Electronic Supplementary Material (ESI) for Green Chemistry.

SUPPLEMENTARY INFORMATION

Synthesis of N-Alkyl-4-vinylpyridinium-based Cross-linked Polymers and their Catalytic Performance for the Conversion of Fructose into 5-Hydroxymethylfurfural

Marc-Philipp Ruby[a] and Ferdi Schüth[a]

a. Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1
D-45470 Mülheim, Germany
E-mail: schueth@kofo.mpg.de

Analytics

HPLC

The reaction mixtures of the catalytic tests were analyzed by HPLC by using a Shimadzu instrument equipped with a Shimadzu CBM-20A controller, an organic acid resin column (300*8 mm), two pumps (Shimadzu LC-20AB & LC-20AD), an auto injector (Shimadzu SIL-20AC), and a column oven (Shimadzu CTO-20A). HMF was detected with a UV detector (Shimadzu SPD-M20A & SPD-M30A). All other compounds were analyzed with a refractive index (RI) detector (Shimadzu LC-10A). Trifluoroacetic acid (2 mM) in water was used as the eluent at 40 °C with a flow rate of 1.0 mL/min.

Thermogravimetric measurements

A NETZSCH thermogravimetry type "Jupiter STA 449 C" was used to check the completeness of the silica removal of the silca hard-templated preparation method of the mesoporous pre-polymer mPoly-VPyr-DVB. A sample of the mesoporous pre-polymer was heated in a gas stream of 40 mL/min of Argon as a protective gas of the balance and 60 mL/min of synthetic air. The sample was heated up from room temperature with a heating rate of 10 K/min until a final temperature of 800 °C. The combustion profile of the mesoporous pre-polymer is shown below in figure S1.

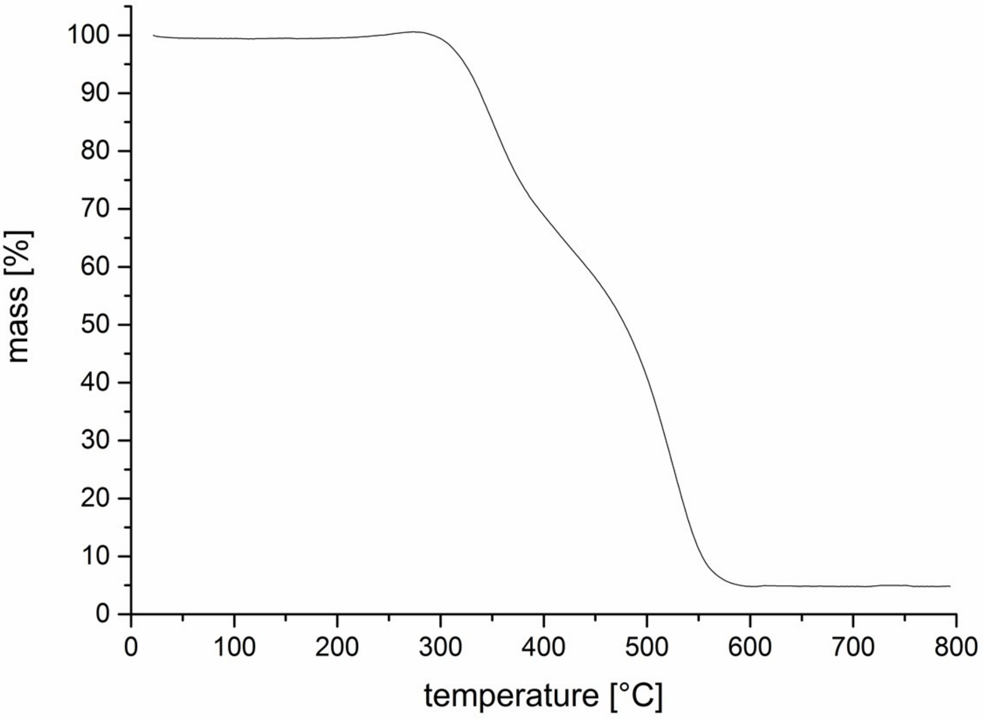

Figure S 1: Thermal combustion profile of the mesoporous pre-polymer mPoly-VPyr-DVB in synthetic air

The mesoporous pre-polymer is fully decomposed at a temperature of about 600 °C. A white solid residue of 4-5 % of the initial sample weight remained in the crucible after a thermal treatment until 800 °C in air, which is silica left from the silica hard-templating preparation method of the mesoporous pre-polymer.

