Insights into the scalability of catalytic upgrading of biomass pyrolysis vapors using micro and bench-scale reactors

Supporting Information

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The supporting information consists of 13 pages, 4 tables, and 18 figures.

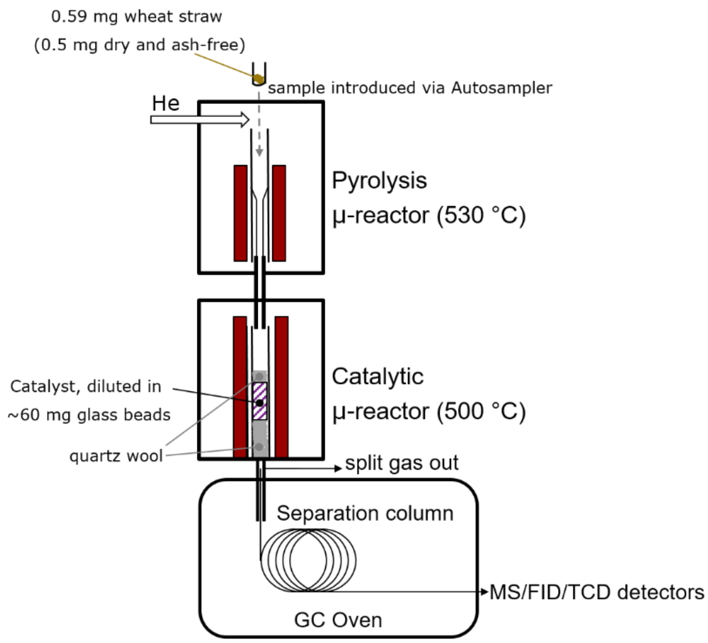

Fig. S1. Schematic of tandem micropyrolyzer-GC-MS/FID/TCD set-up. Cups with biomass were introduced via auto-sampler. Flowrate was 60 ml/min He. Further experimental details can be found in the experimental section.

Table S1. Yields in wt-% of daf wheat straw and standard deviations from three biomass injections using an empty catalytic reactor and a catalytic reactor filled with 2 mg SiC.

	yield (wt-% of daf biomass)	Standard deviation
CO	7.1	0.13
CO_2	17.1	0.22
C_1-C_3	0.1	0.02
C_2-C_3 olefins	0.3	0.01
C_{4+}	0.3	0.01
ALI	0.06	0.005
MAR	0.04	0.002
DAR	0	n.d.
PH	0.13	0.010
ALD	1.76	0.060
AC	2.44	0.091
KET	3.91	0.221
MPH	0.88	0.076
FUR	1.05	0.044
AL	0.75	0.057
EST	0.75	0.050
SUG	0	n.d.
N	0	n.d.

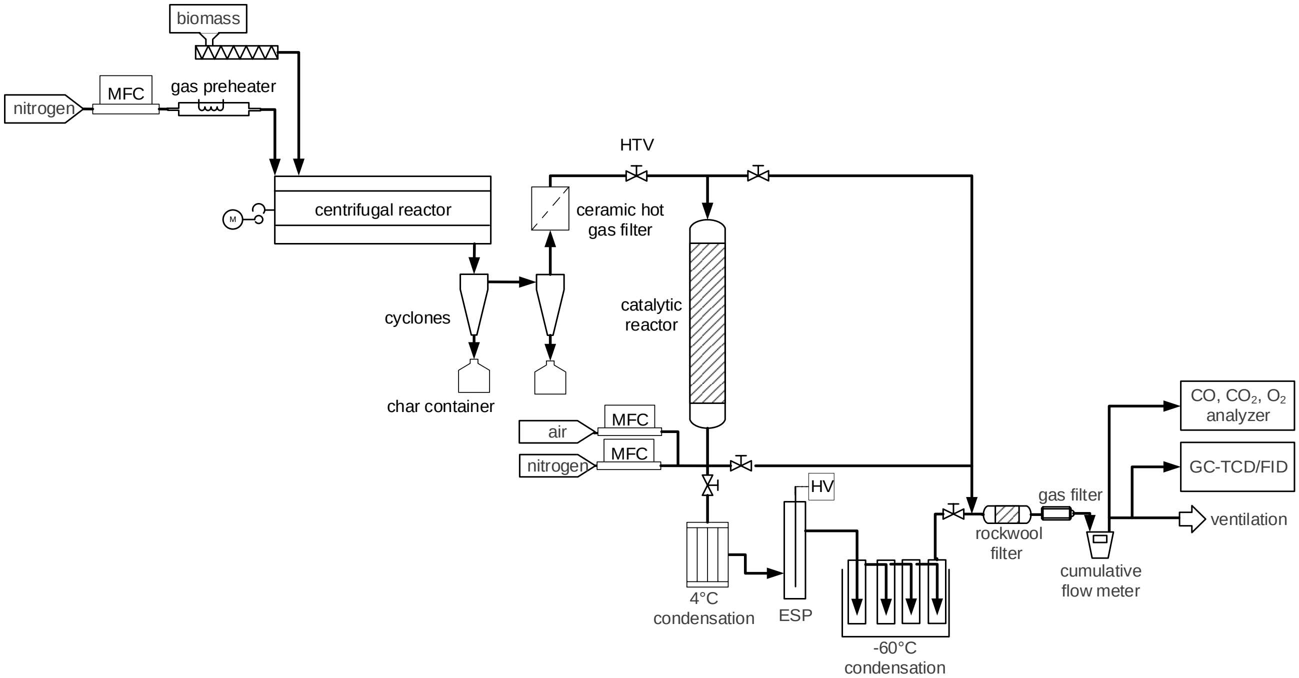

Fig. S2. Pyrolysis unit with fixed bed catalytic reactor for vapor upgrading, bio-oil condensation, and gas analysis.

