

Supporting Information

Enhanced bio-BTX formation by catalytic pyrolysis of glycerol with *in-situ* produced toluene as the co-feed

Fukang Wang,^{a,#} Thomas Sjouke Kramer,^{b,#} Bin Yan,^a Lin Zhu,^a Yuezhaoh Zhu,^a Andre Heeres,^c Diana Ciolca,^d Hero Jan Heeres,^{b,*} and Songbo He^{a,*}

^aJoint International Research Laboratory of Circular Carbon, Nanjing Tech University, Nanjing 211816, PR China

^bGreen Chemical Reaction Engineering, Engineering and Technology Institute Groningen, University of Groningen, 9747 AG Groningen, The Netherlands

^cHanze University of Applied Sciences, 9747 AS Groningen, The Netherlands

^dBioBTX BV, 9747 AA Groningen, The Netherlands

*Corresponding authors. E-mail: h.j.heeres@rug.nl (H.J. Heeres) and songbo.he@njtech.edu.cn (S. He)

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Experimental

Materials. A granular alumina bonded H-ZSM-5 catalyst (H-ZSM-5/Al₂O₃, 60/40 wt.%, ϕ 1.2 - 1.8 mm, SiO₂/Al₂O₃ molar ratio of 28) was produced at Yangzhou Baisheng Catalyst Co., Ltd., PR China. The as-received H-ZSM-5/Al₂O₃ catalyst was calcined at 600 °C 8 h and the calcined catalyst was stored in a vacuum desiccator. Glycerol (> 99.5% purity) was supplied by Boom BV, The Netherlands. Toluene, ethanol, tetrahydrofuran (THF), and n-nonane were of analytical grade and supplied by Sigma-Aldrich. The liquid and gaseous N₂ were supplied by Linde.

Catalytic (co-)pyrolysis experiemnts. The experiments were performed on a well-engineered bench-scale fixed bed reactor setup. The fresh H-ZSM-5/Al₂O₃ catalyst (10 g) was loaded to the isothermal zone of a stainless steel tubular reactor, of which the rest was filled with quartz wool. The reactor was heated to 550 °C under an N₂ flow of 50 ml min⁻¹. The (co-)feed was pumped (10 g h⁻¹) into a preheater (maintained at 350 °C) by using the syringe pump(s) and the gastight syringe(s). The vapor mixed with N₂ gas was first passed to the vent to purge the system for *ca.* 2 h and then introduced to the catalyst reactor. The reactions were continuously performed for a TOS of 12 h. Liquid samples (collected in a 20-ml glass vial) and gas-phase samples (collected in a 5-L FlexFoil Plus sample bag) were taken every 30 min.

Product analysis. The liquid products collected in the 20-ml glass vials were diluted approximately 7 times with a stock solution (*ca.* 20,000 ppm of *n*-nonane in a mixed solvent containing THF and ethanol with a volume ratio of *ca.* 1 to 10) to prepare homogeneous samples for various off-line analyses. The mixtures were analyzed by GC-MS (6890/5973, Hewlett-Packard) and GC-FID (5890, Hewlett-Packard) equipped with a Rtx-1701 column (30 m × 0.25 mm × 0.25 μ m, Restek). The relative response factors of the individual aromatics to the internal standard, *viz.*, *n*-nonane, were applied for the quantification of aromatics. The carbon, hydrogen, and oxygen contents in the samples were analyzed using a EuroEA3000 elemental analyzer (Eurovector). The gaseous products collected in the 5-L gas bags were analyzed by GC-TCD (5890, Hewlett-Packard) equipped with a CP-PoraBOND Q column (50 m × 0.53 mm × 10 μ m, Varian) and an HP-Molsieve column (30m x 0.53 mm x 50 μ m, Agilent). Before and after the analyses, the GC-TCD was pre- and post-calibrated with a standard reference gas mixture containing C₁-C₃, CO, CO₂, and N₂. The carbon yields of products, the

selectivity of individual BTX components, and BTX productivity on the catalyst during the first run were calculated using **Equations 1-3**.

$$\text{Yield (\%, on carbon basis)} = \frac{\text{mol of carbon in the individual product}}{\text{mol of carbon in the feed}} \times 100 \quad (1)$$

$$\text{BTX selectivity (\%)} = \frac{\text{mol of individual BTX component produced}}{\text{mol of total BTX product}} \times 100 \quad (2)$$

$$\text{BTX productivity (mg}_{BTX} \text{ g}_{catalyst}^{-1}) = \frac{\text{weight of BTX produced}}{\text{weight of catalyst loaded in the reactor}} \quad (3)$$

