 1.30 (sex, *J* = 7.6 Hz, 2 H, CH_2), δ 0.86 (t, *J* = 7.6 Hz, 3 H, CH_3); ^{13}C (150 MHz, $CDCl_3$): 170.8, 64.0, 30.2, 20.6, 19.4, 13.6; GC-MS m/*z*; 55.9 (27) and 43.0 (100). This molecule had spectra identical to that already reported in the literature.[1]

[2] *n*-Propyl acetate



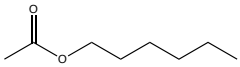
IR νmax (cm^{-1}); 2970, 2884, 1739, 1461, 1366, 1231, 1065, 1045, 966; ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.07 (t, J = 10.6 Hz, 2 H, CH_2), δ 2.06 (s, 3 H, CH_3), δ 1.64 (quin, J = 10.6 Hz, 2 H, CH_2), δ 0.93 (t, J = 10.6 Hz, 3 H, CH_3); ^{13}C (150 MHz, $CDCl_3$): 171.2, 66.0, 22.1, 20.9, 10.3; GC-MS m/*z*; 102.3 (100), 101.4 (68), 79.2 (32) and 39.2 (12). This molecule had spectra identical to that already reported in the literature.[1]

[3] *n*-Pentyl acetate



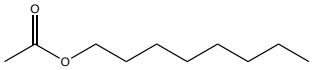
IR νmax (cm^{-1}); 2959, 2868, 1740, 1467, 1365, 1232, 1050, 1039, 97; ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.07 (t, J = 10.2 Hz, 2 H, CH_2), δ 2.05 (s, 3 H, CH_3), δ 1.62 (quin, J = 10.2 Hz, 2 H, CH_2), 1.44 – 1.32 (m, 4H, CH_2CH_2) δ 0.94 (t, J = 11.0 Hz, 3 H, CH_3); ^{13}C (150 MHz, $CDCl_3$): 170.9, 64.4, 31.2, 28.0, 22.2, 20.7, 13.7; GC-MS m/*z*; 102.7 (100), 101.7 (51) and 43.2 (9). This molecule had spectra identical to that already reported in the literature.[2]

[4] *n*-Hexyl acetate



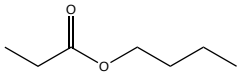
IR νmax (cm^{-1}); 2958, 2860, 1740, 1467, 1388, 1365, 1235, 1033, 895; ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.99 (t, J = 10.3 Hz, 2 H, CH_2), δ 1.98 (s, 3 H, CH_3), δ 1.56 (qu, J = 10.3 Hz, 2 H, CH_2), 1.33 – 1.22 (m, 6H, $CH_2CH_2CH_2$), δ 0.83 (t, J = 10.3 Hz, 3 H, CH_3); ^{13}C (150 MHz, $CDCl_3$): 171.2, 64.8, 31.6, 28.7, 26.1, 22.7, 21.0, 13.9; GC-MS m/*z*; 85.0 (61), 61.1 (100) and 43.1 (35). This molecule had spectra identical to that already reported in the literature.[3]

[5] *n*-Octyl acetate



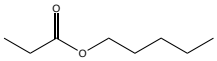
IR νmax (cm^{-1}); 2926, 2857, 1742, 1467, 1388, 1365, 1232, 1038, 724; ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.97 (t, J = 7.0 Hz, 2 H, CH_2), δ 1.96 (s, 3 H, CH_3), δ 1.54 (qu, J = 7.0 Hz, 2 H, CH_2), δ 1.27 – 1.19 (m, 10 H, $CH_2CH_2CH_2$ CH_2CH_2), δ 0.80 (t, J = 7.0 Hz, 3 H, CH_3); ^{13}C (150 MHz, $CDCl_3$): 171.2, 64.6, 31.8, 29.2, 29.2, 28.6, 26.0, 22.6, 20.9, 14.0; GC-MS m/*z*; 71.0 (100), 61.1 (36), 57.1 (21), 43.0 (9) and 39.0 (19). This molecule had spectra identical to that already reported in the literature.[4]