Infrared spectroscopy

To check whether the modification of the synthesized pre-polymers was successful infrared spectra of both pre-polymers and modified polymers have been recorded. A Nicolet "Magna-IR 560 Spectrometer (ESP)" was used, applying attenuated total reflection mode (ATR).

The following three figures show the IR spectra of the modified polymers in comparison to the corresponding pre-polymers (black). Caused by the modification with the corresponding alkylating agent, the appearance of a new band at 1638 cm^{-1} and the disappearance of the band at 1415 cm^{-1} show the successful modification of both the mesoporous and the non-porous pre-polymers. The broad band appearing at 3390 cm^{-1} is caused by adsorbed water while the sample was placed onto the ATR crystal.

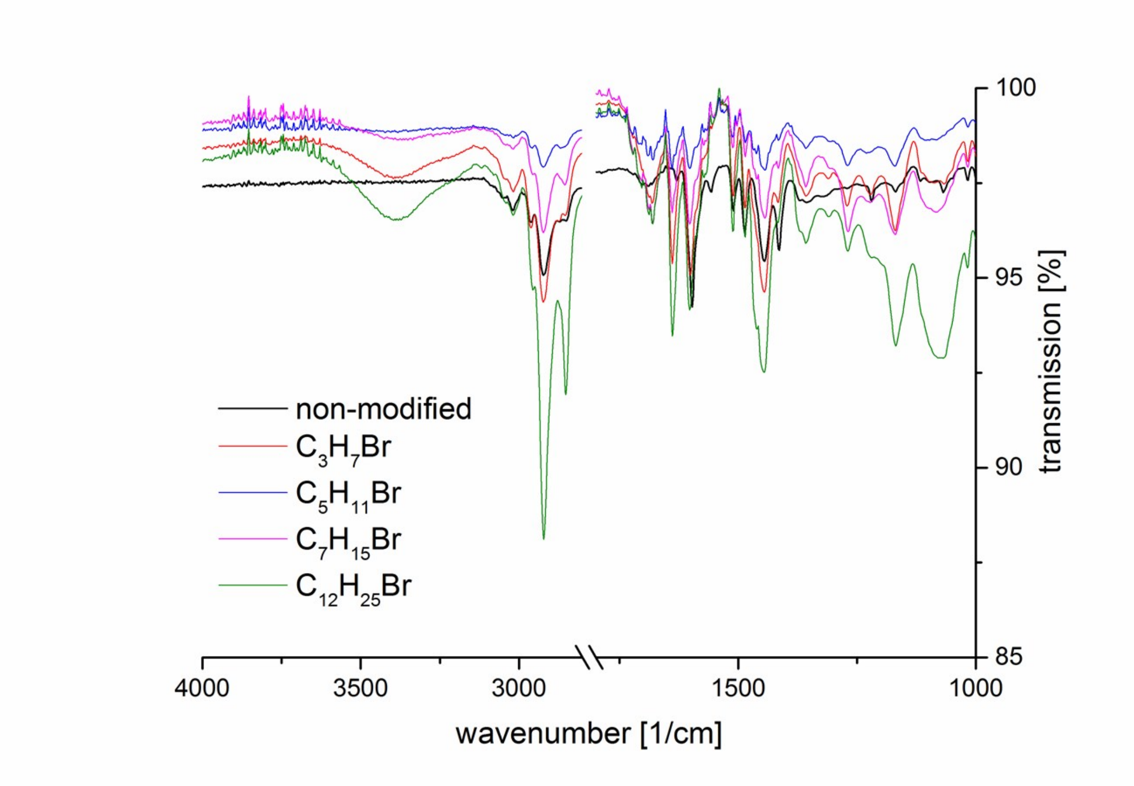

Figure S 2: IR spectra of the mesoporous pre-polymer (black) and its ionic derivatives, modified with 1-bromoalkanes ($C_nH_{2n+1}Br$) with different alkyl chain lengths

