Catalytic fast pyrolysis of biomass: superior selectivity of hierarchical zeolite to aromatics

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Supporting Information:

Fig. S1 Time profiles of various m/z markers as analysed by on-line SPI-MS (Parent HZSM-5), a) first injection of wood (injection 1) over fresh catalyst, b) 14th injection of wood over coked catalyst

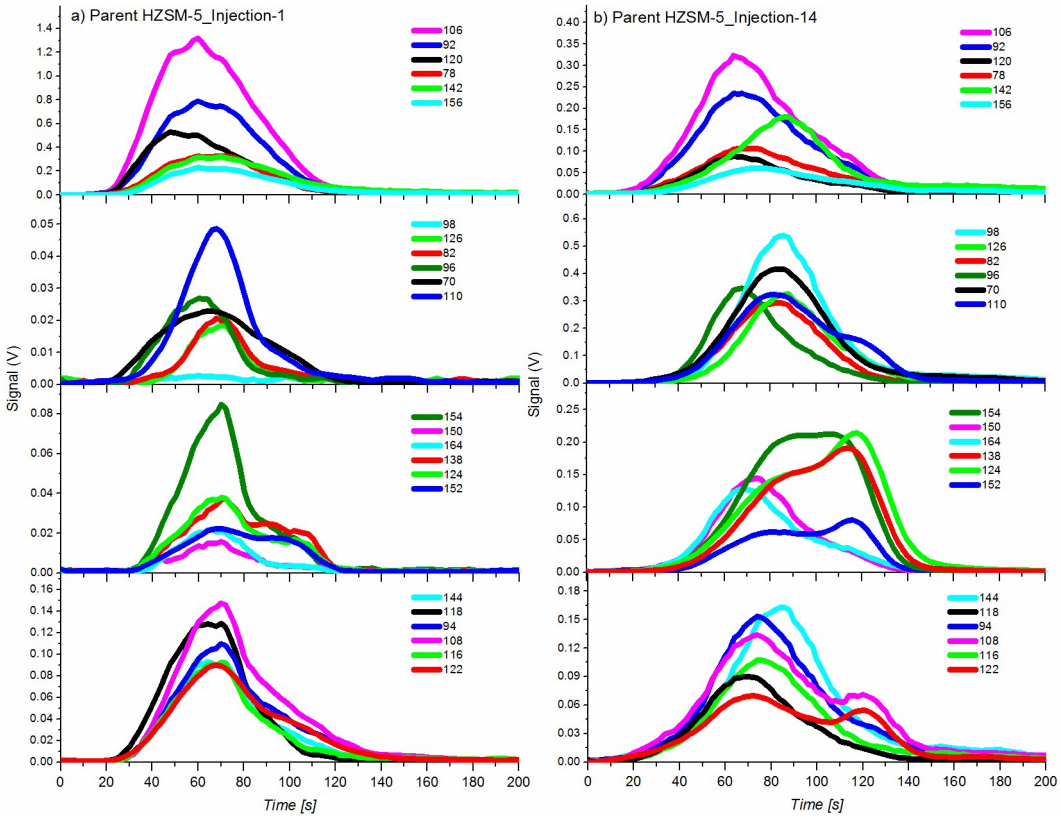


Fig. S2 Time profiles of various m/z markers as analysed by on-line SPI-MS (Hierarchical HZSM-5), a) first injection of wood (injection 1) over fresh catalyst, b) 14th injection of wood over coked catalyst

