Entrainer-intensified vacuum reactive distillation process for the separation of 5-hydroxylmethylfurfural from the dehydration of carbohydrates catalyzed by metal salt/ionic liquid

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1. General information

NMR spectra were recorded on a Rarian PLUS-400 spectrometer in $CDCl_3$. ^{1}H and ^{13}C NMR chemical shifts (δ) are given in ppm relative to TMS. ^{1}H and ^{13}C positive chemical shifts (δ) in ppm are downfield from tetramethylsilane ($CDCl_3$: δ_C =77.000 ppm; residual $CHCl_3$ in $CDCl_3$: δ_H = 7.26 ppm).

Carbohydrates were analyzed by HPLC (Detector: Waters 410 Differential Refractometer; Aminex® HPX-87H column 9 m, 300×7.8 mm), using 5 mmol•l^{-1} H_2SO_4 in ultrapure water as mobile phase at a flow rate of 0.6 ml•min^{-1} and a column temperature of 60 °C. 5-HMF was analyzed by HPLC (UV Detector: Waters 2487; wavelength: 284 nm; SunfireTM C18 column 5 m; 250×4.6 mm), using 70% methanol in ultrapure water as mobile phase at a flow rate of 1 ml•min^{-1} and a column temperature of 35 °C.

2. ^{1}H NMR and ^{13}C NMR spectra of the synthesized [OMIM]Cl

The ^{1}H NMR (400 MHz, $CDCl_3$, 29 °C) spectrum data for the synthesized IL [OMIM]Cl: δ=10.44 (s, $1H_a$), 7.77 (s, $1H_b$), 7.54 (s, $1H_c$), 4.32 (t, J = 7.4 Hz, $2H_d$), 4.13 (s, $3H_e$), 2.00–1.84 (m, $2H_f$), 1.530-1.088 (dd, J = 22.5, 7.4 Hz, $10H_g$), 0.87 (t, J = 6.8 Hz, $3H_h$).