[6] *n*-Butyl propionate



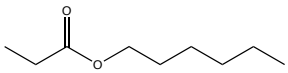
IR νmax (cm^{-1}); 2962, 2877, 1736, 1463, 1382, 1348, 1274, 1182, 1079, 1083, 808; ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.98 (t, *J* = 7.0 Hz, 2 H, CH_2), δ 2.22 (q, J = 7.0 Hz, 2 H, CH_2), δ 1.52 (quin, *J* = 7.8 Hz, 2 H, CH_2), δ 1.28 (sex, *J* = 7.8 Hz, 2 H, CH_2), δ 1.04 (t, *J* = 7.0 Hz, 3 H, CH_3), 0.84 (t, *J* = 7.8 Hz, 3 H, CH_3); ^{13}C (150 MHz, $CDCl_3$): 174.4, 64.0, 30.7, 27.5, 19.1, 13.6, 9.0; GC-MS m/*z*; 130.5 (100), 129.5 (57), 57.0 (85) and 39.0 (64). This molecule had spectra identical to that already reported in the literature.[5]

[7] *n*-Pentyl propionate



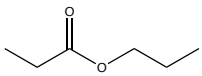
IR νmax (cm^{-1}); 2958, 2873, 1738, 1465, 1349, 1273, 1183, 1083, 1012; ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.96 (t, *J* = 6.8 Hz, 2 H, CH_2), δ 2.20 (q, *J* = 7.5 Hz, 2 H, CH_2), δ 1.51 (quin, *J* = 6.8 Hz, 2 H, CH_2), δ 1.22 (m, 4 H, CH_2CH_2), δ 1.02 (t, *J* = 7.5 Hz, 3 H, CH_3), δ 0.79 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C (150 MHz, $CDCl_3$): 174.6, 64.4, 32.4, 28.0, 27.5, 22.2, 13.8, 9.0; GC-MS m/*z*; 144.5 (15), 75.1 (100), 57.0 (53) and 39.0 (26). This molecule had spectra identical to that already reported in the literature.[6]

[8] *n*-Hexyl propionate



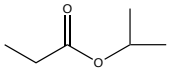
IR νmax (cm^{-1}); 2931, 2860, 1739, 1463, 1348, 1274, 1183, 1083, 1017; ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.95 (t, *J* = 6.9 Hz, 2 H, CH_2), δ 2.20 (q, *J* = 7.7 Hz, 2 H, CH_2), δ 1.51 (quin, *J* = 6.9 Hz, 2 H, CH_2), 1.25 – 1.48 (m, 6 H, $CH_2CH_2CH_2$), δ 1.02 (t, *J* = 7.7 Hz, 3 H, CH_3), δ 0.78 (t, *J* = 6.9 Hz, 3 H, CH_3); ^{13}C (150 MHz, $CDCl_3$): 174.5, 64.4, 31.2, 28.6, 27.6, 25.7, 22.6, 13.9, 9.4; GC-MS m/*z*; 75.2 (100), 57.0 (43) and 39.0 (29). This molecule had spectra identical to that already reported in the literature.[7]

[9] *n*-Propyl propionate



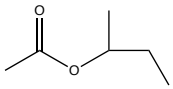
IR νmax (cm^{-1}); 2972, 2884, 1737, 1464, 1353, 1272, 1183, 1082, 941, 809; ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.90 (t, *J* = 6.7 Hz, 2 H, CH_2), δ 2.19 (q, *J* = 6.7 Hz, 2 H, CH_2), δ 1.51 (quin, *J* = 6.7 Hz, 2 H, CH_2), δ 0.99 (t, *J* = 6.7 Hz, 3 H, CH_3), δ 0.80 (t, *J* = 6.7 Hz, 3 H, CH_3); ^{13}C (150 MHz, $CDCl_3$): 174.4, 65.7, 27.5, 22.0, 10.2, 9.0; GC-MS m/*z*; 102.3 (100), 99.2 (50), 61.0 (17) and 39.1 (18). This molecule has identical spectra compared to predicted spectra.[8]

[10] Iso-propyl propionate



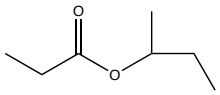
IR νmax (cm^{-1}); 2982, 2941, 2881, 1733, 1373, 1274, 1193, 1109, 1079, 927, 808; ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.93 (sept, *J* = 6.8 Hz, 1 H, CH), δ 2.22 (q, *J* = 7.5 Hz, 2 H, CH_2), δ 1.15 (d, *J* = 7.5 Hz, 6 H, $(CH_3)_2$), δ 1.06 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C (150 MHz, $CDCl_3$): 174.1, 67.2, 27.9, 21.9, 9.1; GC-MS m/*z*; 118.8 (24), 116.8 (24). This molecule had spectra identical to that already reported in the literature.[9]

