

Supporting Information

Catalytic production of Tetrahydropyran (THP): A biomass-derived, economically competitive solvent with demonstrated use in plastic dissolution

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Number of pages: 9

Number of figures: 4

Number of tables: 4

Catalyst characterization

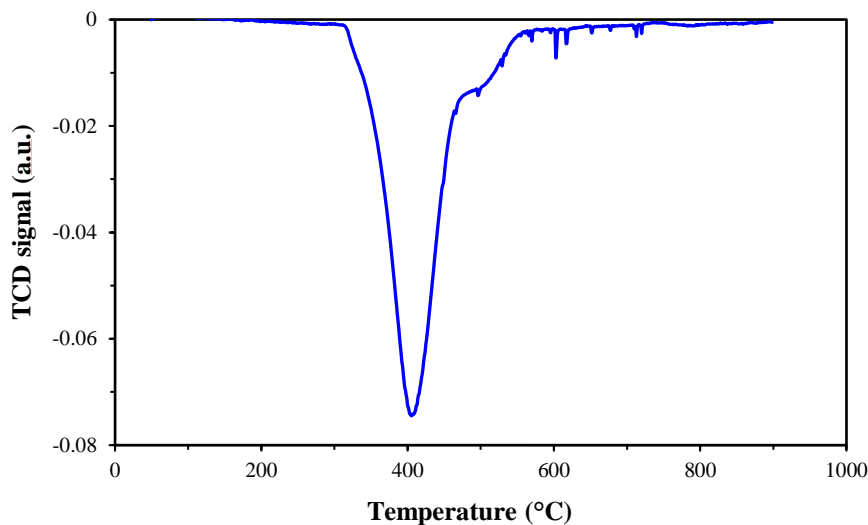


Figure S1. Temperature-programmed reduction (TPR) of 10-Ni/SiO₂ in H₂ flow. Experiment carried out on Micromeritics Autochem II chemisorption analyzer with a thermal conductivity detector (TCD).

Ring opening polymerization:

Materials

Tetrahydrofuran (THF) was purified and dried prior polymerization. High-performance liquid chromatography (HPLC)-grade THF were first sparged extensively with nitrogen during filling 20 L solvent reservoirs and then dried by passage through activated alumina followed by passage through Q-5 supported copper catalyst stainless steel columns. Tetrahydropyran (THP) was purchased from TCI America. THP was degassed and dried over CaH₂ overnight, followed by vacuum distillation (CaH₂ was removed before distillation), and then stored over activated Davison 4 Å molecular sieves. Boron trifluoride diethyl etherate (BF₃·Et₂O) and ytterbium(III) trifluoromethanesulfonate (Yb(OTf)₃) were purchased from Sigma-Aldrich Chemical Co. and used as received. Trifluoromethanesulfonic acid (CF₃SO₃H) was purchased from TCI America and used as received.

Nuclear magnetic resonance (NMR) spectroscopy

¹H spectra were recorded on a Bruker Advance NEO 400 MHz. Chemical shifts for all spectra were referenced to internal solvent resonances and were reported as parts per million relative to SiMe₄.

Thermal Analysis

Melting transition (T_m) and cold crystallization (T_c) temperatures were measured by differential scanning calorimetry (DSC) on an Auto Q20, TA Instrument. All T_m and T_g values were obtained from a second scan after the thermal history was removed from the first scan. The second heating rate was 10 °C/min and cooling rate was 10 °C/min unless indicated otherwise in the polymerization tables. Decomposition temperatures (T_d , defined by the temperature of 5 % weight loss) and maximum rate decomposition temperatures (T_{max}) of the polymers were measured by thermal gravimetric analysis (TGA) on a Q50 TGA Analyzer, TA Instrument. Polymer samples were heated from ambient temperature to 700 °C at a heating rate of 10 °C/min. Values of T_{max} were obtained from derivative (wt %/°C) vs. temperature (°C) plots, while T_d and T_{onset} values (initial and end temperatures) were obtained from wt % vs. temperature (°C) plots.