Table S2. Overview of surface area, acidity, micro and mesopore volume

catalyst	V_{micro}[a] [cc/g]	V_{meso}[b] [cc/g]	BET area[b] [m^2/g]	acidity [mmol NH_3/g]	basicity [mmol CO_2/g]	promoter loading [wt.%]
Z30	0.21	0.11	416	0.51[c]	n.d.	-
Z55	0.22	0.12	424	0.30[c]	n.d.	-
Z80	0.20	0.08	419	0.24[c]	n.d.	-
mZ30	0.15	0.41	620	0.44[c]	n.d.	-
mZ55	0.19	0.37	426	0.25[c]	n.d.	-
mZ80	0.20	0.23	454	0.24[c]	n.d.	-
γ-Al_2O_3	0	0.53	201	0.31[c]	0.004	-
mZ80/γ- Al_2O_3	0.07	0.38	251	0.33[c]	n.d.	-
Na/Al_2O_3	0	0.34	125	0.06	0.018	9.6
Pt/TiO_2[d]	0	0.43	51	0.25	n.d.	0.6
Mo/Al_2O_3[d]	0	n.d.	n.d.	0.50	n.d.	n.d.[e]
MoO_3/TiO_2[d]	0	0.23	54	0.19	n.d.	5.8

[a]from Ar physisorption; [b]from N_2 physisorption; [c]catalyst was steam treated; [d]acidity was determined for reduced catalyst, [e]not determined due to proprietary reasons; [f]loading of molybdenum

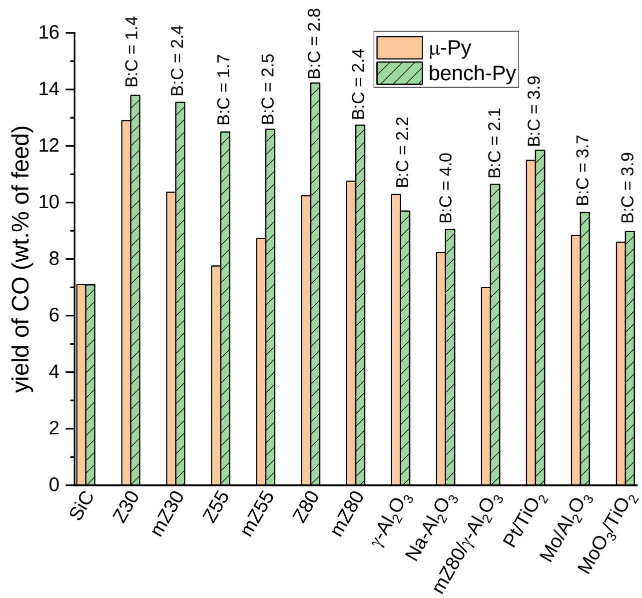

Fig. S3. Product yields of CO (wt.% of feed) for vapor upgrading in μ-Py (2 mg catalyst) and bench-Py (100–150 g). Z30, Z55, and Z80 refer to HZSM-5 with Si/Al =16, 28, and 39. mZ30, mZ55, and mZ80 refer to desilicated HZSM-5 with added mesoporosity.

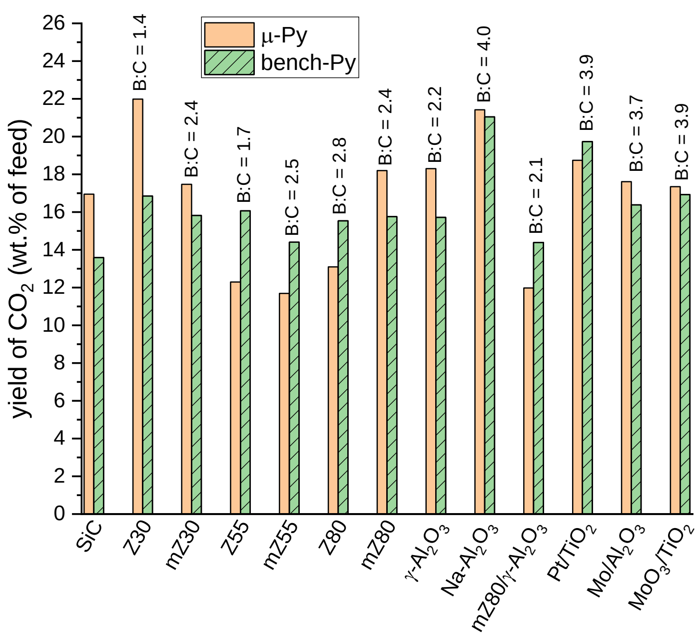

Fig. S4. Product yields of CO_2 (wt.% of feed) for vapor upgrading in μ-Py (2 mg catalyst) and bench-Py (100–150 g). Z30, Z55, and Z80 refer to HZSM-5 with Si/Al =16, 28, and 39. mZ30, mZ55, and mZ80 refer to desilicated HZSM-5 with added mesoporosity.

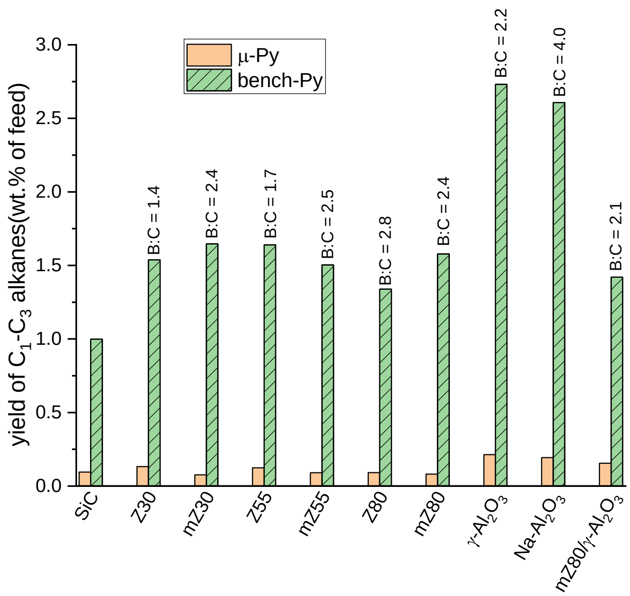

Fig. S5. Product yields of C_1-C_3 alkanes (wt.% of feed) for vapor upgrading in µ-Py (2 mg catalyst) and bench-Py (100–150 g). Z30, Z55, and Z80 refer to HZSM-5 with Si/Al =16, 28, and 39. mZ30, mZ55, and mZ80 refer to desilicated HZSM-5 with added mesoporosity.