Calculation procedure for the calculated data shown in Figs. 3, 4, S3, and S4

The following general calculation equation was used:

Calculated carbon yield of the co-feed = Experimental performance data of Feed A × carbon fraction (C.%) of Feed A in the co-feed + Experimental performance data of Feed B × carbon fraction (C.%) of Feed B in the co-feed

The mass ratio of glycerol and toluene in the co-feed was 93/7 wt.%.

The carbon ration of glycerol and toluene in the co-feed was 85/15 C.%.

Calculated data in Figs. 3 and S3

	Glycerol (Experimental)	Toluene (Experimental)	Glycerol/Toluene (85/15 C.%) (Calculated)
Carbon yield of benzene (C.%) [#]	4.4	26.7	$4.4 \times 0.85 + 26.7 \times 0.15 = 7.7$
Carbon yield of toluene (C.%) [#]	9.5	41.3	$9.5 \times 0.85 + 41.3 \times 0.15 = 14.3$
Carbon yield of xylenes (C.%) [#]	5.3	15.7	$5.3 \times 0.85 + 15.7 \times 0.15 = 6.8$

[#]The average value of the carbon yields at TOS of 1.5, 2, and 2.5 h.

Calculated data in Fig. 4

	Glycerol (Experimental)	Toluene (Experimental)	Glycerol/Toluene (85/15 C.%) (Calculated)
Overall carbon yield of benzene (C.%)	2.1	22.1	$2.1 \times 0.85 + 22.1 \times 0.15 = 5.1$
Overall carbon yield of toluene (C.%)	5.3	46.2	$5.3 \times 0.85 + 46.2 \times 0.15 = 11.4$
Overall carbon yield of xylenes (C.%)	3.6	16.4	$3.6 \times 0.85 + 16.4 \times 0.15 = 5.5$

Calculated data in Fig. S4

	Glycerol (Experimental)	Toluene (Experimental)	Glycerol/Toluene (93/7 wt.%) (Calculated)
Productivity of benzene on the catalyst during the first run ($\text{mg g}^{-1}_{\text{catalyst}}$)	79	1859	$79 \times 0.93 + 1859 \times 0.07 = 204$
Productivity of toluene on the catalyst during the first run ($\text{mg g}^{-1}_{\text{catalyst}}$)	206	3926	$206 \times 0.93 + 3926 \times 0.07 = 466$
Productivity of xylenes on the catalyst during the first run ($\text{mg g}^{-1}_{\text{catalyst}}$)	141	1409	$141 \times 0.93 + 1409 \times 0.07 = 230$

BTX prices are collected from the weekly report of Ethanol Market and Pricing Data by U.S. Grains Council.
The reports are available at https://grains.org/ethanol_report/