Molecular Weight Measurements

Measurements of polymer weight-average molecular weight (M_w), number-average molecular weight (M_n), and molecular weight distributions or dispersity indices ($D = M_w/M_n$) were performed via gel-permeation chromatography (GPC). The GPC instrument consisted of an Agilent HPLC system equipped with one guard column and two PLgel 5 µm mixed-C gel permeation columns and coupled with a Wyatt DAWN HELEOS II multi (18)-angle light scattering detector and a Wyatt Optilab TrEX dRI detector; the analysis was performed at 40 °C using chloroform as the eluent at a flow rate of 1.0 mL/min, using Wyatt ASTRA 7.1.2 molecular weight characterization software.

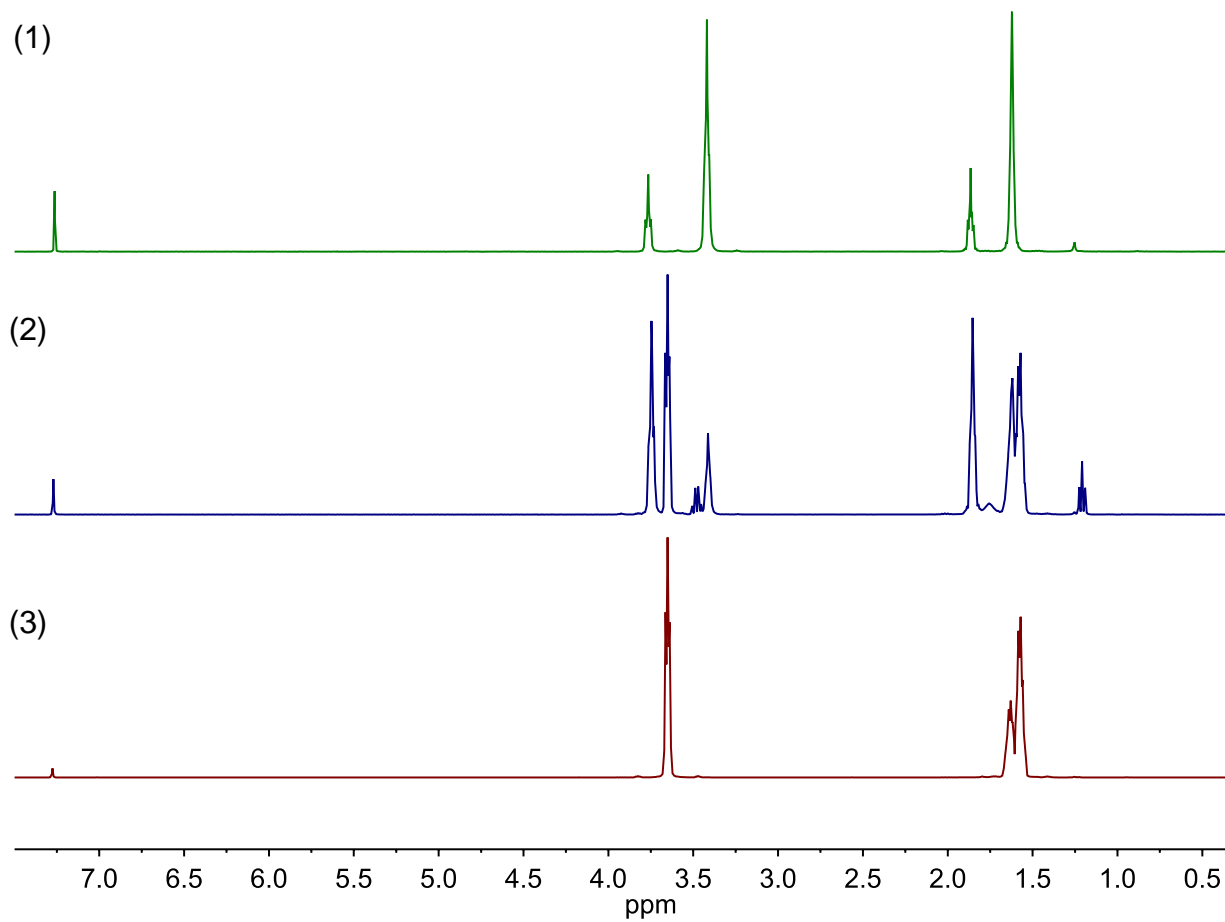


Figure S2. ¹H NMR (23 °C, CDCl₃) spectra stack of: **(1)** THF polymerization catalyzed by CF₃SO₃H with [THF]/[THP]/[CF₃SO₃H] = 100/100/1 at 0 °C. **(2)** copolymerization of THF and THP catalyzed by BF₃·Et₂O with [THF]/[THP]/[BF₃·Et₂O] = 100/100/10 at 0 °C. **(3)** THP for reference.