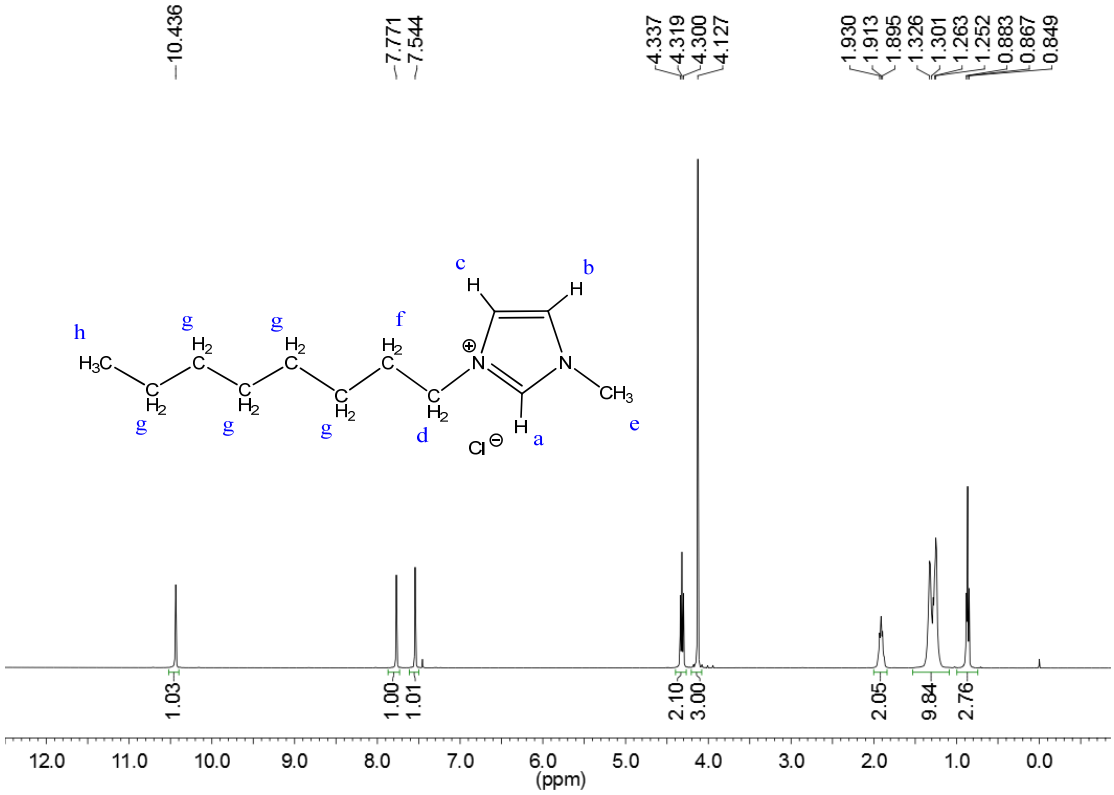

Figure 1s ^{1}H NMR spectrum of the synthesized [OMIM]Cl

The ^{13}C NMR (101 MHz, $CDCl_3$, 29 °C) spectrum data for the synthesized IL [OMIM]Cl: δ_C=137.03 ($1C_a$), 123.37 ($1C_b$), 121.50 ($1C_c$), 49.65 ($1C_d$), 36.21 ($1C_e$), 31.30 ($1C_f$), 29.99 ($1C_g$), 28.66 ($1C_h$), 28.60 ($1C_i$), 25.92 ($1C_j$), 22.22 ($1C_k$), 13.74 ($1C_l$).