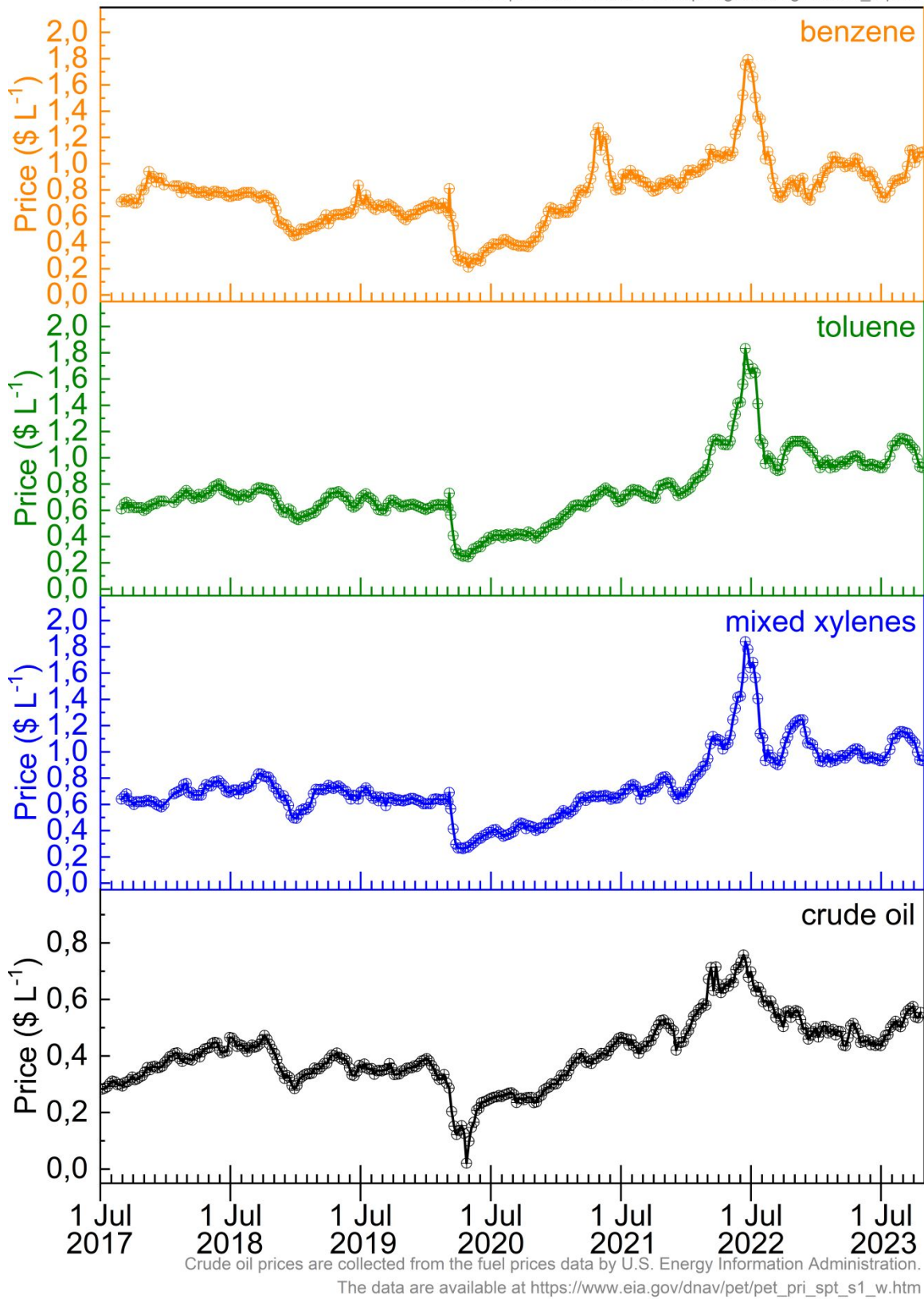


Figure S1. Pricing for benzene, toluene, mixed xylenes, and crude oil in 2017 - 2023.^{S1-S2}