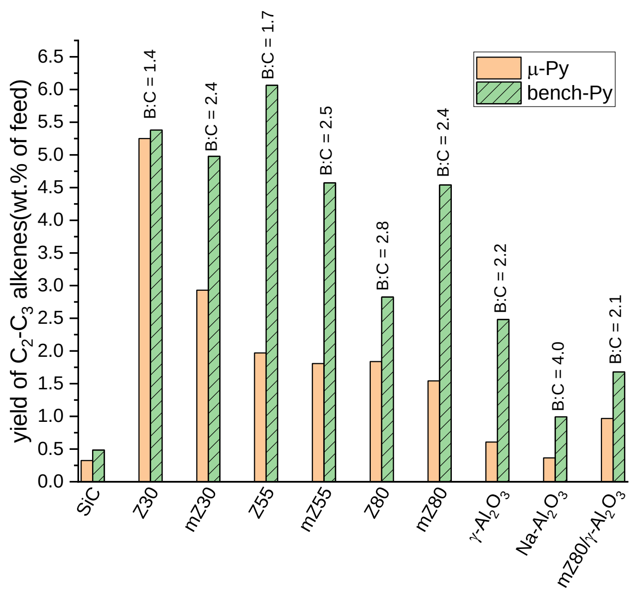

Fig. S6. Product yields of C_2-C_3 alkenes (wt.% of feed) for vapor upgrading in µ-Py (2 mg catalyst) and bench-Py (100–150 g). Z30, Z55, and Z80 refer to HZSM-5 with Si/Al =16, 28, and 39. mZ30, mZ55, and mZ80 refer to desilicated HZSM-5 with added mesoporosity.