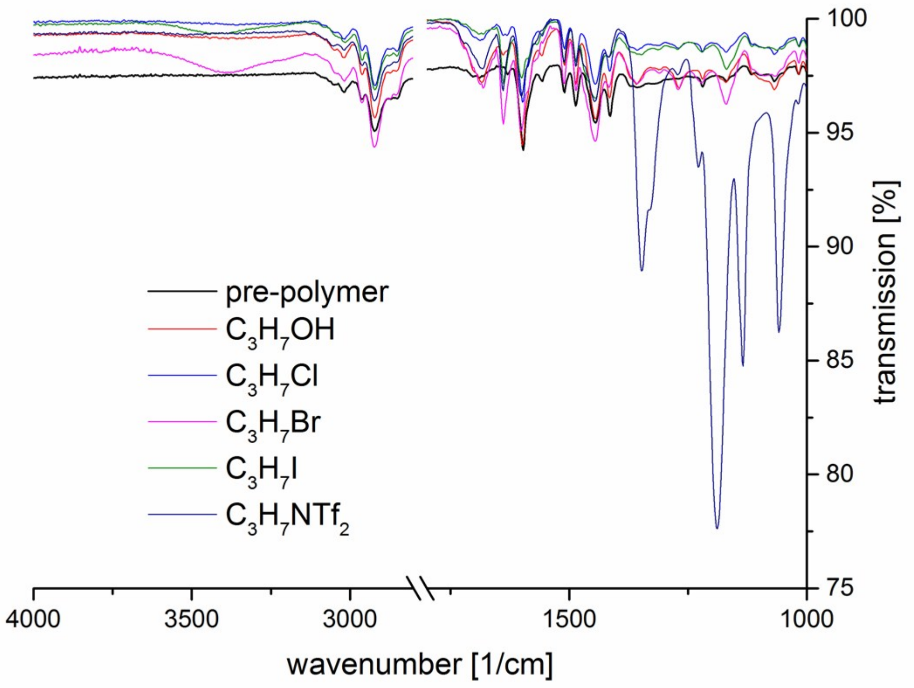

Figure S 3: IR spectra of the mesoporous pre-polymer (black) and its ionic derivatives, modified with 1-bromoalkanes (C_3H_7X) with different anions

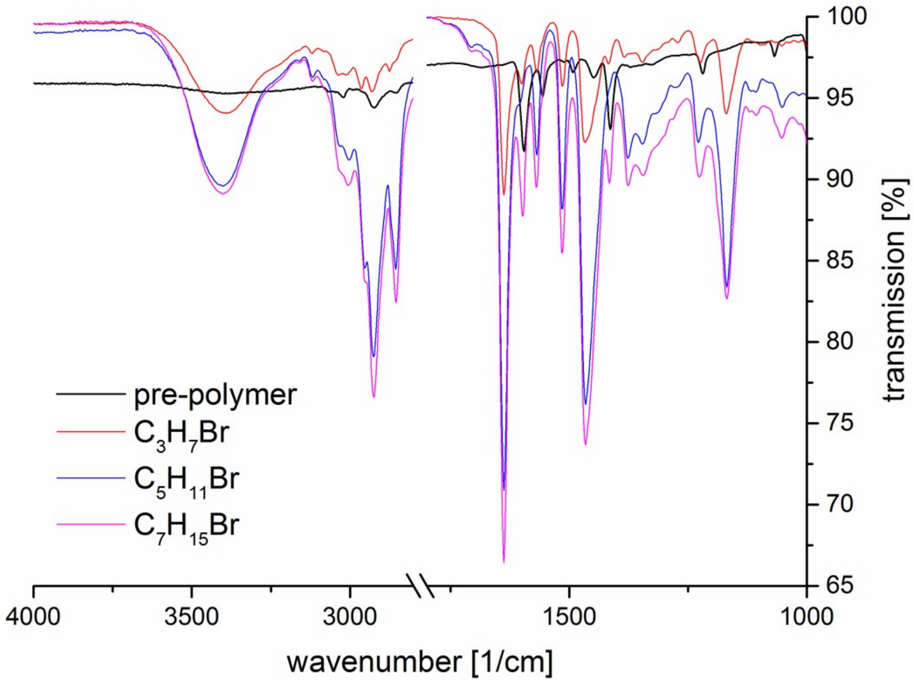

Figure S 4: IR spectra of the non-porous pre-polymer (black) and its ionic derivatives, modified with 1-bromoalkanes ($C_nH_{2n+1}Br$) with different alkyl chain lengths

N_2 Physisorption measurements of the mesoporous polymers mPoly-AlkVPyrX-DVB

To determine the specific surface areas, the pore volume and the pore diameter of the polymer catalysts prepared via silica hard-templating method nitrogen physisorption measurements were carried out with a “ASAP 2000” from Micromeritics. The N_2 adsorption isotherms were measured at 77 K, using isothermal jackets around the sorption tubes during the measurements. The N_2 adsorption isotherms at 77 K of the mesoporous polymer catalysts mPoly-AlkVPyrX-DVB depending on the counter ion and the alkyl chain length are shown in figure S5 and figure S6, respectively.