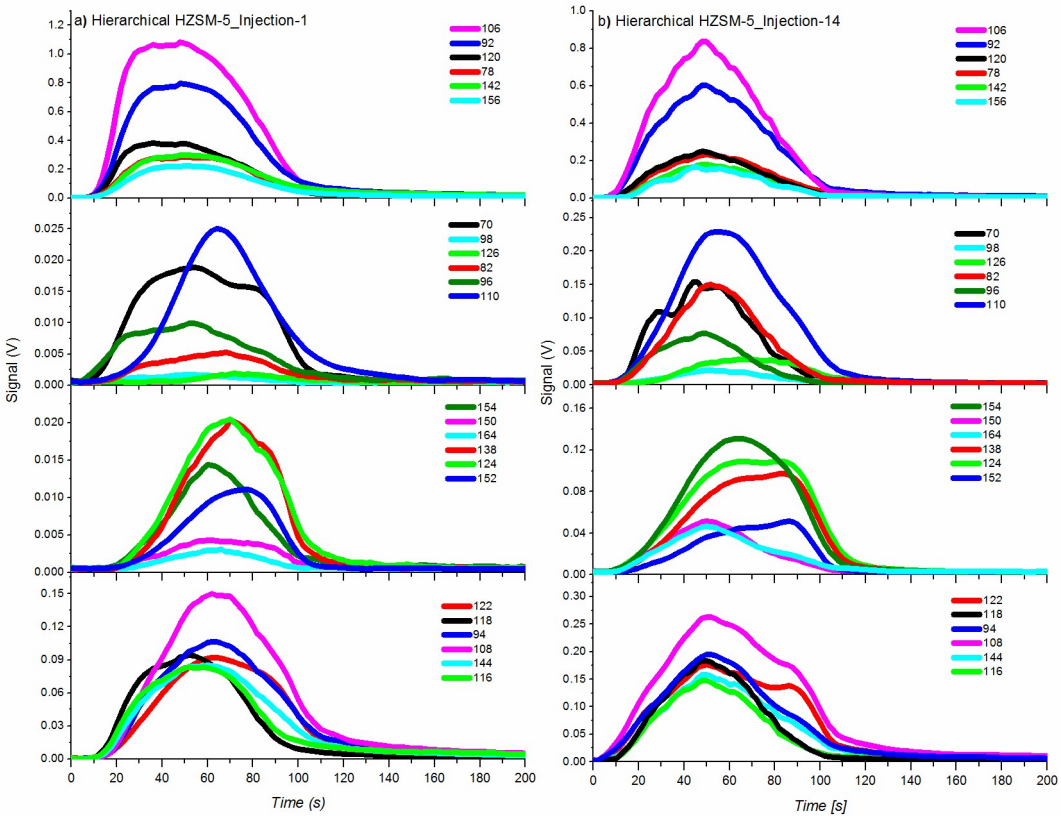


Fig. S3 Char yields for sand particles and the two zeolites for the multiple injections (up to 14 injection of wood for zeolites).

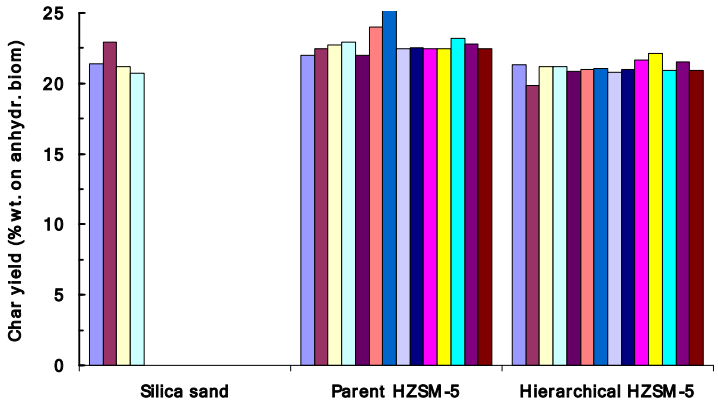
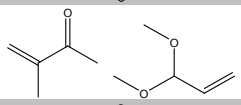
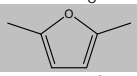
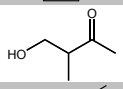
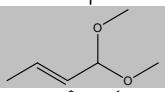
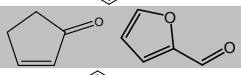
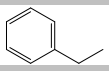
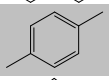
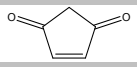
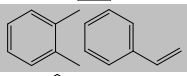
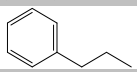
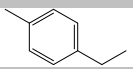
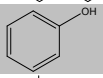
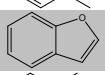
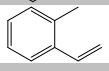
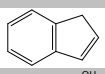
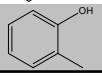
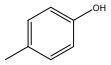
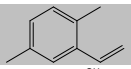
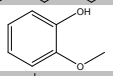
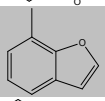
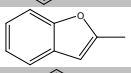
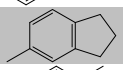
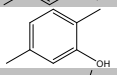
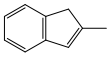
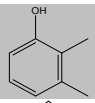
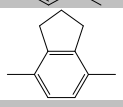
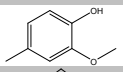
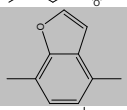
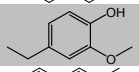
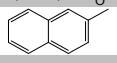
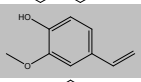
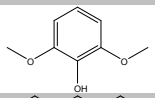
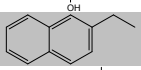
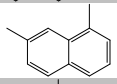
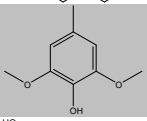
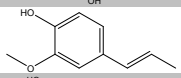
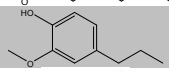
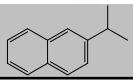


