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

Eschenbacher, Andreas; Saraeian, Alireza; Shanks, Brent H.; Jensen, Peter Arendt; Henriksen, Ulrik Birk; Ahrenfeldt, Jesper; Jensen, Anker Degn

Published in:
Sustainable Energy & Fuels

Link to article, DOI:
[10.1039/D0SE00303D](https://doi.org/10.1039/D0SE00303D)

Publication date:
2020

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Eschenbacher, A., Saraeian, A., Shanks, B. H., Jensen, P. A., Henriksen, U. B., Ahrenfeldt, J., & Jensen, A. D. (2020). Insights into the scalability of catalytic upgrading of biomass pyrolysis vapors using micro and bench-scale reactors. *Sustainable Energy & Fuels*, 2020(4), 3780-3796 . <https://doi.org/10.1039/D0SE00303D>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

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

Supporting Information

Andreas Eschenbacher^a, Alireza Saraeian^b, Brent H. Shanks^b, Peter Arendt Jensen^a, Ulrik Birk Henriksen^a,

Jesper Ahrenfeldt^a, Anker Degn Jensen^{a,*}

*corresponding author: aj@kt.dtu.dk

^aDepartment of Chemical and Biochemical Engineering, Technical University of Denmark (DTU), 2800 Kgs. Lyngby, Denmark

^bDepartment of Chemical and Biological Engineering, Iowa State University, Ames, IA 50011, United States

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 ₂ O ₃	0	0.53	201	0.31 ^c	0.004	-
mZ80/ γ - Al ₂ O ₃	0.07	0.38	251	0.33 ^c	n.d.	-
Na/Al ₂ O 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 ₂ O 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

^afrom Ar physisorption; ^bfrom N₂ physisorption; ^ccatalyst was steam treated; ^dacidity was determined for reduced catalyst, ^enot determined due to proprietary reasons; ^floading 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 CO₂ (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 C₁-C₃ 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 C₂-C₃ 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 CO₂. (c) Molar CO/CO₂ ratio. (d-f) Yields of C₁-C₃ alkanes, C₂-C₃ alkenes, and C₄-C₅ gases. Labels A-M refer to catalyst identifiers shown in Table 2 of main article.

Fig. S8. Product yield of C₄+ 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 C₄+ 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 $\sim$ 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

- [1] S.D. Stefanidis, K.G. Kalogiannis, E.F. Iliopoulou, A.A. Lappas, P.A. Pilavachi, In-situ upgrading of biomass pyrolysis vapors: Catalyst screening on a fixed bed reactor, *Bioresour. Technol.* 102 (2011) 8261–8267. doi:10.1016/j.biortech.2011.06.032.
- [2] E.F. Iliopoulou, S.D. Stefanidis, K. Kalogiannis, A.C. Psarras, A. Delimitis, K.S. Triantafyllidis, A.A. Lappas, Pilot-scale validation of Co-ZSM-5 catalyst performance in the catalytic upgrading of biomass pyrolysis vapours, *Green Chem.* 16 (2014) 662–674. doi:10.1039/C3GC41575A.
- [3] P.T. Williams, P.A. Horne, The influence of catalyst regeneration on the composition of zeolite-upgraded biomass pyrolysis oils, *Fuel*. 74 (1995) 1839–1851. doi:10.1016/0016-2361(95)80017-C.
- [4] K. Iisa, R.J. French, K.A. Orton, A. Dutta, J.A. Schaidle, Production of low-oxygen bio-oil via ex situ catalytic fast pyrolysis and hydrotreating, *Fuel*. 207 (2017) 413–422. doi:10.1016/j.fuel.2017.06.098.
- [5] P.T. Williams, N. Nugranad, Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks, *Energy*. 25 (2000) 493–513. doi:10.1016/S0360-5442(00)00009-8.
- [6] H. Hernando, S. Jiménez-Sánchez, J. Feroso, P. Pizarro, J.M. Coronado, D.P. Serrano, Assessing biomass catalytic pyrolysis in terms of deoxygenation pathways and energy yields for the efficient production of advanced biofuels, *Catal. Sci. Technol.* 6 (2016) 2829–2843. doi:10.1039/c6cy00522e.