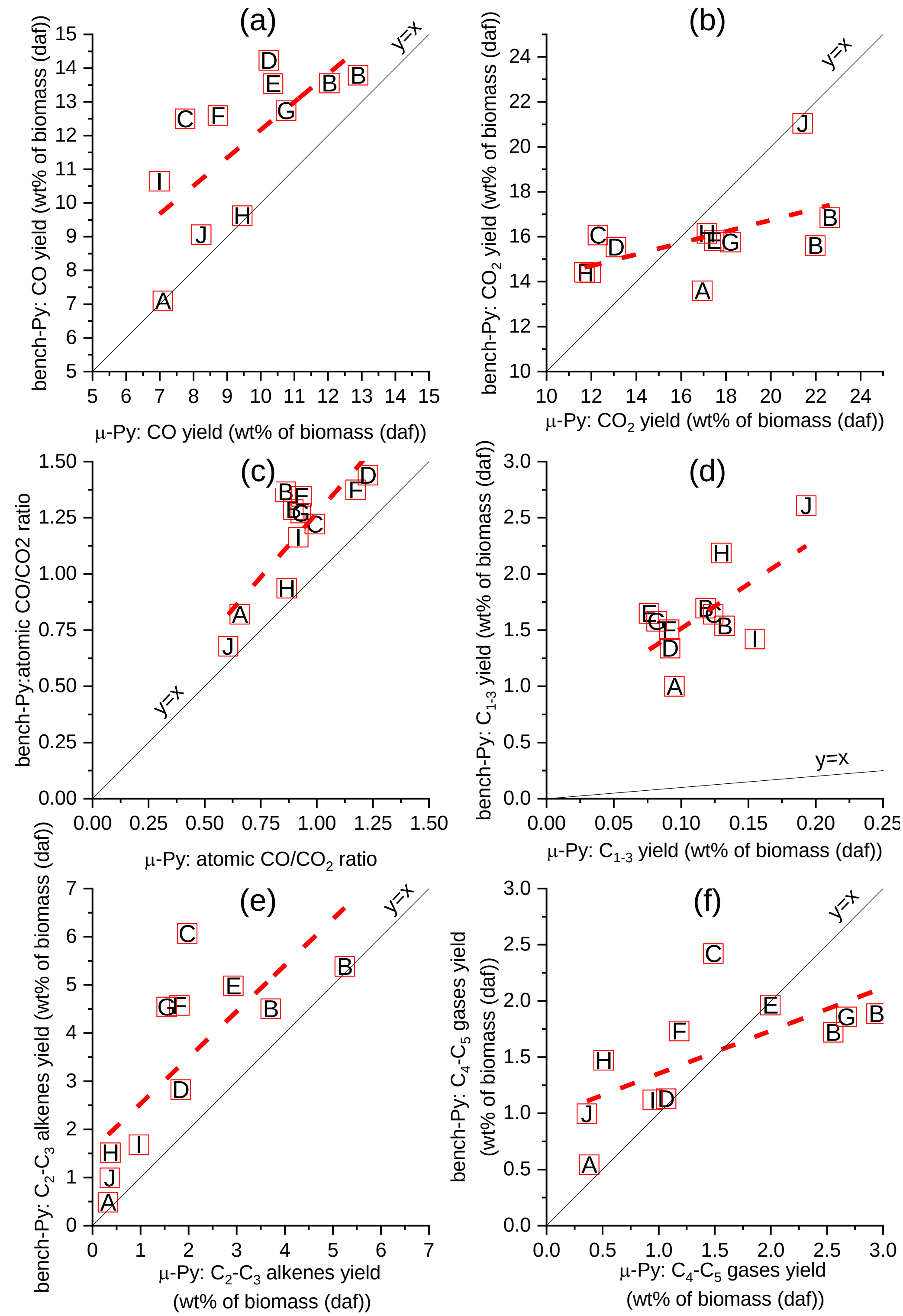

Fig. S7. Gas yields obtained by catalytic upgrading of vapors generated in a bench scale fast pyrolysis unit (bench-Py) and a tandem micro pyrolyzer (μ-Py). (a-b) Yield of CO and CO_2. (c) Molar CO/CO_2 ratio. (d-f) Yields of C_1-C_3 alkanes, C_2-C_3 alkenes, and C_4-C_5 gases. Labels A-M refer to catalyst identifiers shown in Table 2 of main article.

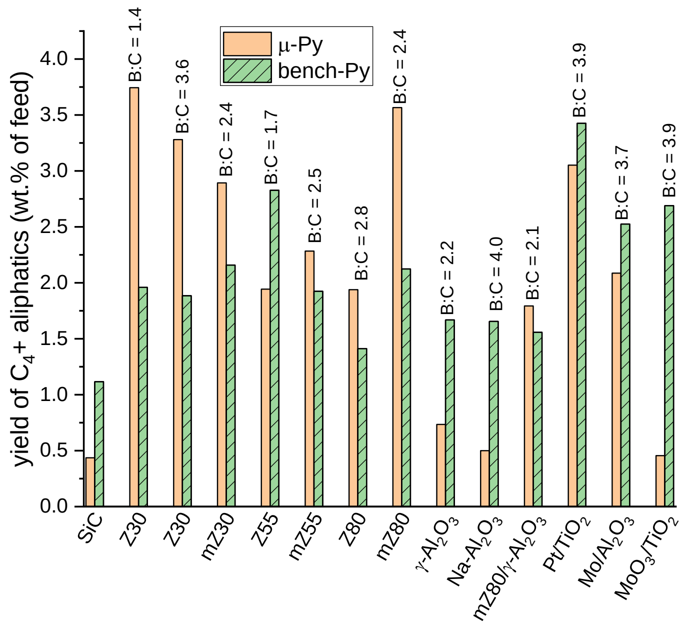

Fig. S8. Product yield of C_4+ aliphatics (wt.% of feed) for vapor upgrading in µ-Py (2 mg catalyst) and bench-Py (100–150 g). Z30, Z55, and Z80 refer to HZSM-5 with Si/Al =16, 28, and 39. mZ30, mZ55, and mZ80 refer to desilicated HZSM-5 with added mesoporosity. For bench-Py, both the C_4+ aliphatics detected in gas phase and condensed liquid are included.

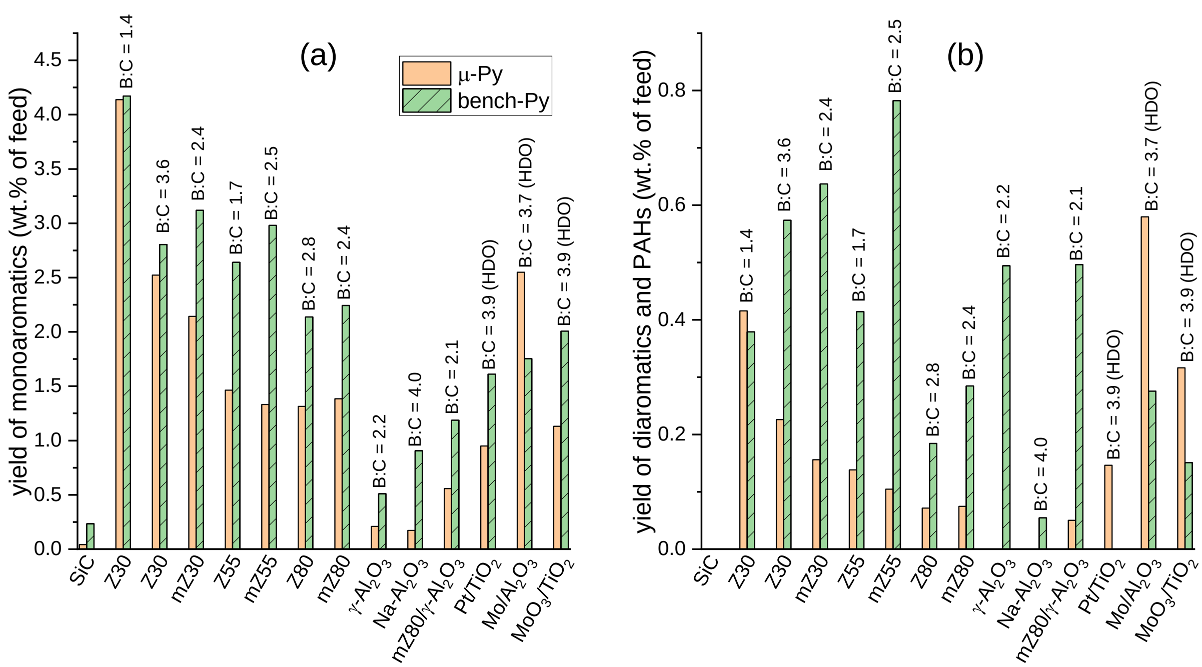

Fig. S9. (a) Product yield of monoaromatics (wt.% of feed) and (b) product yield of diaromatics and PAHs (wt.% of feed) for vapor upgrading in µ-Py (2 mg catalyst) and bench-Py (100–150 g). Z30, Z55, and Z80 refer to HZSM-5 with Si/Al =16, 28, and 39. mZ30, mZ55, and mZ80 refer to desilicated HZSM-5 with added mesoporosity.