Table S1. Main species identified by GC/MS in bio-oil produced by the CFP of biomass by the 2 zeolites Peak numbers refer to the numbers in chromatograms presented in the following figure.

Label	Retention time (min)	Mw (g/mol)	Name	Chemical structure	Main component as identified by multivariate analysis PC1: hydrocarbons, PC2: intermediates (furans, phenols) PC3 : Primary oxygenated products
1	4.601	82	2-methylfuran		3
2	4.985	60	Acetic acid		3
3	5.353	78	Benzene		1
4	5.656	84 &102	3-Buten-2-one, 3-methyl & Acrolein, dimethyl acetal		3
5	6.268	96	Furan, 2,5-dimethyl-		3
6	7.064	102	2-butanone,4-hydroxy-3-methyl-		3
7	7.579	116	2-Butene, 1,1-dimethoxy-		3
8	7.934	92	Toluene		1
9	10.397	82 &96	2-Cyclopenten-1-one & Furfural		3
10	11.362	106	Ethylbenzene		1
11	11.681	106	p-xylene		1
12	12.401	96	2-Cyclopentene-1,4-dione		3
13	12.582	106/104	o-Xylene & Styrene		1
14	15.084	120	Benzene, propyl-		1
15	15.143	142	Unknown compounds (see supplementary material)		3
16	15.390	120	1-ethyl-4-methylbenzene or 1-ethyl-2-methylbenzene		1
17	16.018	94	Phenol		2
18	16.596	120	1,2,3-trimethylbenzene or 1,2,4-trimethylbenzene		1
19	16.746	118	Benzofuran		2
20	17.823	118	Benzene, 1-ethenyl-2-methyl-		2
21	18.236	118	Indane		2
22	18.575	116	Indene		2
23	18.777	108	Phenol, 2-methyl-		2

24	19.528	108	Phenol, 4-methyl-		2
25	19.907	132	Benzene, 2-ethenyl-1,4-dimethyl-		2
26	20.155	124	Phenol, 2-methoxy-		3
27	20.703	132	Benzofuran, 7-methyl-		2
28	20.971	132	Benzofuran, 2-methyl-		2
29	21.979	132	1H-Indene, 2,3-dihydro-5-methyl-		2
30	22.243	122	Phenol, 2,5-dimethyl-		2
31	22.432	130	1H-Indene, 1-methyl-		2
32	22.628	130	2-Methylindene		2
33	22.800	122	Phenol, 2,3-dimethyl-		2
34	23.461	146	1H-Indene, 2,3-dihydro-4,7-dimethyl-		2
35	23.623	128	Naphthalene		1
36	23.723	138	Phenol, 2-methoxy-4-methyl		3
37	24.545	146	Benzofuran, 4,7-dimethyl-		2
38	26.009	144	Naphthalene, 1,2-dihydro-4-methyl-		2
39	26.518	152	Phenol, 4-ethyl-2-methoxy-		3
40	27.230	142	Naphthalene, 2-methyl		1
41	27.617	150	2-Methoxy-4-vinylphenol		3
42	28.695	154	Phenol, 2,6-dimethoxy-		3
43	30.204	156	Naphthalene, 2-ethyl-		1
44	30.542	156	Naphthalene, 1,7-dimethyl-		1
45	31.463	168	Syringol, 4-methyl		2&3
46	31.701	164	Phenol, 2-methoxy-4-(1-propenyl)		3
47	31.988	166	phenol, 2-methoxy-4-(1-propyl)-		3
48	33.145	162	β-D-Glucopyranose, 1,6-anhydro-		3
49	33.324	170	Naphthalene, 2-(1-methylethyl)-		1