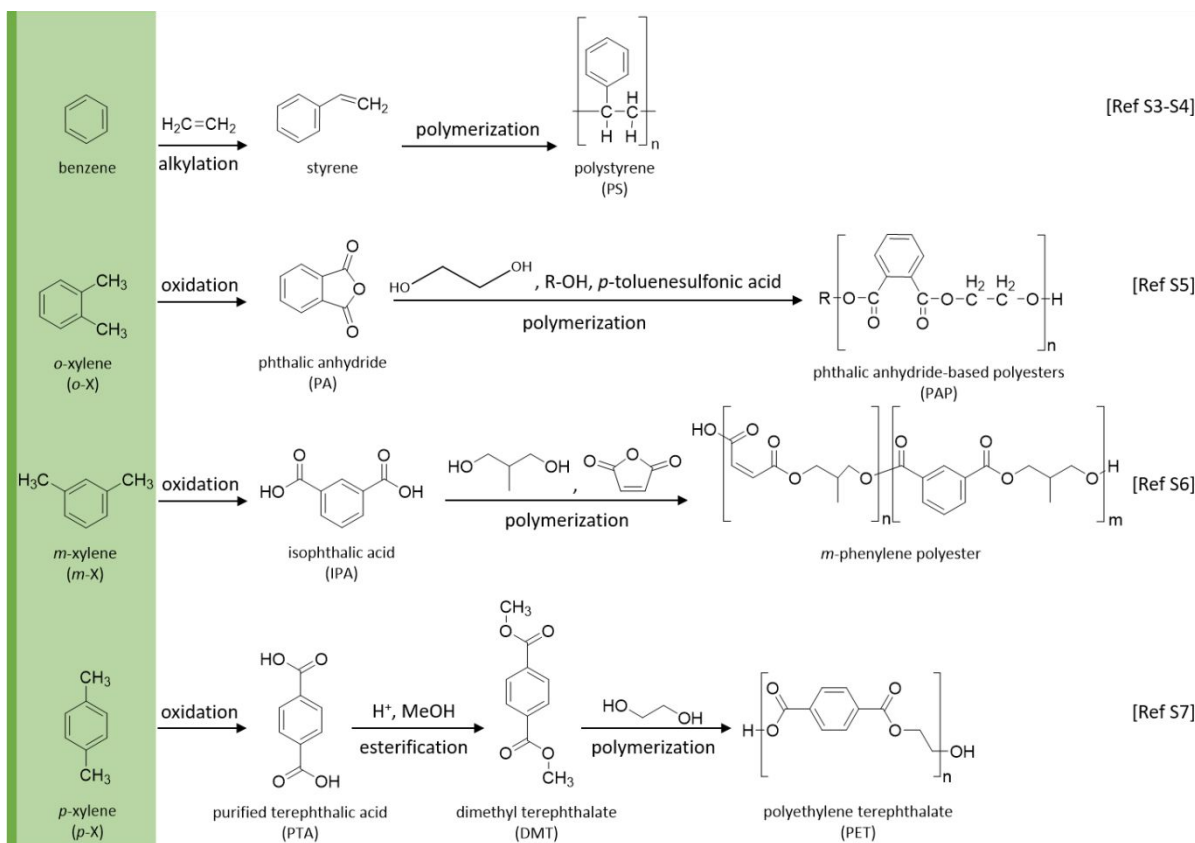


Figure S2. Synthesis of bio-based polymers from bio-based benzene and xylenes.^{S3-S7}