[11] Sec-Butyl acetate



IR νmax (cm^{-1}); 2975, 2942, 2880, 1734, 1372, 1239 1127, 1116, 1030, 1027, 868; ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.83 (sex, *J* = 6.8 Hz, 1 H, CH), δ 2.05 (s, 3 H, CH_3), δ 1.63-1.59 (m, 2 H, CH_2), δ 1.21 (d, *J* = 6.8 Hz, 3 H, CH_3), δ 0.89 (t, *J* = 6.8 Hz, 3 H, CH_3); ^{13}C (150 MHz, $CDCl_3$): 171.0, 72.3, 28.8, 21.3, 19.7, 9.8; GC-MS m/*z*; 116.2 (51), 57.0 (49) and 39.1 (46). This molecule has identical spectra compared to predicted spectra. [8]

[12] Sec-Butyl propionate



IR νmax (cm^{-1}); 2980, 2942, 2880, 1733, 1377, 1191, 1126, 1115, 1086, 868; ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.68 (sex, *J* = 6.5 Hz, 1 H, CH), δ 2.14 (q, *J* = 7.5 Hz, 2 H, CH_2), δ 1.47 – 1.40 (m, 2 H, CH_2), δ 1.06 – 1.03 (m, 3 H, CH_3), δ 0.97 (t, *J* = 6.5 Hz, 3 H, CH_3), δ 0.73 (t, *J* = 6.5 Hz, 3 H, CH_3); ^{13}C (150 MHz, $CDCl_3$): 171.1, 71.8, 28.8, 27.9, 22.7, 19.5, 9.5; GC-MS m/*z*; 75.0 (100), 57.0 (38) and 39.1 (11). This molecule has identical spectra compared to predicted spectra.[8]