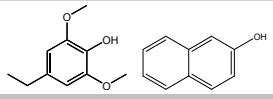
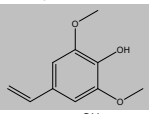
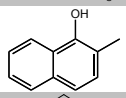
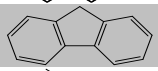
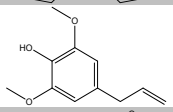
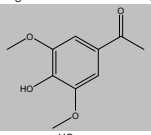
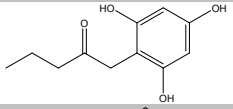
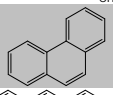
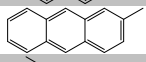
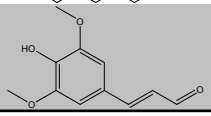
50	33.639	182 &144	Syringol, 4-ethyl, & β-naphthol		*m/z* 182 : 2&3 *m/z* 144 : 2
51	34.708	180	4-vinylsyringol		3
52	36.400	158	1-naphthalenol, 2-methyl-		2
53	36.724	166	Fluorene		2
54	38.171	194	Phenol, 2,6-dimethoxy-4-(2-propenyl)-		2&3
55	39.043	196	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-		2&3
56	39.960	210	2-pentanone, 1-(2,4,6-trihydroxyphenyl)		2&3
57	40.900	178	Phenanthrene		2&3
58	43.664	192	Anthracene, 2-methyl-		2&3
59	44.818	208	3,5-dimethoxy-4-hydroxycinnamaldehyde		3