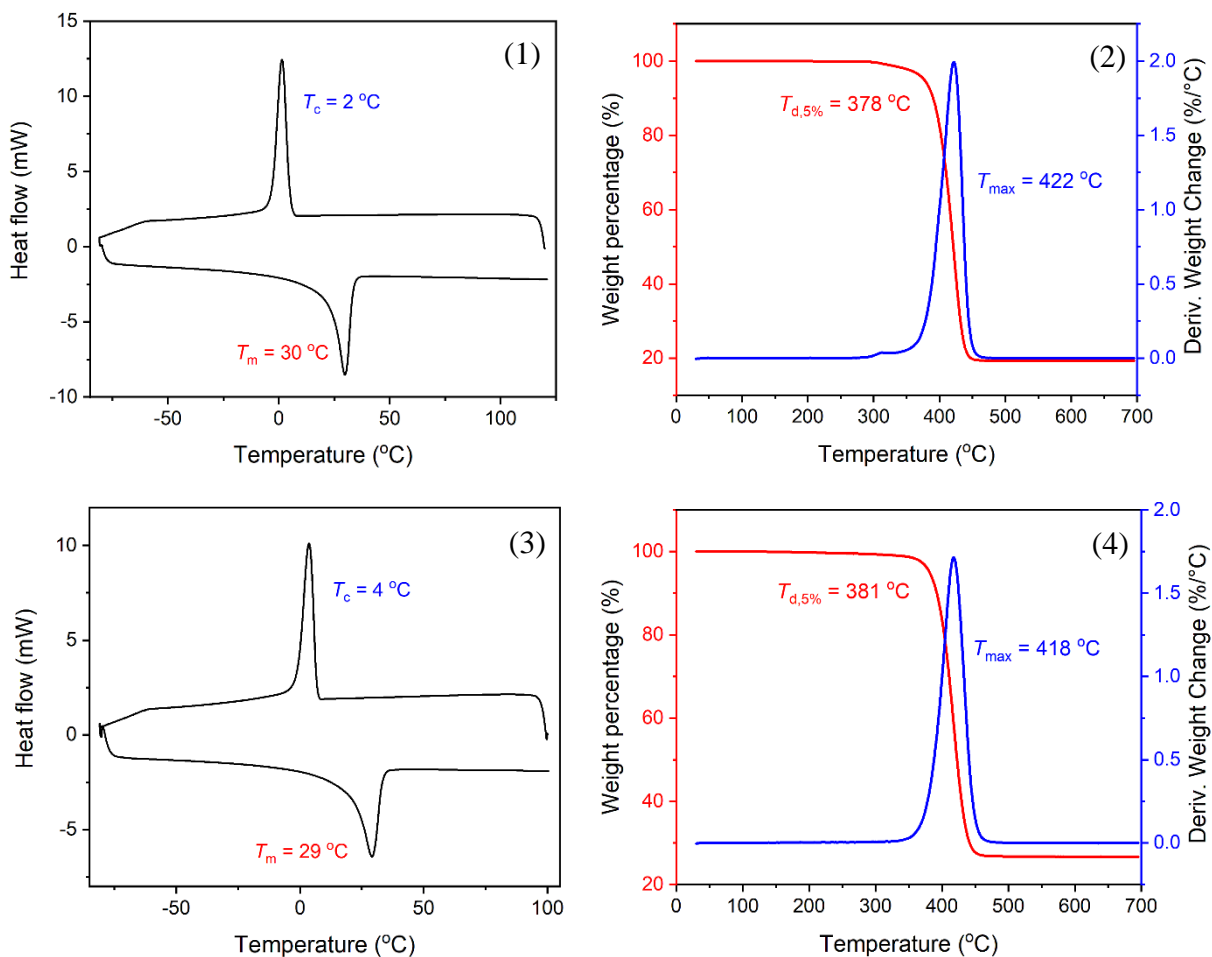


Figure S3. For poly(THF) produced by polymerization of THF: (1) DSC trace; (2) TGA and DTG curves. For poly(THF) produced by copolymerization of THF and THP: (3) DSC trace; (4) TGA and DTG curves.