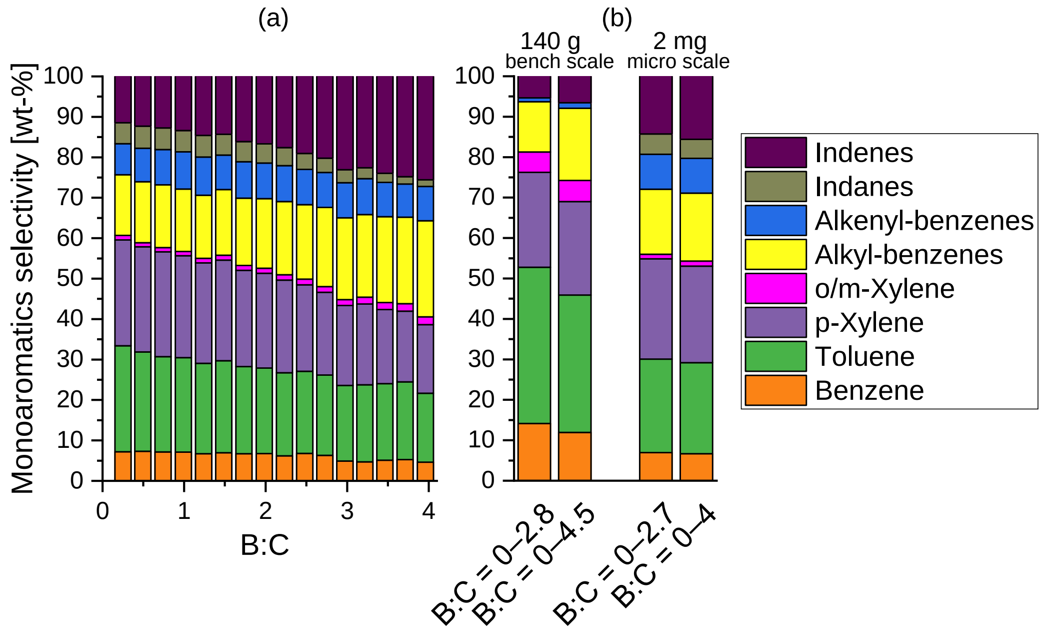

Fig. S10. (a) Selectivity of monoaromatics for each injection in μ-Py using Z55 (HZSM-5 with Si/Al ~28) as catalyst.(b) Comparison of cumulative selectivity to monoaromatics at similar B:C for bench scale and micro-scale.

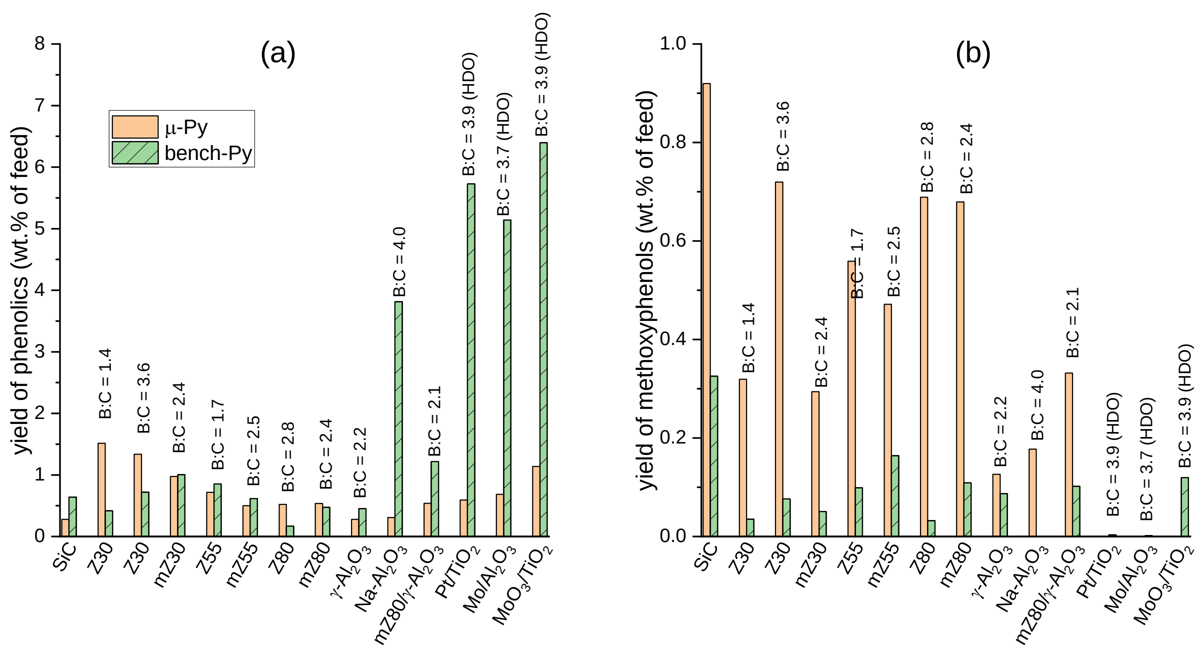

Fig. S11. (a) Product yield of phenolics (wt.% of feed) and (b) product yield of methoxy-phenols (wt.% of feed) for vapor upgrading in μ-Py (2 mg catalyst) and bench-Py (100–150 g). Z30, Z55, and Z80 refer to HZSM-5 with Si/Al =16, 28, and 39. mZ30, mZ55, and mZ80 refer to desilicated HZSM-5 with added mesoporosity.