Fig. S4 EIMS of unidentified compound eluted at 15.143min on GC/MS chromatograms

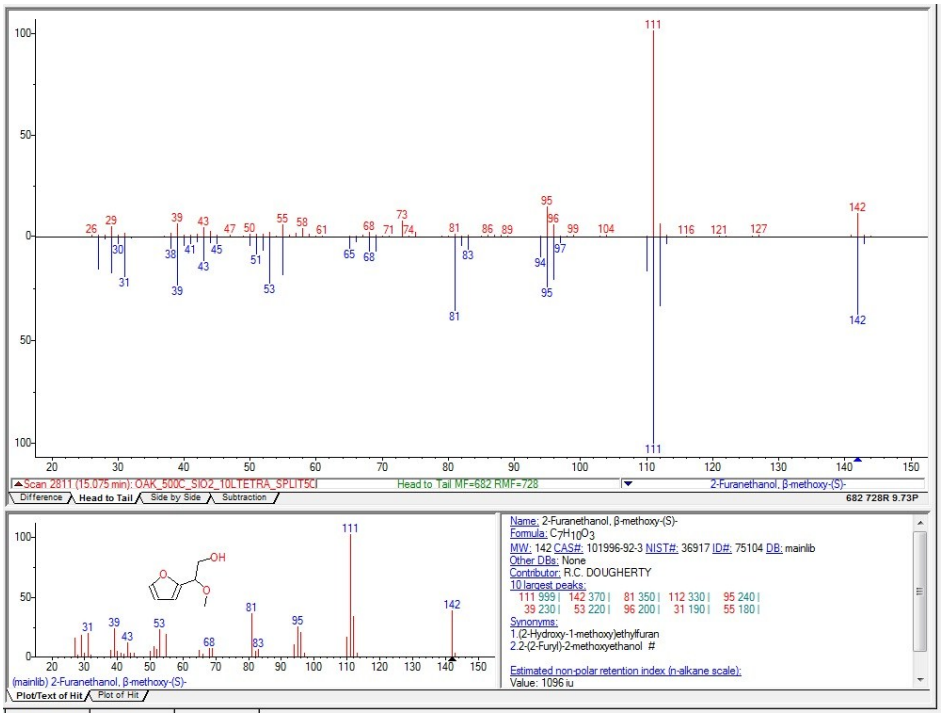
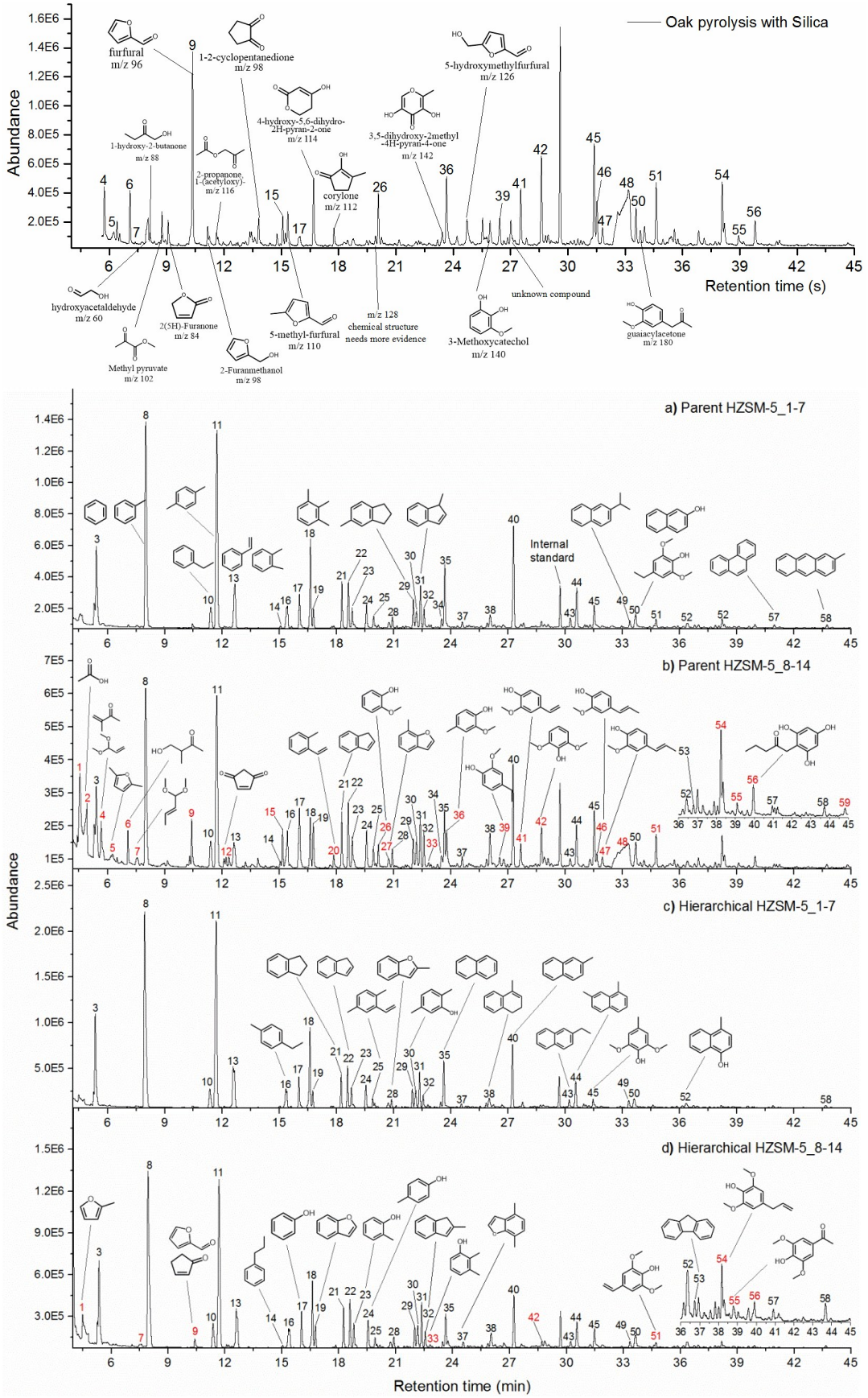


Fig. S5 GC/MS chromatogram with silica sand in the micro-fluidized bed reactor (no zeolite) and for two zeolites, parent a) injections of wood 1 to 7 and b) injection 8 to 14 and hierarchical c) 1 to 7 and d) 8 to 14.



Chromatograms a) and c) present the analysis of the bio-oils accumulated in the cold traps from the first injection of wood (fresh catalyst) to the 7th injection (up to a biomass-to-catalyst ratio of 0.85). Chromatograms b) and d) present

the analysis of the bio-oils accumulated in the cold traps from the 8th injection (coked catalyst with a biomass-to-catalyst ratio of 0.85) to the 14th injection (biomass-to-catalyst ratio 1.7).