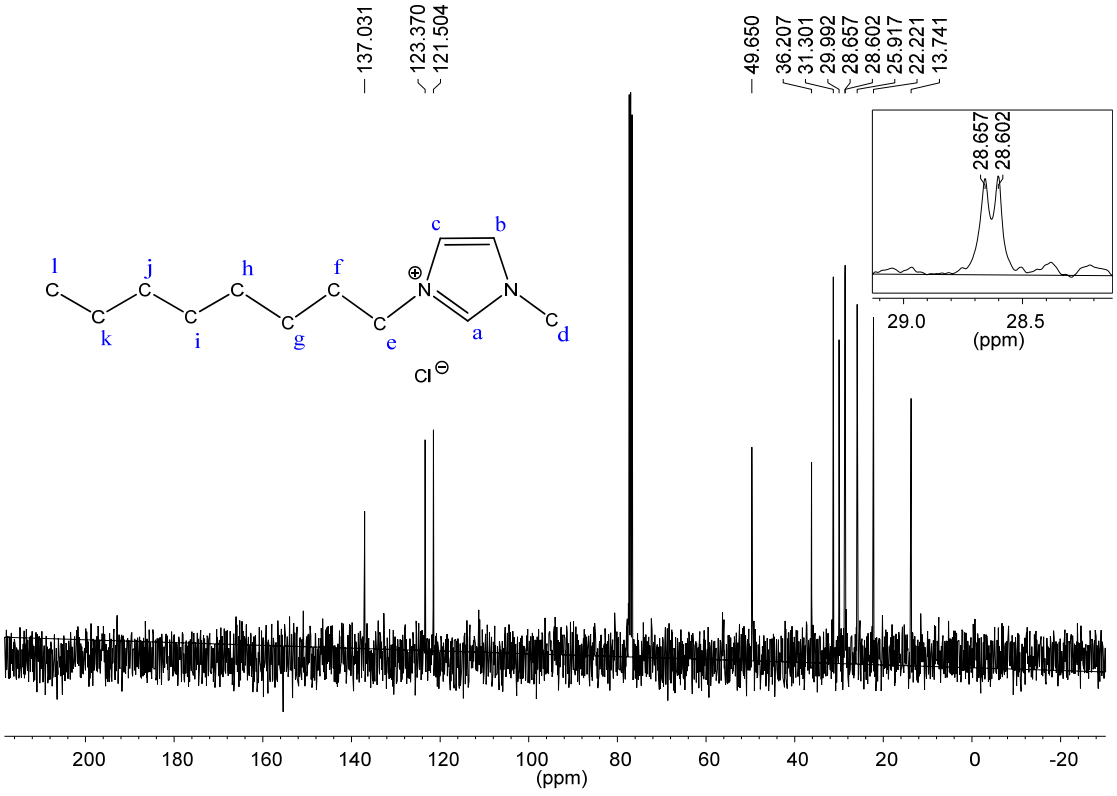

Figure 2s ^{13}C NMR spectrum of the synthesized [OMIM]Cl

3. ^{1}H NMR and ^{13}C NMR spectra of the synthesized [OMIM]Cl after the dehydration reaction

The ^{1}H NMR (400 MHz, $CDCl_3$, 29 °C) spectrum data for the synthesized IL [OMIM]Cl after five times reused for the dehydration of fructose: δ=10.31 (s, $1H_a$), 7.71 (s, $1H_b$), 7.49 (s, $1H_c$), 4.31 (t, J = 7.4 Hz, $2H_d$), 4.11 (s, $3H_e$), 2.00–1.84 (m, $2H_f$), 1.43-1.17 (dd, $10H_g$), 0.87 (t, J = 6.8 Hz, $3H_h$).

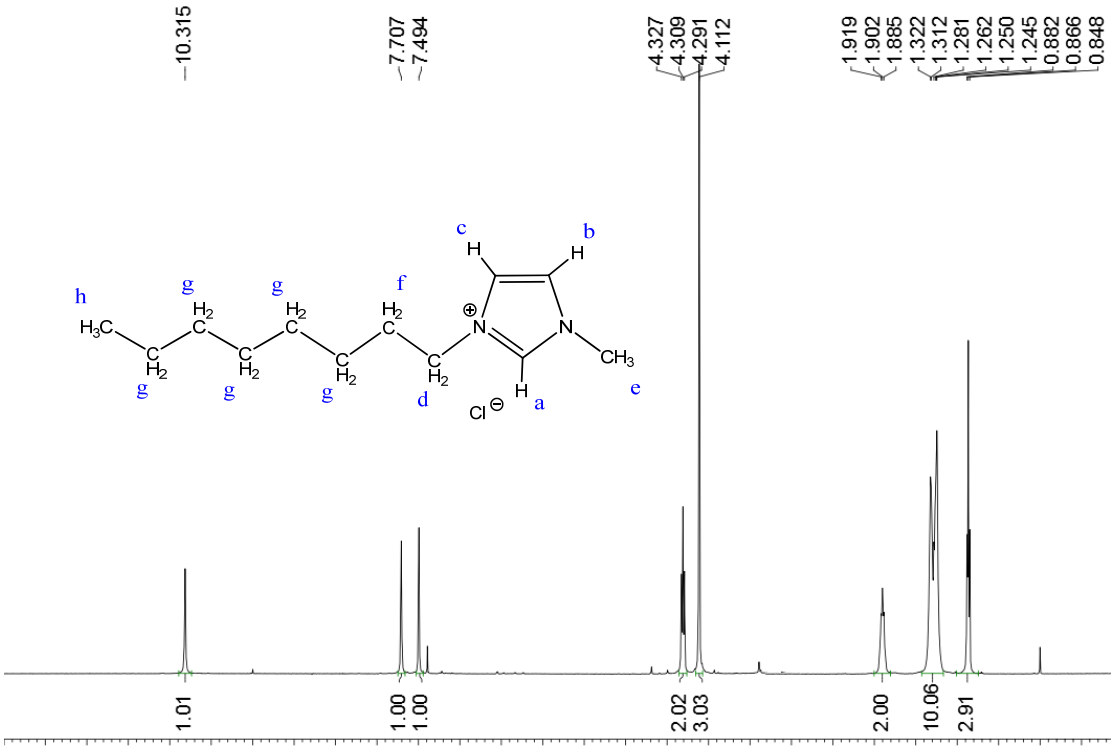

Figure 3s ^{1}H NMR spectrum of the synthesized [OMIM]Cl after five times reused for the dehydration of fructose