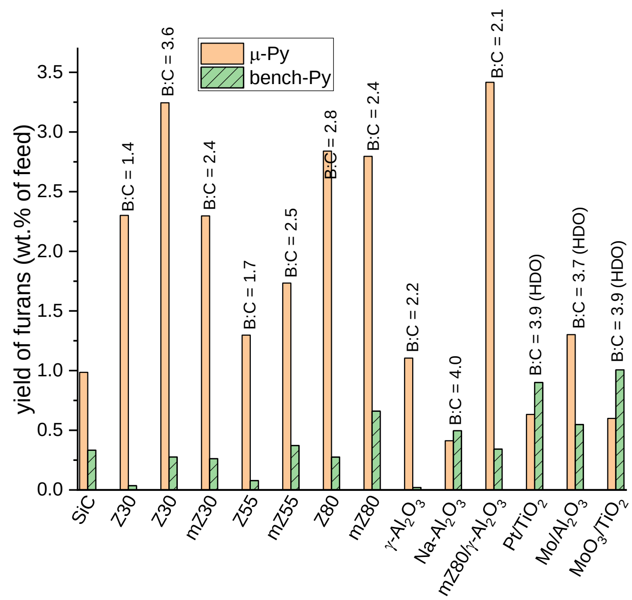

Fig. S12. Product yield of furans (wt.% of feed) for vapor upgrading in μ-Py (2 mg catalyst) and bench-Py (100–150 g). Z30, Z55, and Z80 refer to HZSM-5 with Si/Al =16, 28, and 39. mZ30, mZ55, and mZ80 refer to desilicated HZSM-5 with added mesoporosity.

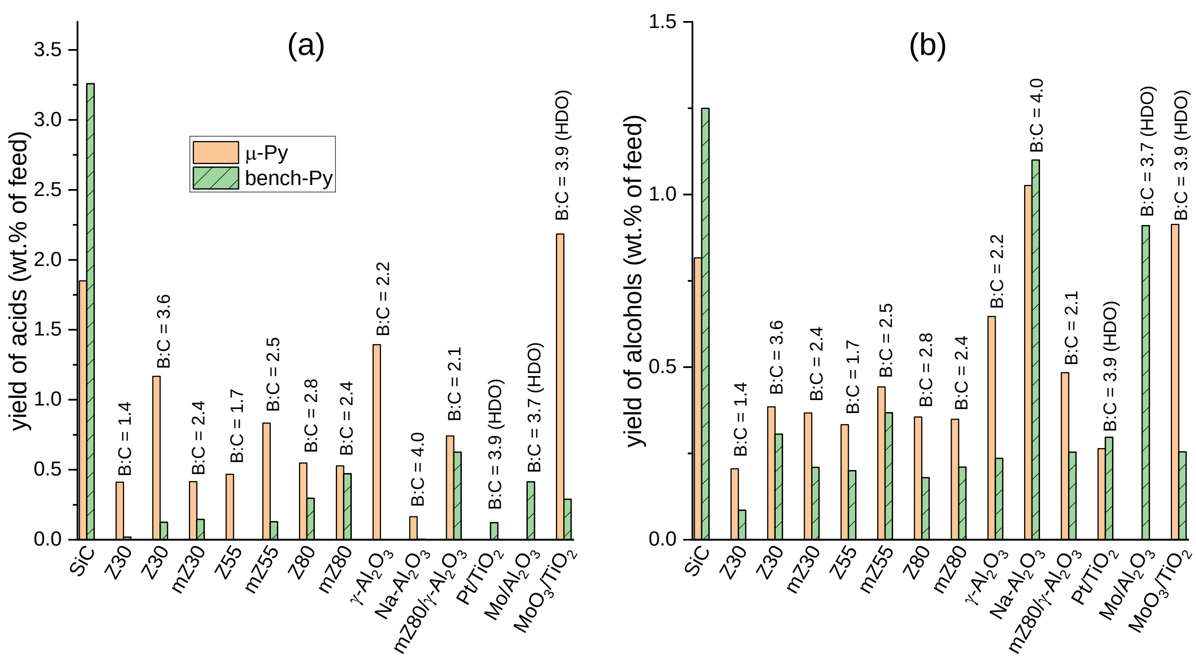

Fig. S13. Product yield of (a) acids (wt.% of feed) and (b) product yield of alcohols (wt.% of feed) for vapor upgrading in μ-Py (2 mg catalyst) and bench-Py (100–150 g). Z30, Z55, and Z80 refer to HZSM-5 with Si/Al =16, 28, and 39. mZ30, mZ55, and mZ80 refer to desilicated HZSM-5 with added mesoporosity.