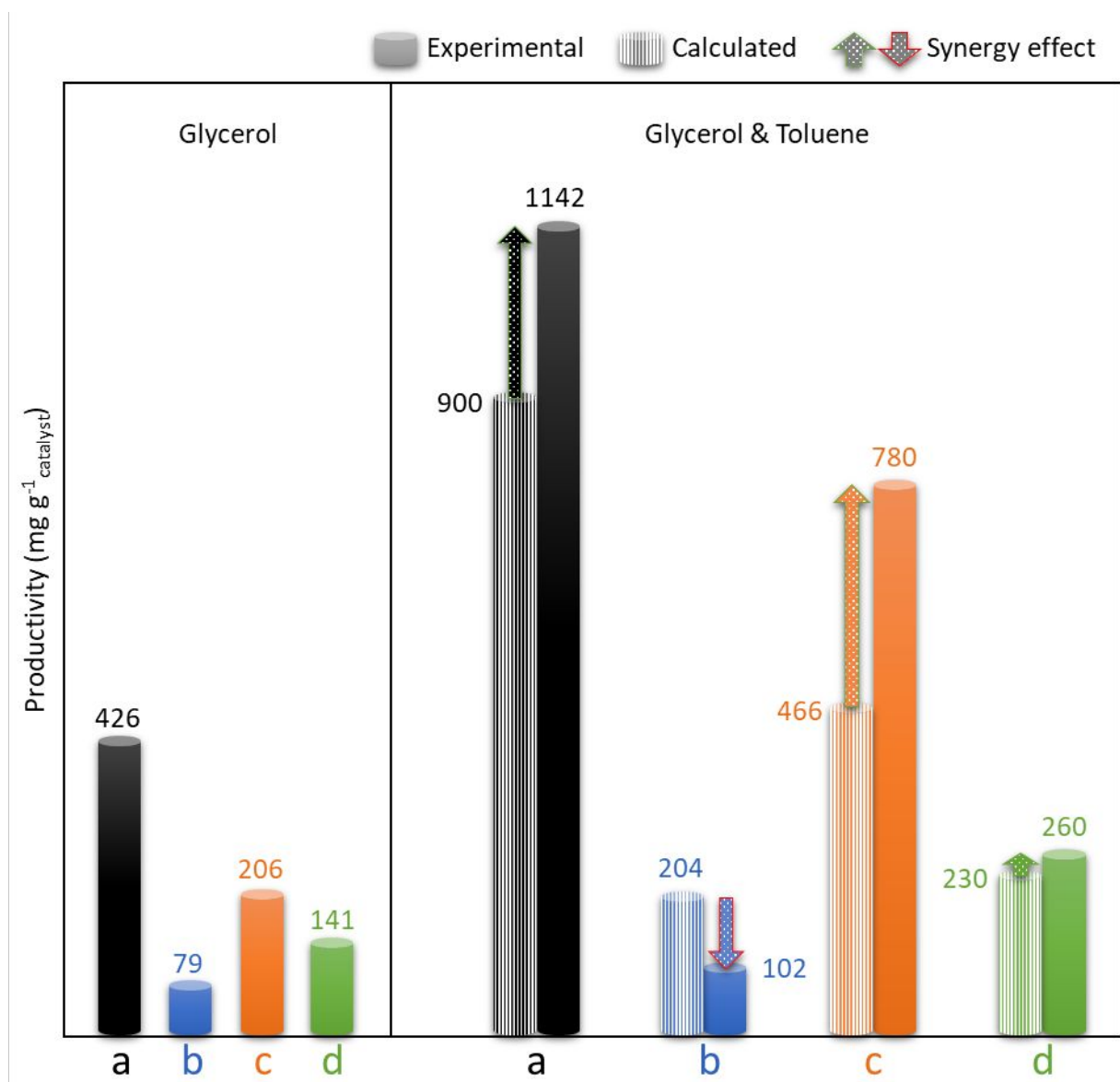


Figure S3. Productivity of (a) total BTX, (b) benzene, (c) toluene, and (d) xylenes on the catalyst during the first run for catalytic conversion of glycerol (left) and co-conversion of glycerol and toluene (93/7 wt.%, right). Reaction conditions: H-ZSM-5/Al₂O₃ (60/40 wt.%) catalyst of 10 g, WHSV of the (co-)feeds of 1 h⁻¹, N₂ flow of 50 ml min⁻¹, reactor temperature of 550 °C, atmospheric pressure, and TOS of 8.5 h.

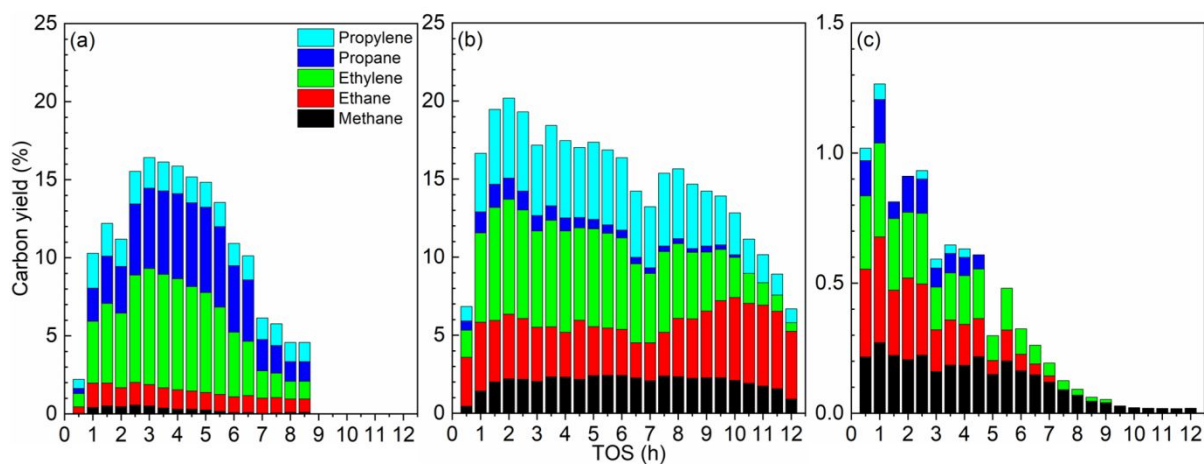


Figure S4. Carbon yields of low-molecular-weight hydrocarbons *versus* TOS for catalytic conversion of individual glycerol (a) and toluene (c), and catalytic co-conversion of glycerol and toluene (93/7 wt.%, b). Reaction conditions: H-ZSM-5/Al₂O₃ (60/40 wt.%) catalyst of 10 g, WHSV of the (co-)feeds of 1 h⁻¹, N₂ flow of 50 ml min⁻¹, reactor temperature of 550 °C, and atmospheric pressure.