Technoeconomic analysis:

Table S1. Temperature, pressure and mass flow of each stream based on the process flow diagram in **Figure 1**.

| Stream | Temperature (°C) | Pressure (bar) | Total flow (kg/h) | H₂ (kg/h) | DHP (kg/h) | THP (kg/h) | 1-Pentanol (kg/h) |
|---------------------------------|-----------------------------|---------------------------|------------------------------|---------------------------------|-----------------------|-----------------------|------------------------------|
| 1 | 27.92 | 14.8 | 2,069.78 | - | 2,069.78 | - | - |
| 2 | 200 | 14.8 | 4,331.30 | 1,683.77 | 2,079.50 | 567.88 | 0.15 |
| 3 | 200 | 14 | 4,331.30 | 1,634.65 | 43.02 | 2,639.90 | 13.73 |
| 4 | 25 | 14 | 2,230.25 | 1,634.61 | 10.02 | 585.47 | 0.16 |
| 5 | 36.63 | 14.8 | 2,163.31 | 1,585.56 | 9.72 | 567.88 | 0.15 |
| 6 | 498.92 | 14.8 | 98.21 | 98.21 | - | - | - |
| 7 | 200 | 14.8 | 2,261.52 | 1,683.77 | 9.72 | 567.88 | 0.15 |
| H₂ makeup | 25 | 1.01 | 98.21 | 98.21 | - | - | - |
| Purge | 36.63 | 14.8 | 66.91 | 49.04 | 0.3 | 17.56 | 0 |
| DHP | 25 | 1 | 2,069.78 | - | 2,069.78 | - | - |
| THP | 25 | 14 | 2,101.05 | 0.05 | 33 | 2,054.43 | 13.57 |

Table S2. Economic parameters and assumptions.¹

| | |
|--|-------------------------|
| Plant operating hours per year (hours/year) | 7880 |
| Plant life (year) | 30 |
| Internal rate of return (%) | 10 |
| Plant depreciation (year) | 7 |
| Loan terms | 10 years loan at 8% APR |
| Construction time (year) | 3 |
| First 12 months' expenditure | 8 |
| Next 12 months' expenditure | 60 |
| Last 12 months' expenditure | 32 |
| Federal tax rate (%) | 21 |
| Financing (% of equity) | 40 |
| Start-up time (month) | 6 |
| Revenue during start-up (%) | 50 |
| Variable operating costs during start-up (%) | 75 |
| Fixed operating costs during start-up (%) | 100 |
| Variable operating cost | |
| Electricity purchase (\$/kWh) | 0.07 |
| Hydrogen purchase (\$/ton) | 1507 |
| 30 wt% Ni/SiO ₂ ^a | 185.4 |
| Steam purchase (\$/kJ) | 2.50×10^{-6} |
| Cooling water purchase (\$/kJ) | 2.12×10^{-7} |
| Fixed operating cost | |
| Labor costs ^b | \$75,000 |
| Annual maintenances | 3.0% of ISBL |
| Property insurances | 0.7% of FCI |

^aWe assumed that catalyst was refurbished after every 3 months at 20% of the initial catalyst cost.²

^bWe assumed that the DHP production process can be operated by one full-time operator.

Table S3. Summary of capital costs of the THP production process at a DHP feed rate of 16,300 ton per year.

| Cost components | | Cost (1,000\$) |
|--|----------------|-----------------------|
| Inside-battery-limits (ISBL) equipment cost | | 8,698 |
| Outside-battery-limits (ISBL) equipment cost | 40.0% of ISBL | 3,479 |
| Warehouse | 4.0% of ISBL | 348 |
| Site development | 9.0% of ISBL | 783 |
| Additional piping | 4.5% of ISBL | 391 |
| Total direct costs (TDC) | | 13,700 |
| Prorateable expenses | 10.0% of TDC | 1,370 |
| Field expenses | 10.0% of TDC | 1,370 |
| Home office and construction fee | 20.0% of TDC | 2,740 |
| Project contingency | 40.0% of TDC | 5,480 |
| Other costs (start-up, Permits, etc.) | 10.0% of TDC | 1,370 |
| Total indirect costs (TIC) | | 12,330 |
| Fixed capital investment (FCI) | TDC+TIC | 26,030 |
| Land and working capital | 5.0% of FCI | 1,302 |
| Total capital investment (TCI) | | 27,332 |