The ^{13}C NMR (101 MHz, $CDCl_3$, 29 °C) spectrum data for the synthesized IL [OMIM]Cl after five times reused for the dehydration of fructose: δ_C=137.11 ($1C_a$), 123.43 ($1C_b$), 121.55 ($1C_c$), 49.78 ($1C_d$), 36.36 ($1C_e$), 31.44 ($1C_f$), 30.10 ($1C_g$), 28.79 ($1C_h$), 28.73 ($1C_i$), 26.05 ($1C_j$), 22.35 ($1C_k$), 13.87 ($1C_l$).

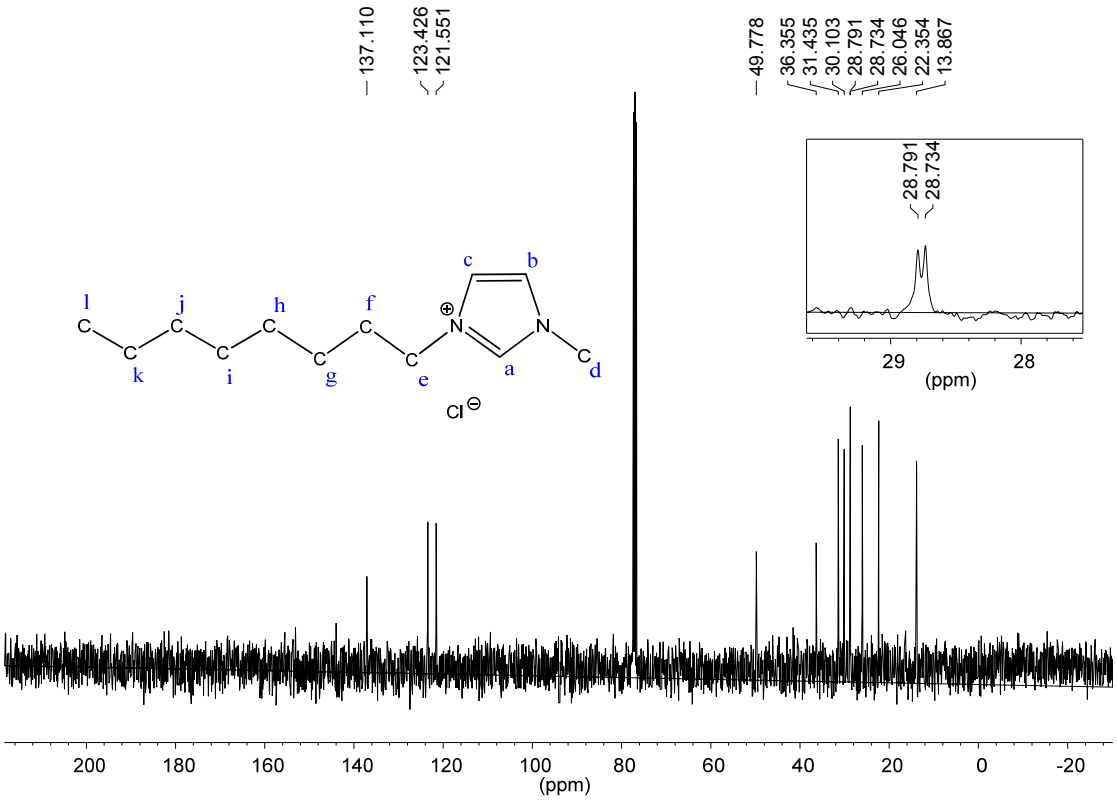

Figure 4s ^{13}C NMR spectrum of the synthesized [OMIM]Cl after five times reused for the dehydration of fructose

4. ^{1}H NMR and ^{13}C NMR spectra of the obtained 5-HMF

The ^{1}H NMR (400 MHz, $CDCl_3$, 29 °C) spectrum data for obtained 5-HMF: δ=9.56 (s, $1H_a$), 7.21 (d, J = 3.5 Hz, $1H_b$), 6.51 (d, J = 3.5 Hz, $1H_c$), 4.71 (s, $2H_d$), 2.73 (s, $1H_e$).