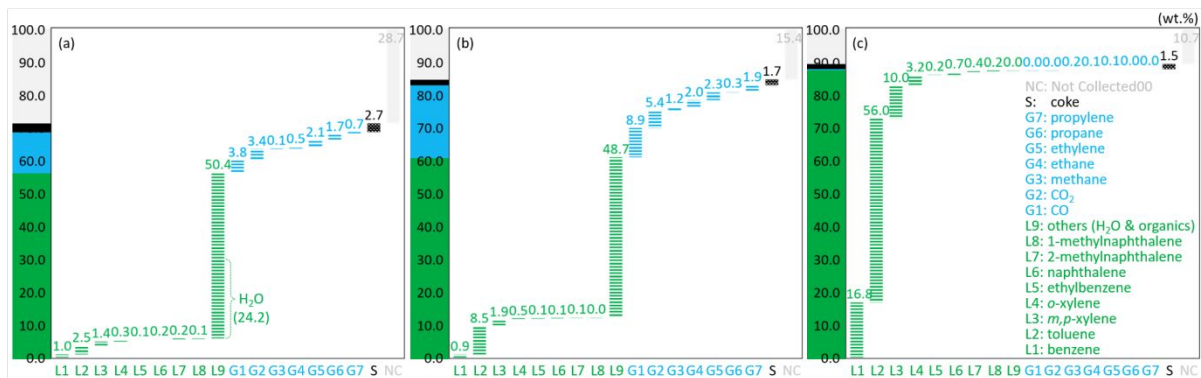


Figure S5. Mass balance for catalytic conversion of individual glycerol (a) and toluene (c), and catalytic co-conversion of glycerol and toluene (93/7 wt.%, b). Reaction conditions: H-ZSM-5/Al₂O₃ (60/40 wt.%) catalyst of 10 g, WHSV of the (co-)feeds of 1 h⁻¹, N₂ flow of 50 ml min⁻¹, reactor temperature of 550 °C, and atmospheric pressure.

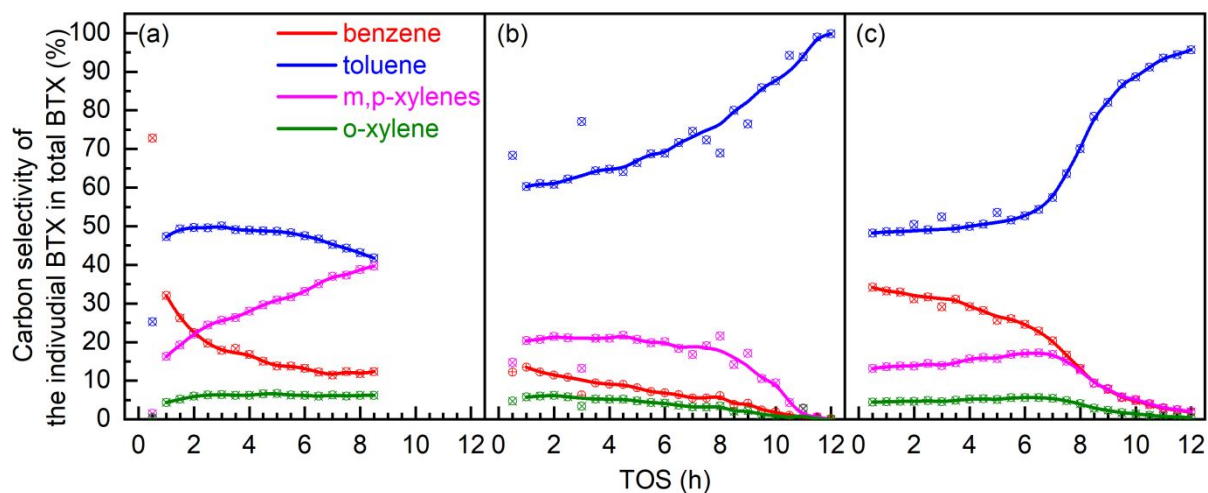


Figure S6. Carbon selectivity of the individual BTX in total BTX *versus* TOS for catalytic conversion of individual glycerol (a) and toluene (c), and catalytic co-conversion of glycerol and toluene (93/7 wt.%, b). Reaction conditions: H-ZSM-5/Al₂O₃ (60/40 wt.%) catalyst of 10 g, WHSV of the (co-)feeds of 1 h⁻¹, N₂ flow of 50 ml min⁻¹, reactor temperature of 550 °C, and atmospheric pressure.