Table S4. Summary of operating costs of the THP production process at a DHP feed rate of 16,300 ton per year.

| Cost components | Cost (\$/year) |
|---------------------------------|-----------------------|
| Cooling water | 19,029 |
| Steam | 24,903 |
| Electricity | 209,845 |
| DHP feed stock | 24,467,400 |
| Hydrogen | 1,166,650 |
| Catalyst | 6,674 |
| Variable operating costs | 25,894,500 |
| Labor costs | 75,000 |
| Annual maintenance | 260,953 |
| Property insurance | 182,211 |
| Fixed operating costs | 518,164 |

Computational modeling

MD simulation setup

Atomistic MD simulations were performed in the isothermal-isobaric ensemble using *Gromacs 2016*.³ The simulation contains 1 LDPE oligomer ($C_{40}H_{82}$) and 216 solvent (THP or water) molecules. All molecules were parameterized using Antechamber and the Generalized AMBER force fields.^{4,5} The simulation system was initialized with a cubic box containing a single polymer. The system was then solvated, energy minimized, and equilibrated for 20 ns in an *NPT* simulation at 300 K and 1 bar using a velocity-rescale thermostat and Berendsen barostat. A 100 ns *NPT* simulation was then performed at the same temperature and pressure using the Nose-Hoover thermostat and Parrinello-Rahman barostat. All simulations were performed using a leapfrog integrator with a 2-fs timestep. Verlet lists were generated using a 1.2 nm neighbor list cutoff. Van der Waals interactions were modeled with a shifted Lennard-Jones potential and Verlet cutoff-scheme that was smoothly shifted to zero at 1.2 nm. Electrostatic interactions were calculated using the smooth Particle Mesh Ewald method with a short-range cutoff of 1.2 nm, grid spacing of 0.14 nm, and 4th order interpolation. Bonds were constrained using the LINCS algorithm. All thermostats used a 2.0 ps time constant and all barostats used a 2.0 ps time constant with an isothermal compressibility of $3.0 \times 10^{-5} \text{ bar}^{-1}$.

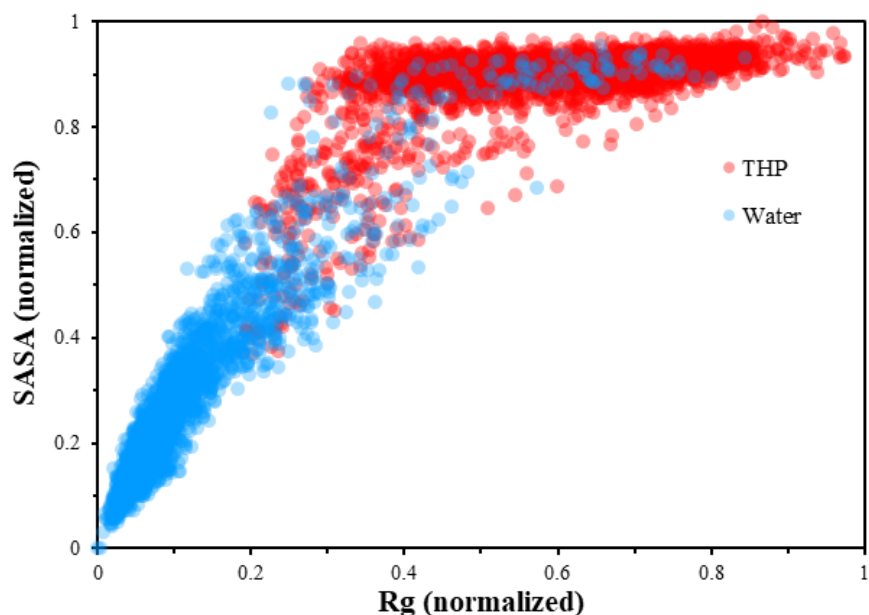


Figure S4. R_g -SASA scatter plot of LDPE oligomer in THP and water. R_g and SASA were calculated from MD simulations.

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