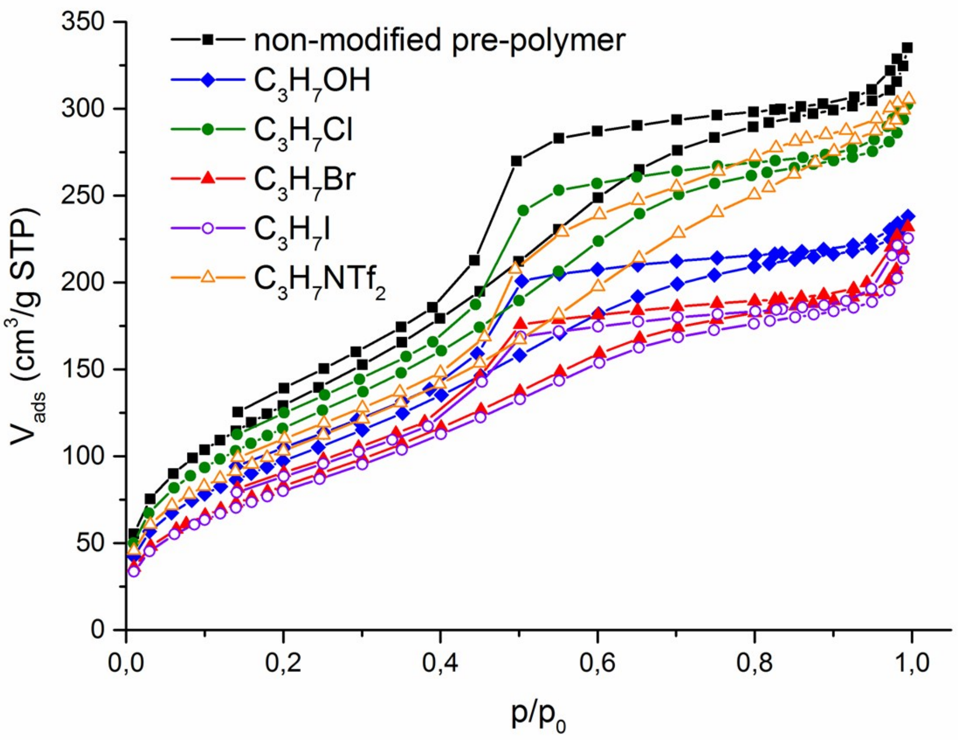

Figure S 5: N_2 physisorption isotherms at 77 K of mesoporous DVB cross-linked N-propyl-4-vinylpyridinium polymers with different anions