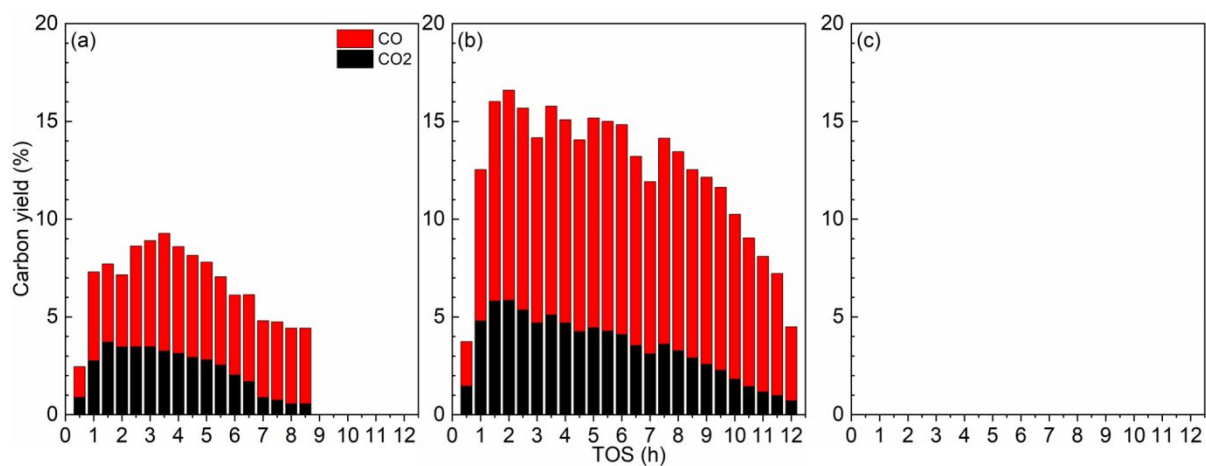


Figure S7. Carbon yields of CO and CO₂ versus TOS for catalytic conversion of individual glycerol (a) and toluene (c), and catalytic co-conversion of glycerol and toluene (93/7 wt.%, b).

Reaction conditions: H-ZSM-5/Al₂O₃ (60/40 wt.%) catalyst of 10 g, WHSV of the (co-)feeds of 1 h⁻¹, N₂ flow of 50 ml min⁻¹, reactor temperature of 550 °C, and atmospheric pressure.