Fig. S6 Evolution of main m/z markers upon wood injections (biomass-to-catalyst ratio)

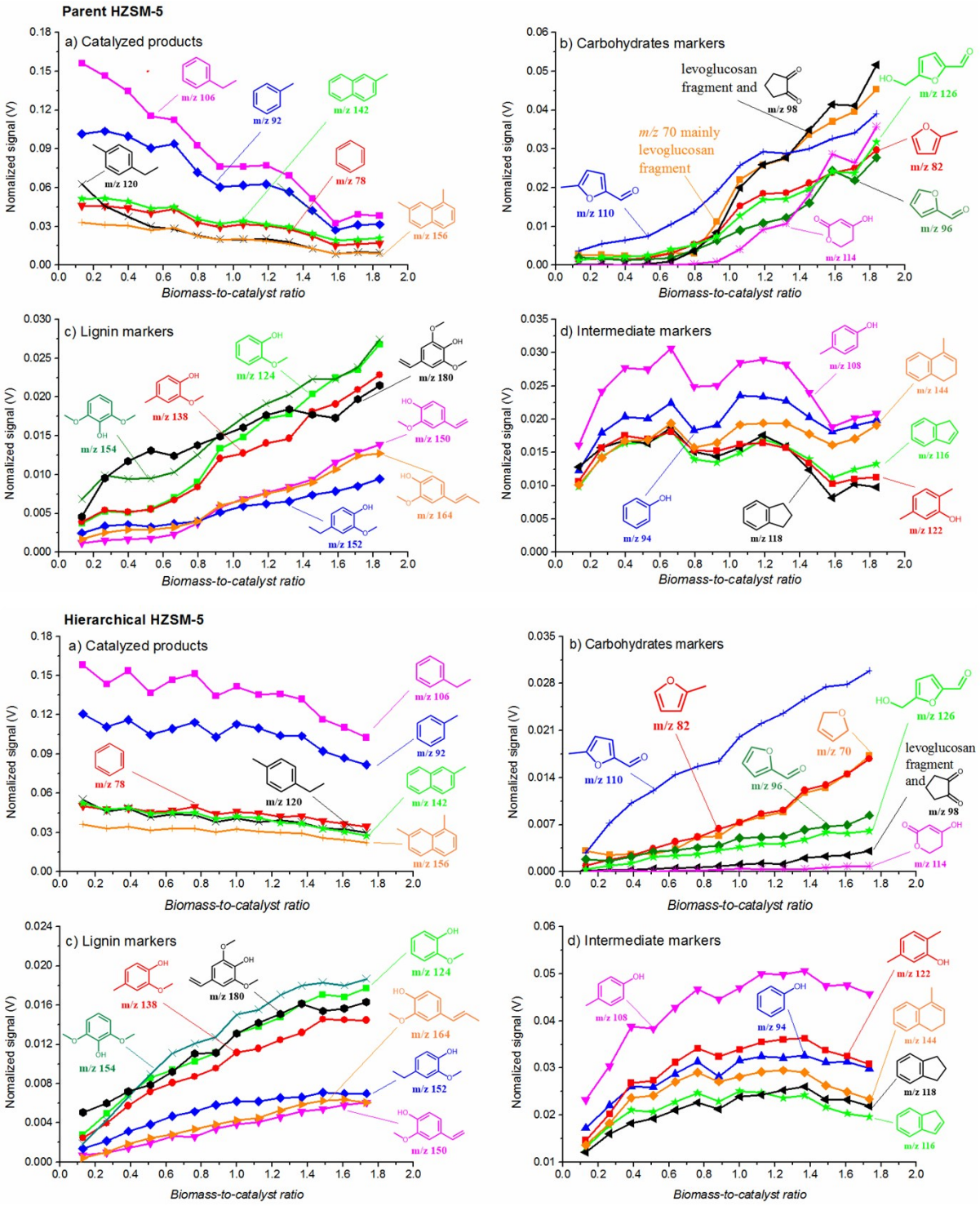
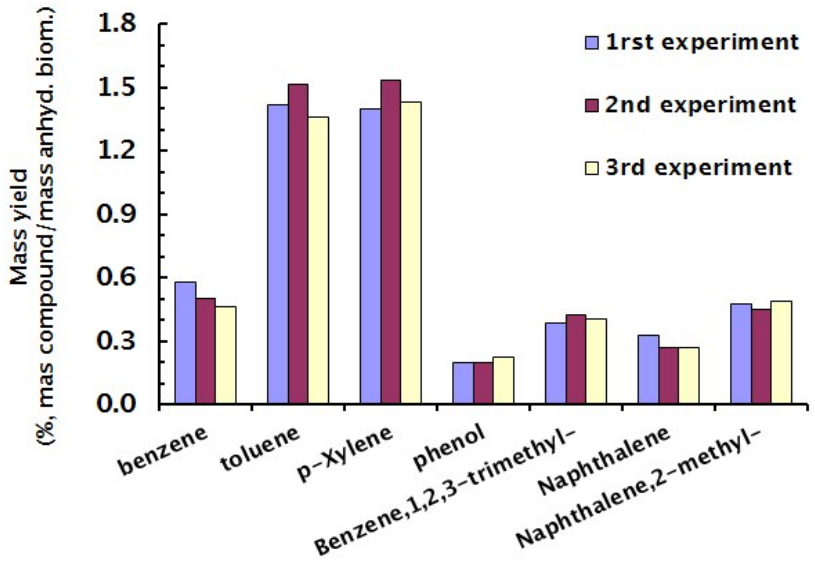