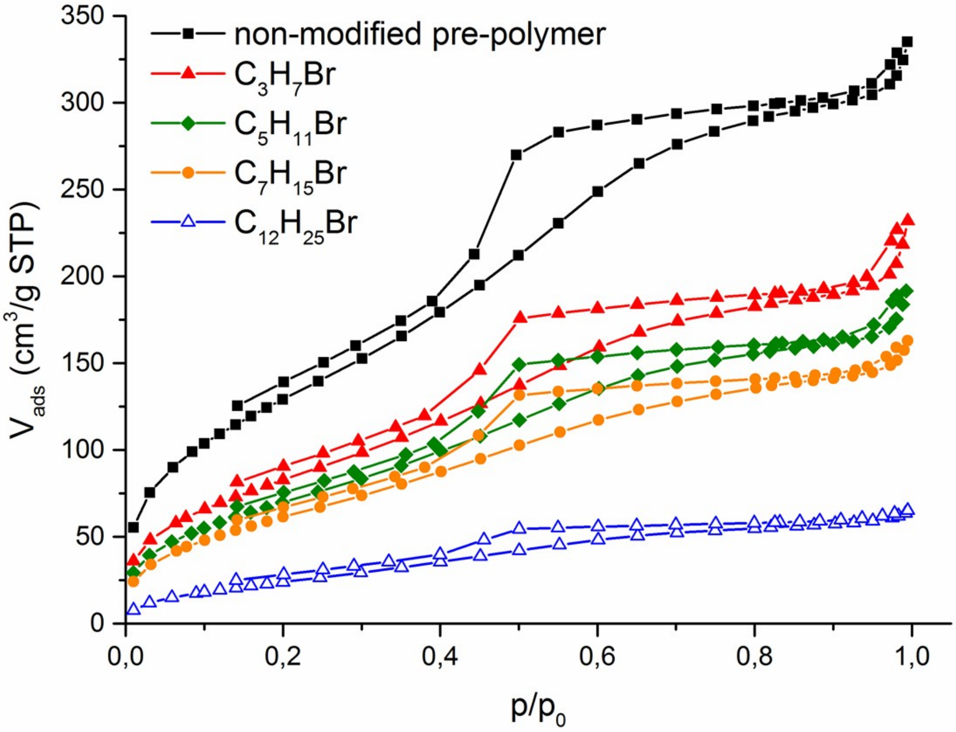

Figure S 6: N_2 physisorption isotherms at 77 K of mesoporous DVB cross-linked N-alkyl-4-vinylpyridinium bromide polymers with different alkyl chain length at the pyridinium nitrogen

In the following table S1 BET surface areas, pore volumes and pore diameters of the mesoporous polymer catalysts mPoly-AlkVPyrX-DVB are listed, derived from the N_2 adsorption isotherms at 77 K shown in figure S5 and figure S6.

Table S 1: Results of the N_2-physisorption measurements at 77 K of mesoporous DVB cross-linked N-alkyl-4-vinylpyridinium polymers

Sample	**BET surface area STP [m²/g]**	**Pore volume [cm³/g]**	**Pore diameter [nm]**
mPoly-VPyr-DVB (non-modified)	498	0,518	4,2
mPoly-PropVPyrOH-DVB	367	0,348	3,8
mPoly-PropVPyrCl-DVB	437	0,435	4,0
mPoly-PropVPyrI-DVB	305	0,349	4,6
mPoly-PropVPyrNTf$_2$-DVB	252	0,252	4,0
mPoly-PropVPyrBr-DVB	315	0,359	4,6
mPoly-PentVPyrBr-DVB	267	0,296	4,4
mPoly-HepVPyrBr-DVB	237	0,252	4,3
mPoly-DodecVPyrBr-DVB	95	0,094	4,0

Elemental analysis (C, H, N)

To modify the non-porous and mesoporous DVB cross-linked 4-vinylpyridine polymers, their elemental composition needed to be known, especially the nitrogen content of the pre-polymers. Therefor elemental analyses for the chemical elements carbon, hydrogen and nitrogen of the pre-polymers were carried out with a "vario MICRO cube" from elementar. Both of the pre-polymers were analyzed four times. The contents of carbon, hydrogen and nitrogen of the non-porous and mesoporous pre-polymer are listed below in table S3 and table S4, respectively. Within reasonable accuracies, the elemental composition of the non-porous pre-polymer is closed to 100 % by carbon, hydrogen and nitrogen, as expected. In case of the mesoporous pre-polymer 4-5 weight-% are missing, which is silica, confirmed by the results of the thermogravimetric analysis of the mesoporous pre-polymer, yielding 4-5 weight-% of a white solid residue after full combustion in air.

Table S 2: Elemental composition of the non-porous DVB cross-linked 4-vinylpyridine polymer (pre-polymer of the ionic non-porous polymer catalysts)

	Carbon	**Hydrogen**	**Nitrogen**
1	84,5	7,0	10,7
2	83,7	7,2	10,6
3	84,5	7,3	10,6
4	83,2	7,2	10,7
Average	83,9	7,2	10,7

Table S 3: Elemental composition of the mesoporous DVB cross-linked 4-vinylpyridine polymer (pre-polymer of the ionic mesoporous polymer catalysts)

	Carbon	**Hydrogen**	**Nitrogen**
1	85,6	7,6	2,6
2	86,1	7,5	2,6
3	86,5	7,6	2,6
4	86,4	7,6	2,6
Average	86,2	7,6	2,6

Based on the results of the elemental analyses the concentration of anions of the final polymer catalysts were calculated, depending on the modification agents. These results are listed in the following table S5. With respect to the initial fructose concentration, the desired amount of each polymer catalyst to provide 10 mol-% of anions in a typical catalytic reaction for the dehydration of fructose into HMF is listed in table S5 a well.