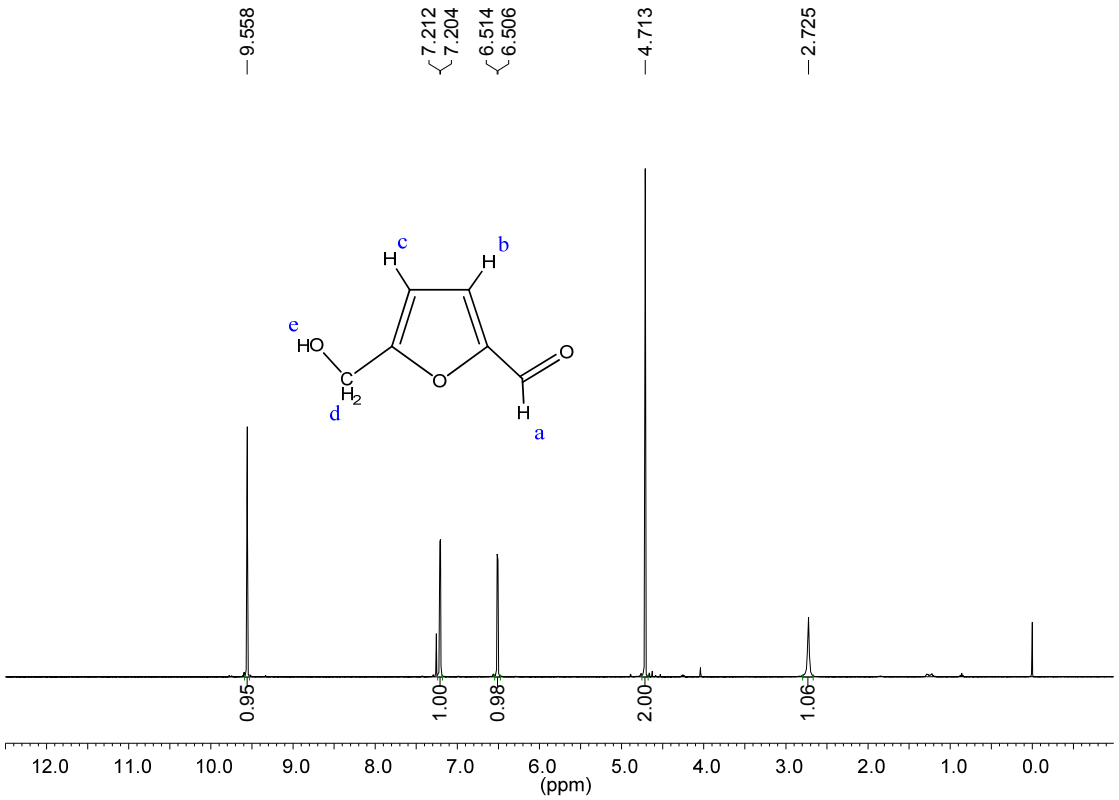

Figure 5s ^{1}H NMR spectrum of the obtained 5-HMF

The ^{13}C NMR (101 MHz, $CDCl_3$, 29 °C) spectrum data for the obtained 5-HMF: δ_C=177.40 ($1C_a$), 160.42 ($1C_b$), 152.12 ($1C_c$), 122.68 ($1C_d$), 109.90 ($1C_e$), 57.62 ($1C_f$).