Fig. S7 Reproducibility on quantitative GC/MS-FID analysis (Parent HZSM-5 after 7 injections of wood, biomass-to-catalyst ratio of 0.85)



FigS8. Mass yield in main products in double fixed bed and reproducibility

A first fixed bed of biomass (85mg) is injected in a preheated furnace (500°C) and vapours are directly up-graded into a 2nd fixed bed of zeolite (100mg) pre-heated at 500°C following the same procedure as the pretreatment in microfluidized bed (same temperature program for catalyst activation). The reproducibility is excellent.

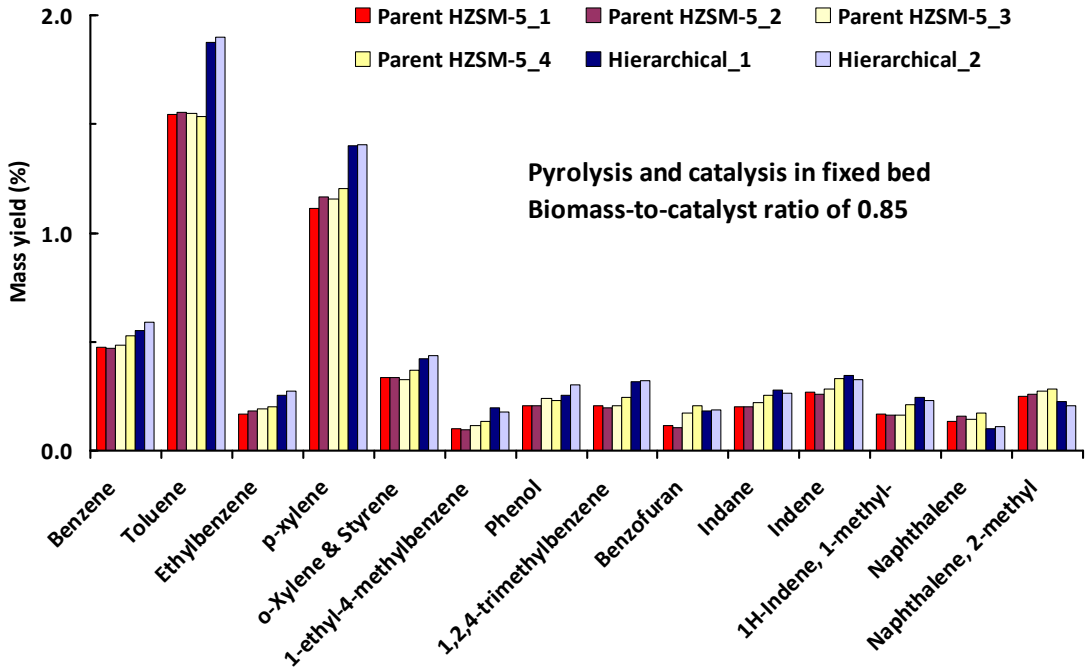


Fig. S9 Evolution of CO_2/CO molar ratio as a function of biomass-to-catalyst ratio