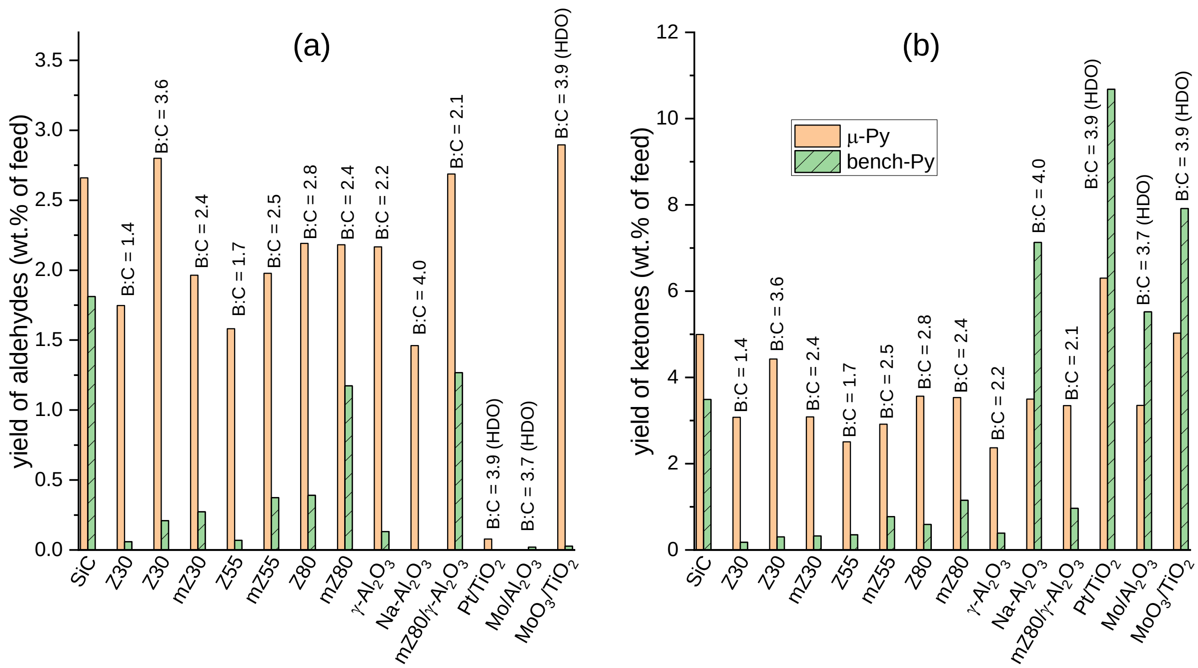

Fig. S14. (a) Product yield of aldehydes (wt.% of feed) and (b) product yield of ketones (wt.% of feed) for vapor upgrading in µ-Py (2 mg catalyst) and bench-Py (100–150 g). Z30, Z55, and Z80 refer to HZSM-5 with Si/Al =16, 28, and 39. mZ30, mZ55, and mZ80 refer to desilicated HZSM-5 with added mesoporosity.

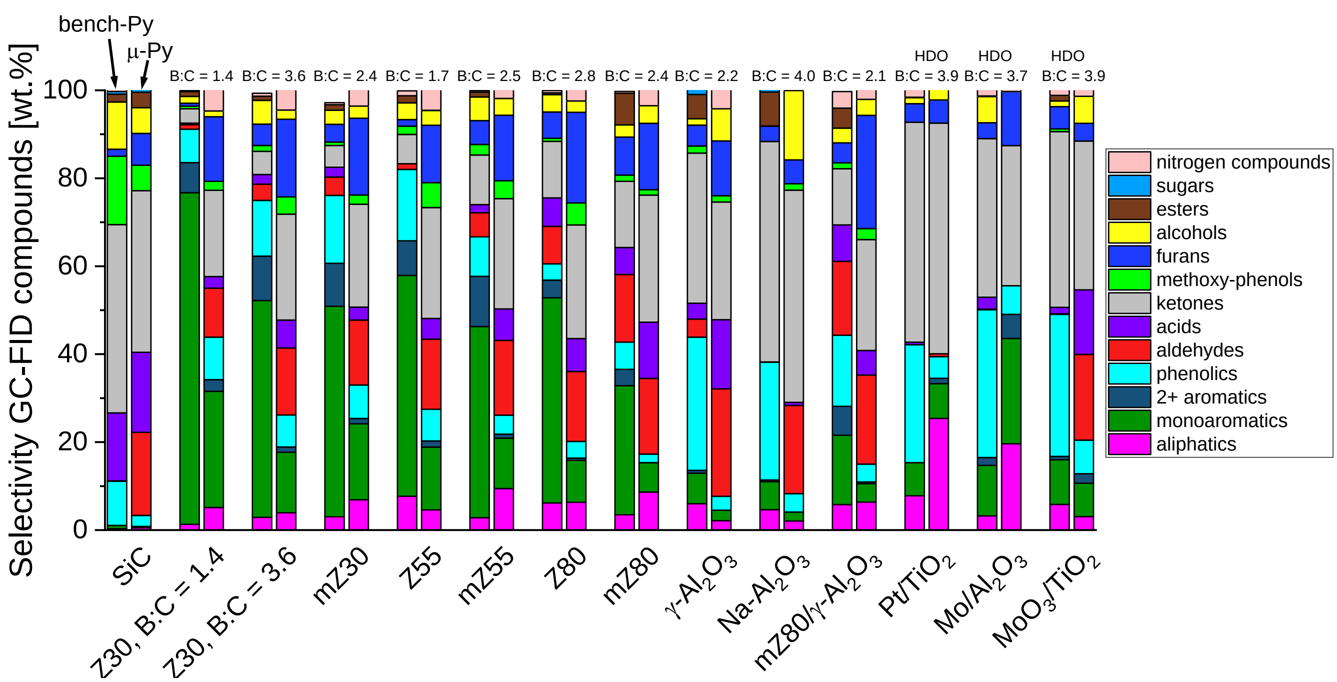

Fig. S15. Selectivity amongst compounds identified by GC-FID (wt.%) for bio-oil from bench-Py and non-condensed vapor from µ-Py.