Table S 4: Anion concentration of the polymer catalysts and the amount of each polymer used for the catalytic reactions

Polymer	Anion concentration [mmol/g][a]	m(Polymer) [mg][b]
Poly-PropVPyrBr-DVB	3,93	70,6
Poly-PentVPyrBr-DVB	3,54	78,4
Poly-HepVPyrBr-DVB	3,22	86,2
mPoly-PropVPyrOH-DVB	1,66	167
mPoly-PropVPyrCl-DVB	1,61	172
mPoly-PropVPyrI-DVB	1,41	197
mPoly-PropVPyrNTf$_2$-DVB	1,16	240
mPoly-PropVPyrBr-DVB	1,51	184
mPoly-PentVPyrBr-DVB	1,45	192
mPoly-HepVPyrBr-DVB	1,39	200
mPoly-DodecVPyrBr-DVB	1,15	242

[a] anion concentration based on the nitrogen content of the pre-polymer, calculated for quantitative modification
[b] amount of polymer catalyst to provide 10 mol-% anions in a reaction with 500 mg fructose

To check whether modification of the two types of pre-polymer was quantitative the nitrogen content was measured by elemental analyses and compared to the theoretical nitrogen content assuming quantitative modification. The results obtained from fourfold measurements are listed in the following table S6.

Table S 5: Nitrogen content of the modified pre-polymers found by elemental analyses compared to the theoretical nitrogen content assuming quantitative modification

modifying agent	mesoporous polymers (starting from 2,6 wt-% N)		non-porous polymers (starting from 10,7 wt-% N)	
	theoretical	found	theoretical	found
C_3H_7Br	2.1 %	1.9 %	5.5 %	5.9 %
$C_5H_{11}Br$	2.0 %	1,9 %	4.7 %	4.9 %
$C_7H_{15}Br$	2.0 %	1,9 %	4.5 %	4.7 %
$C_{12}H_{25}Br$	1.8 %	1.8 %		
"C_3H_7OH"	2.3 %	2.3 %		
C_3H_7Cl	2.3 %	2.4 %		
C_3H_7I	2.0 %	2.1 %		
"$C_3H_7NTf_2$"	3.2 %	2.9 %		

The results in table S6 show that the pre-polymers were successfully modified quantitatively. The deviations compared to the theoretical values are within the precision of the elemental analyzer. Therefore the pre-polymers are assumed to be quantitatively modified.

Gas chromatography

To identify the main by-products and consecutive products in our catalytic system for the dehydration of fructose into HMF, a gas chromatograph from Agilent Technologies was used, equipped with a 30 m column with a stationary phase of poly(ethylene glycol) and a layer thickness of 0.25 µm. Figure S7 displays the gas chromatogram of a reaction mixture after 6 h at 180 °C, applying an isothermal step at 40 °C for 5 min, a heating step until 260 °C with a heating rate of 8 K/min, followed by a final isothermal step for 5 min. The compounds were identified by a mass spectrometer.

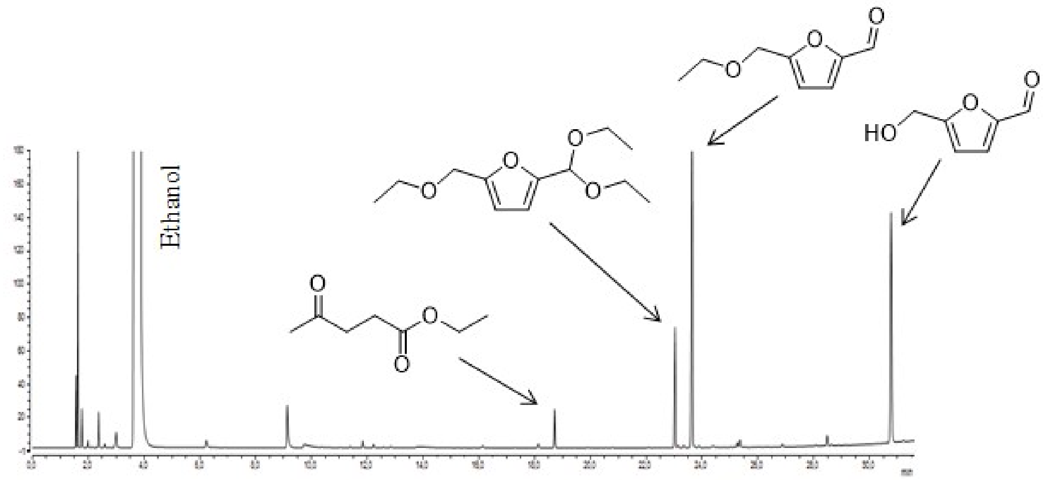

Figure S 7: Gas chromatogram of a reaction mixture after 6 h at 180 °C for the dehydration of fructose into HMF in ethanol as solvent