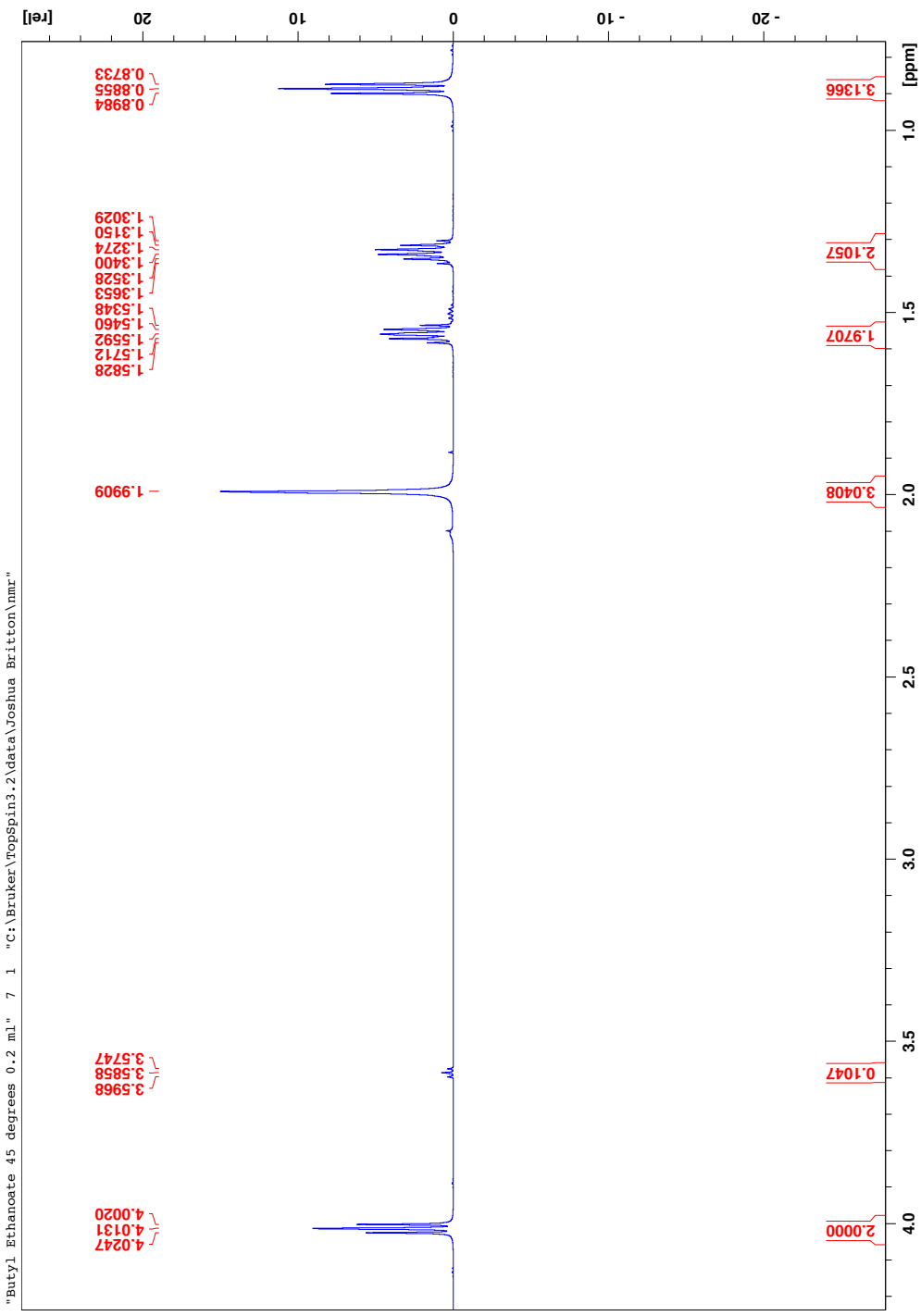


Figure 1. ^{1}H NMR of *n*-butyl acetate showing the small alcohol peak at 3.59 ppm that was taken into consideration when calculating yields. Purity eg. (2/2.1407) *100 = 93.4 % of product, with 6.4 % being *n*-butanol.

Recycling through the VFD

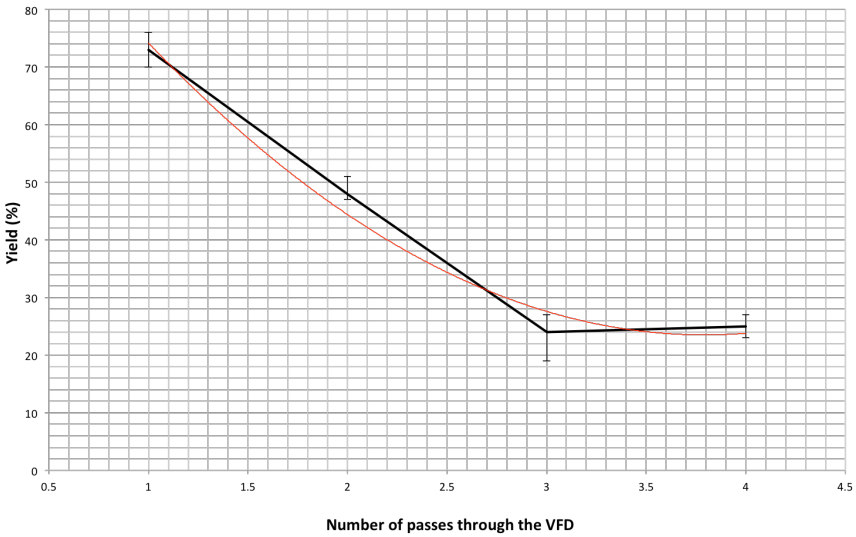


Chart 1. The effect of multiple passes through the VFD on the yield for the esterification of *n*-butyl acetate at a 45 ° tilt angle relative to the horizontal position, for a flow rate of 0.50 mL/min and 5250 rpm rotational speed, housing a 17.5 mm internal diameter NMR tube.

Variation in acid concentration for the synthesis of *n*-butyl acetate

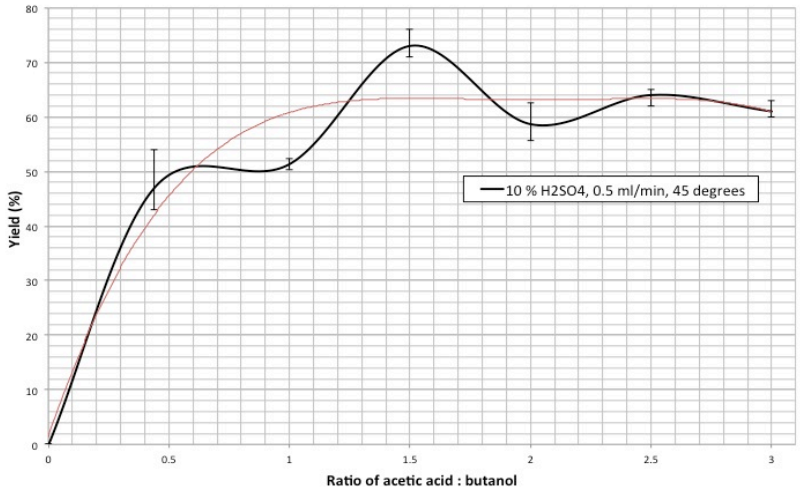


Chart 2. Change in the ratio of acetic acid to *n*-butanol versus yield at a 45 ° tilt angle relative to the horizontal position for a flow rate of 0.50 mL/min and 5250 rpm rotational speed, housing a 17.5 mm internal diameter NMR tube.