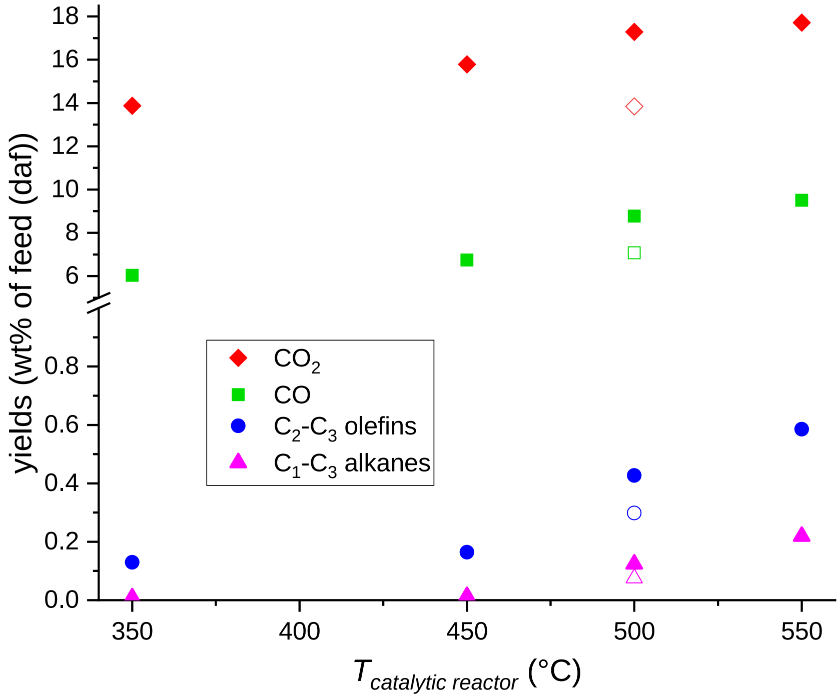

Fig. S16. Gas yields (wt.% of feed (daf)) for passing fast pyrolysis vapors over 8 mg char at different reactor temperatures (full symbols). Empty symbols at 500 °C were obtained with SiC as a highly inert reference.

Table S3. Product yields (wt.% of feed (daf)) in non-condensed vapors from the µ-Py reactor.

yield (wt.% of feed (daf))	2 mg SiC (500 °C)	8 mg char (350 °C)	8 mg char (450 °C)	8 mg char (500 °C)	8 mg char (550 °C)
ALI	0.06	0.03	0.04	0.05	0.05
MAR	0.04	0.04	0.05	0.09	0.08
PH	0.28	0.36	0.41	0.58	0.54
ALD	2.66	1.30	1.69	2.15	2.10
AC	1.85	0.82	1.13	0.84	0.64
KET	4.99	4.13	4.71	3.88	3.51
MPH	0.92	1.06	1.12	0.71	0.46
FUR	0.99	0.34	0.46	0.48	0.49
ALC	0.82	0.84	0.82	0.79	0.77
EST	0.64	0.33	0.31	0.22	0.20
SUG	0.06	0.21	0.15	0.10	0.09

Table S4. Oxygen content of non-condensed vapors from the µ-Py reactor.

	2 mg SiC (500 °C)	8 mg char (350 °C)	8 mg char (450 °C)	8 mg char (500 °C)	8 mg char (550 °C)
wt.% O in vapors	36.6	34.4	34.2	32.2	32.0

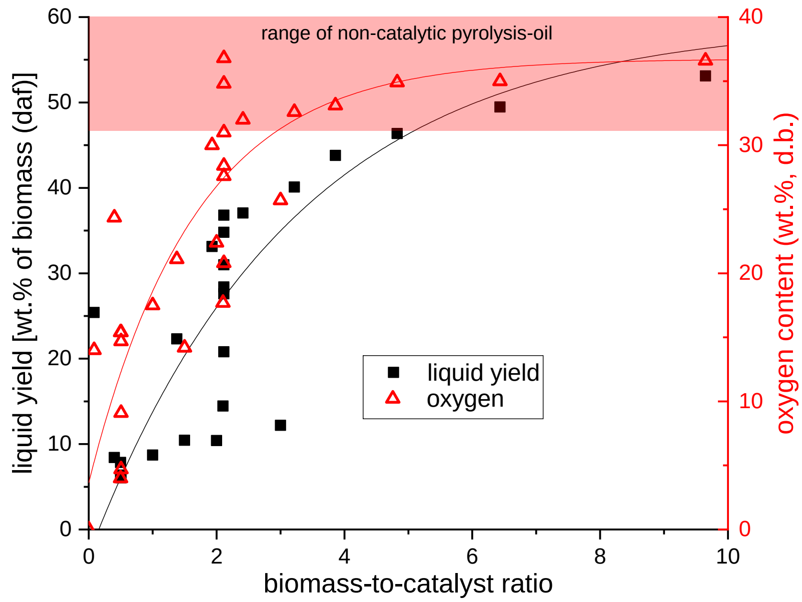

Fig. S17. Correlation of bio-oil liquid yield and oxygen content in the bio-oil as a function of cumulative biomass-to-catalyst ratio (w/w) for HZSM-5 based catalysts at ~400-500 °C. Data was obtained from several authors for FP of woody biomass [1–4], rice husks [5], and acid-washed wheat straw [6] at scales that allowed collection of sufficient liquid for further analysis of moisture content and elemental composition.

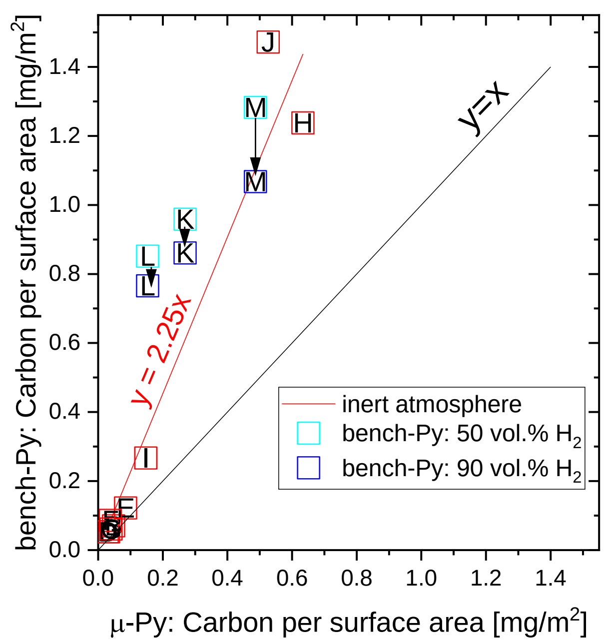

Fig. S18. Surface based coking comparison for catalysts tested in bench-Py (~100–150 g catalyst) and tandem μ-Py (2 mg catalyst) for the same pyrolysis and catalyst temperatures under inert atmosphere (□), and under hydrogen containing atmosphere in 50 vol.% H_2 (□) and 90 vol% H_2 (□).

References

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