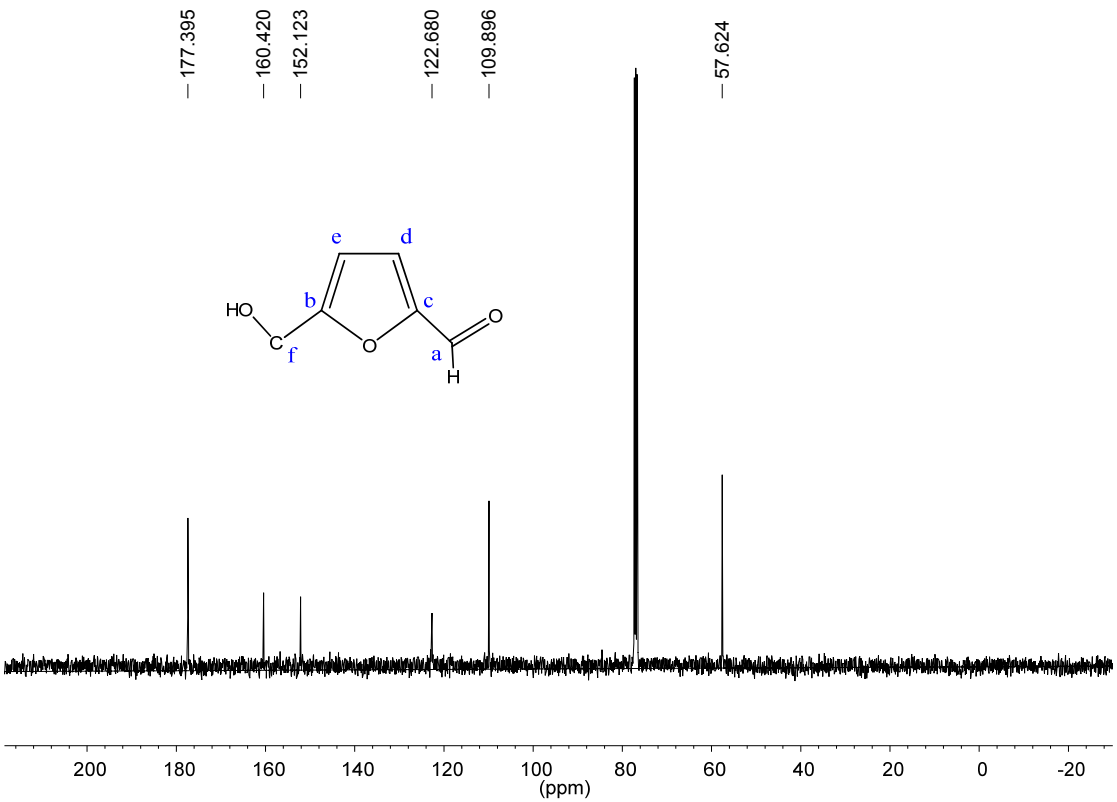

Figure 6s ^{13}C NMR spectrum of the obtained 5-HMF

5. HPLC chromatograms for the analysis of reaction bulks

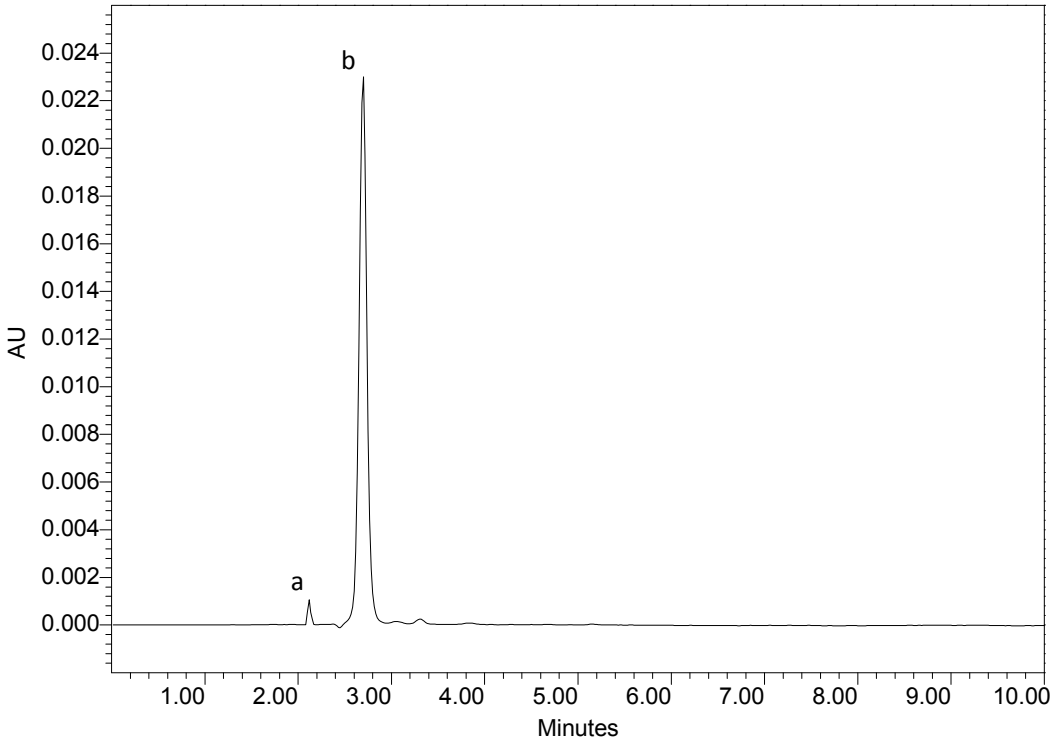

Figure 7s Typical HPLC chromatogram for the analysis of 5-HMF from reaction bulk (peak a belongs to [OMIM]Cl, with r.t. 2.05 min, peak b belongs to 5-HMF, with r.t 2.72 min)