Variation in acid catalyst for the synthesis of *n*-butyl acetate

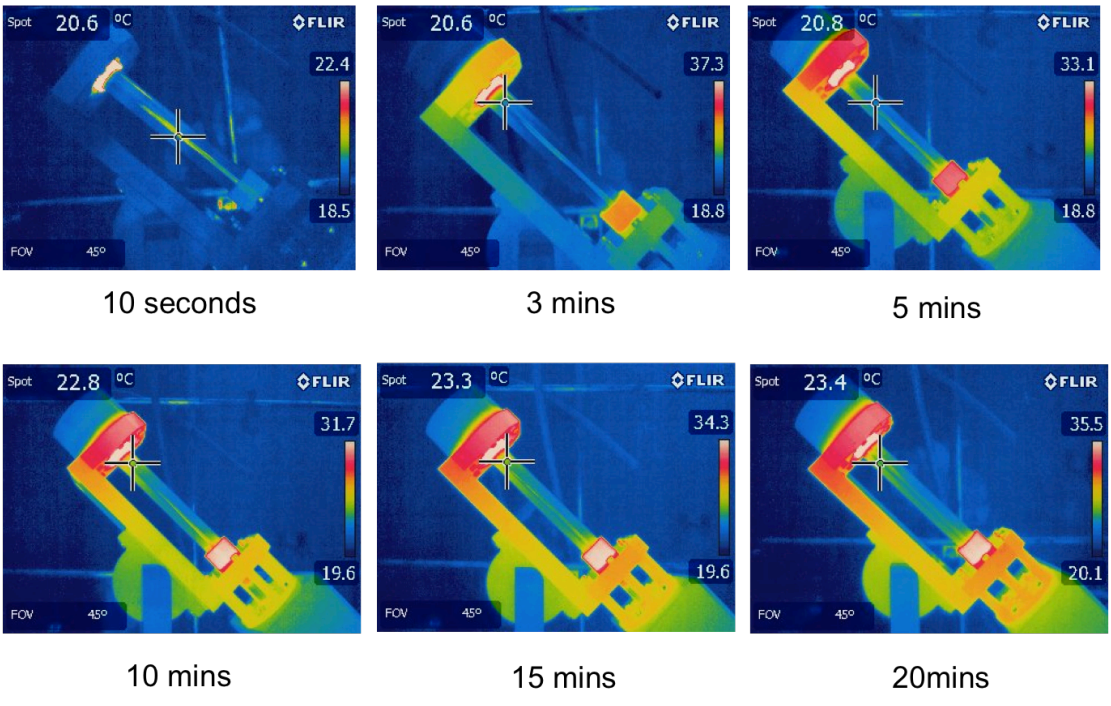
Catalyst	Yield (%)
Sulfuric Acid	73
Nitric Acid	0
ortho-phosphoric Acid	0
Hydrochloric Acid	20
p-toluenesulfonic Acid	30

Table 1. Percent conversion for a ratio of *n*-butanol to acetic acid of 1:1.5 as a function of choice of acid catalyst, for the VFD (17.5 mm internal diameter NMR tube) operating at θ 45°, and 5250 rpm, for a flow rate of 0.50 mL/min.

Fabrication of a high contact angle surface 20 mm VFD tube

A 17.5 mm internal diameter NMR tube was filled with fresh piranha solution and left for one hour. Following this, the tube was rinsed with Milli-Q water (10 x 25 mL) and then placed in the over at 150 °C for 16 hrs. The tube was removed from the oven and 75 % volume was filled with toluene, following this trichlorododecyl silane (2 mL) was added and then toluene was added until the NMR tube was full, and after standing for 24 hrs, the solution was removed and the tube then rinsed with toluene (2 x 10 mL), followed by water (2 x 10 mL).

Thermal imaging of a rotating tube devoid of solvent



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[6] WSS: Spectral data was obtained from Wiley subscription services, INC. (US).
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