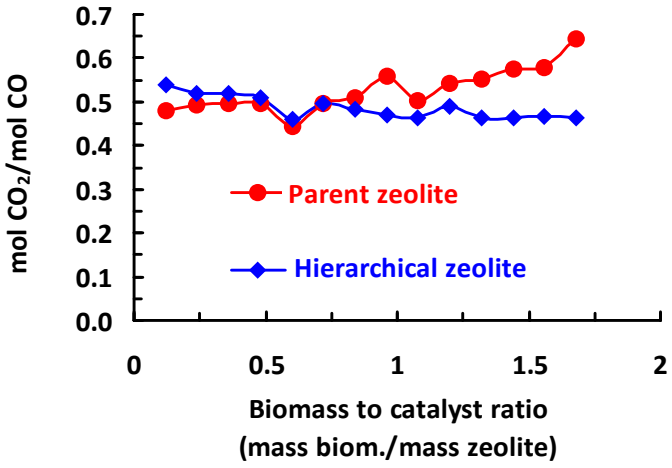
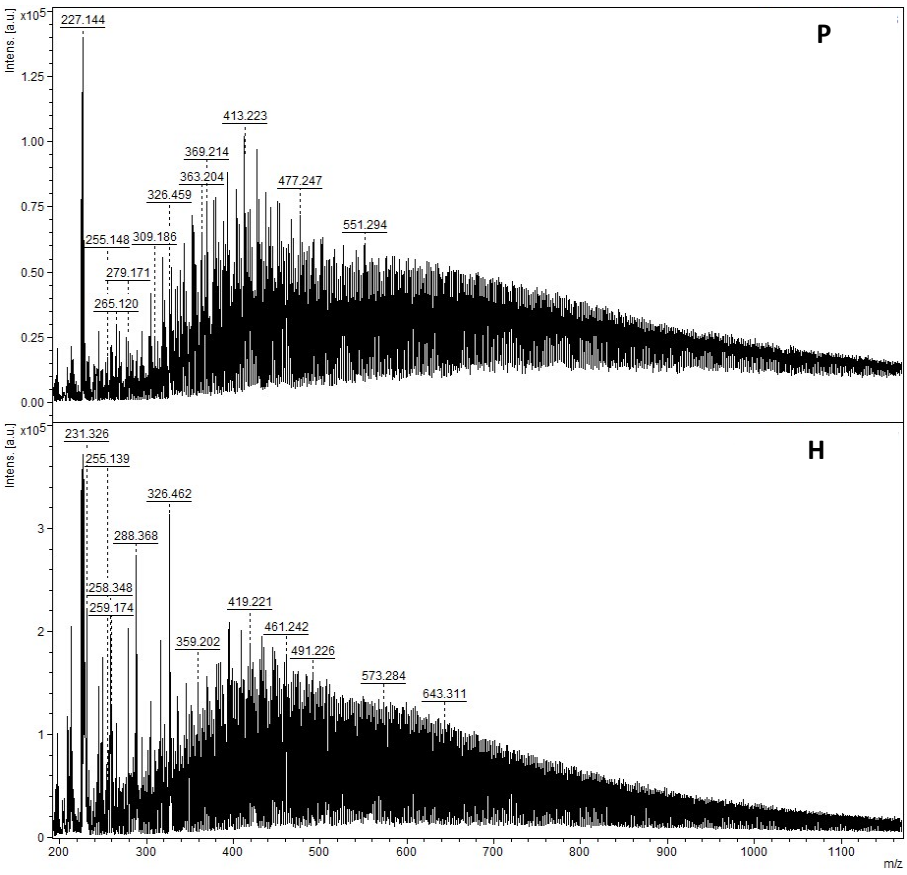


Fig. S10 Characterization by MALDI-TOF/MS of coke insoluble in CH_2Cl_2 and recovered after zeolite digestion with HF



Video S1 One video taken through the quartz window of the micro-fluidized bed reactor during operation, for bubbling zeolite at 500°C under N_2, before wood injection (white); one video for bubbling zeolite, under same conditions, after first wood injection: it becomes black.