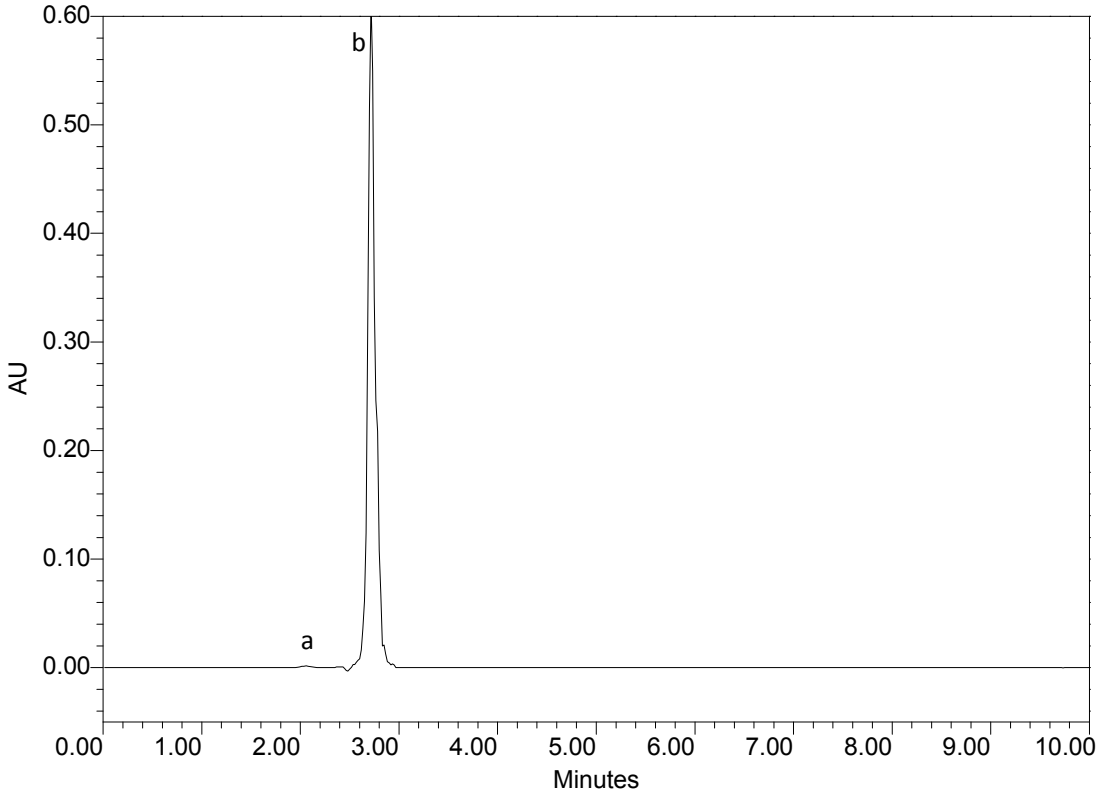

Figure 8s Typical HPLC chromatogram for the analysis of 5-HMF from recovery flask (peak a belongs to [OMIM]Cl, with r.t. 2.07 min, peak b belongs to 5-HMF, with r.t 2.73 min)

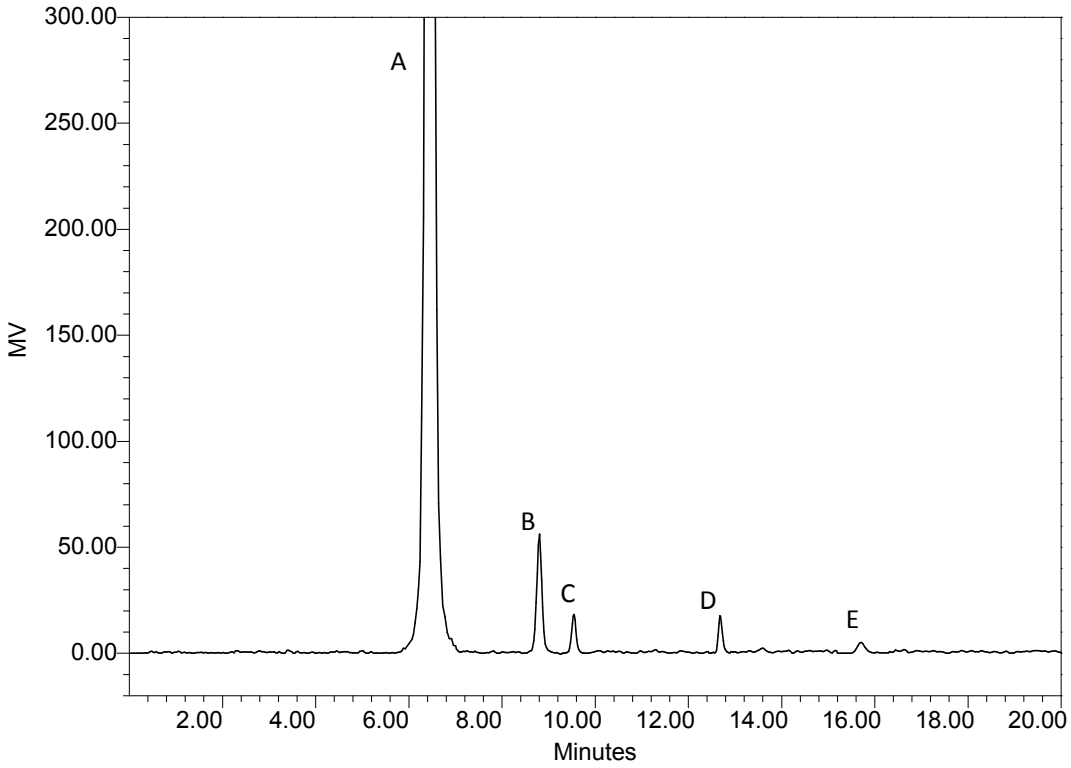

Figure 9s Typical HPLC chromatogram for the analysis of fructose and glucose (peak A belongs to [OMIM]Cl, with r.t. 6.45 min; peak B belongs to glucose, with r.t 8.80 min, peak C belongs to fructose, with r.t. 9.55 min; peak D and E are two unkown byproducts with r.t. 12.7 min and 15.7 min, respectively.)