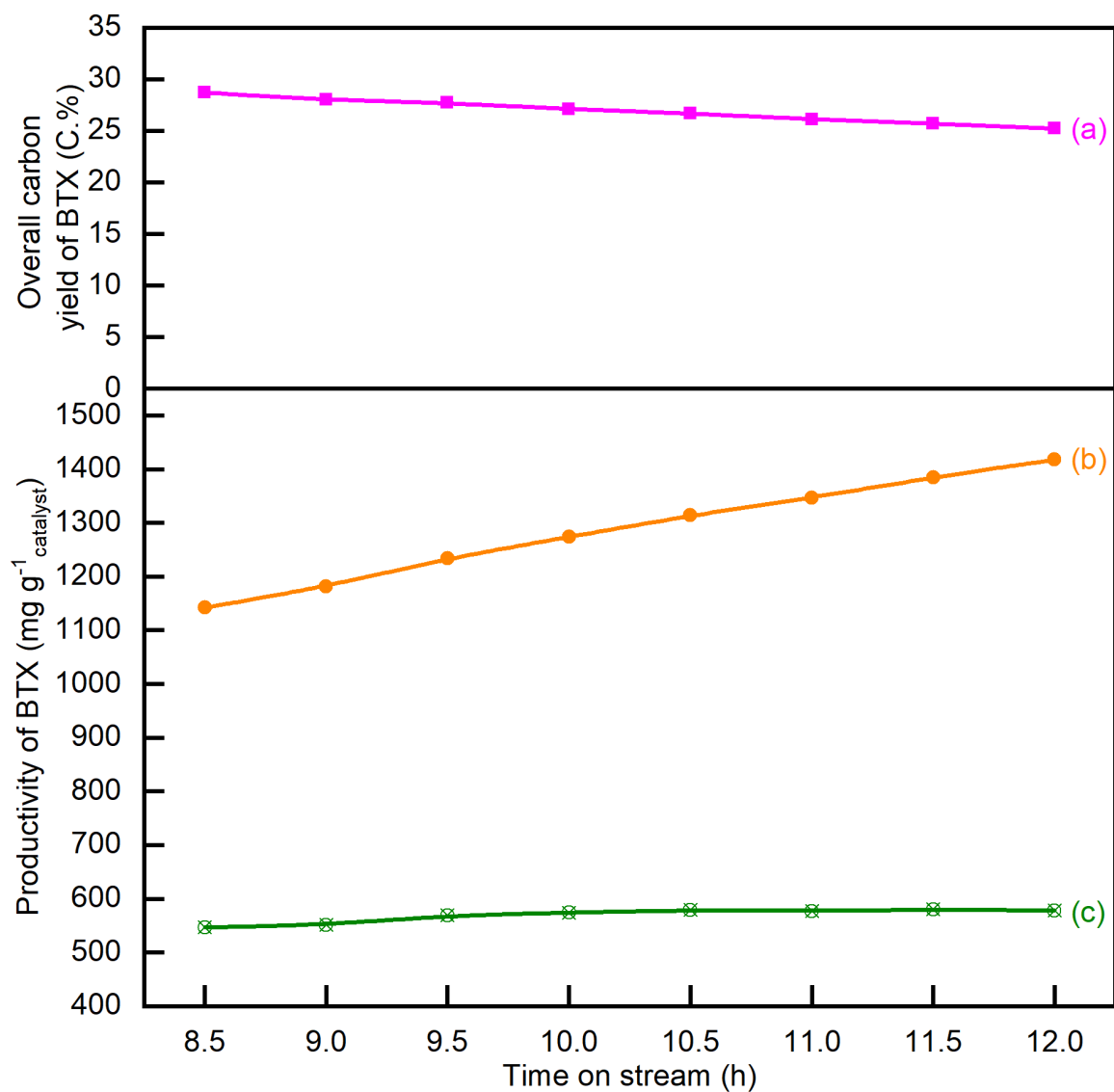


Figure S8. Overall BTX carbon yield (a), productivity of BTX on the catalyst during the first run including the toluene fraction for the recycle in co-feed (b), and productivity of BTX on the catalyst during the first run excluding the toluene fraction recycled in co-feed (c) for co-conversion of glycerol and toluene (93/7 wt.%). Reaction conditions: H-ZSM-5/Al₂O₃ (60/40 wt.%), WHSV of co-feed of 1 h⁻¹, N₂ flow of 50 ml min⁻¹, reactor temperature of 550 °C, atmospheric pressure, and TOS varied from 8.5 to 12 h.

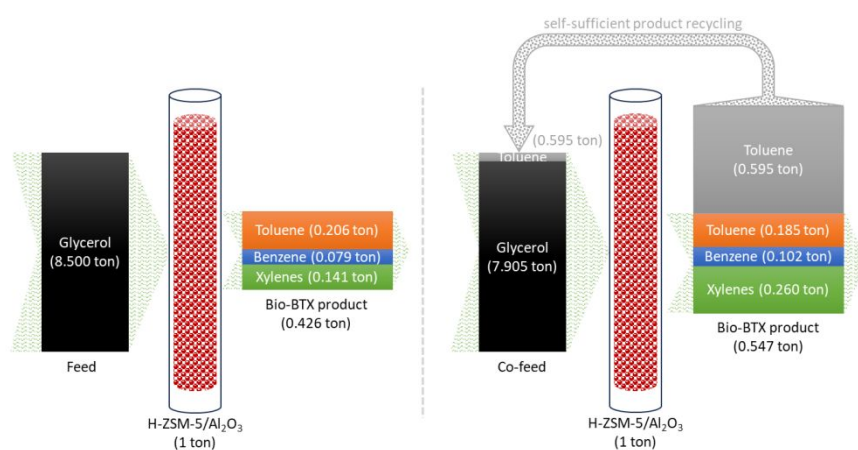


Figure S9. Enhanced production of bio-BTX aromatics (in particular xylenes) for catalytic conversion of glycerol (left) by self-sufficient toluene product recycling (right). Reaction conditions: H-ZSM-5/Al₂O₃ (60/40 wt.%), WHSV of the (co-)feeds of 1 h⁻¹, N₂ flow of 50 ml min⁻¹, reactor temperature of 550 °C, atmospheric pressure, and TOS of 8.5 h.

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