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

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ABSTRACT

Tetrahydropyran (THP) is a five-carbon heterocyclic ether that is non-carcinogenic, non-peroxide forming, biodegradable, and economically competitive with tetrahydrofuran (THF) as a solvent. In this work, THP has been synthesized from renewable biomass at >99.8% selectivity and 98% yield via hydrogenation of furfural-derived 3,4-dihydropyran (DHP) over Ni/SiO₂ in a continuous flow reactor at 150-200°C. The apparent activation energy of THP formation is 31 kJ/mol, and the reaction orders with respect to the partial pressures of H₂, DHP, and THP are: 2, 1, and -0.3. The kinetic data has been fitted to a Hougen-Watson model where the rate limiting step is the hydrogenation of adsorbed DHP. Ni/SiO₂ is shown to have a low deactivation rate constant of 0.012 h⁻¹ over 100 h time on stream and can be regenerated *in situ*. As a performance advantage, THP is shown to be resistant to ring opening polymerization under strongly acidic conditions that THF is not, revealing it to be a superior solvent. The minimum selling price of THP is competitive with the market price of THF (\$900-1400/ton) at a DHP feedstock cost of \$1,000/ton. Conductor-like Screening Model for Real Solvents (COSMO-RS) and molecular dynamics (MD) simulations with 1,008 solvents and 8 common plastics have demonstrated that THP can serve as an alternative solvent to THF, 2-methyltetrahydrofuran (MeTHF), and cyclopentyl methyl ether (CPME) for plastic dissolution, especially low-density polyethylene (LDPE), polypropylene (PP), polystyrene (PS) and polyvinyl chloride (PVC). This work establishes THP as a green solvent with excellent thermal, chemical and peroxidative stability that can be used for numerous applications, including waste plastic recycling.


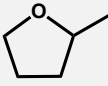

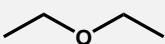
INTRODUCTION

Catalytic upgrading of lignocellulosic biomass offers a sustainable route to green solvents with superior properties.^{1, 2} The global solvent market is projected to reach \$67 billion in 2028,³ but most industrial solvents in use today are petroleum-derived.⁴ Ethers and aromatic solvents are also extremely hazardous as peroxide formers,⁵ carcinogens,⁶ reproductive hazards,⁷ and/or neurotoxins.⁸ While some research has demonstrated the production of ether solvents from biomass, they suffer from peroxide formation⁹ and the high price of precious metal catalysts/reactants.¹⁰ In this work, we introduce an approach to produce tetrahydropyran (THP) from biobased furfural. THP is a five-carbon heterocyclic ether that is non-carcinogenic,¹¹ biodegradable,¹² and non-peroxide forming even after 30 days of exposure to air.¹³

The solvent properties of THP, 2-methyl-THF (MeTHF), tetrahydrofuran (THF), and diethyl ether are shown in **Table 1**. THP has the highest boiling point (88°C) among the listed solvents, imparting it with the lowest vapor pressure and excellent thermal stability. Separation and recovery of THP from aqueous reaction mixtures is simpler since it has a lower solubility in water compared to THF (8.57 wt% solubility for THP vs miscibility of THF in water). Moreover, THP has the highest autoxidation stability to peroxide

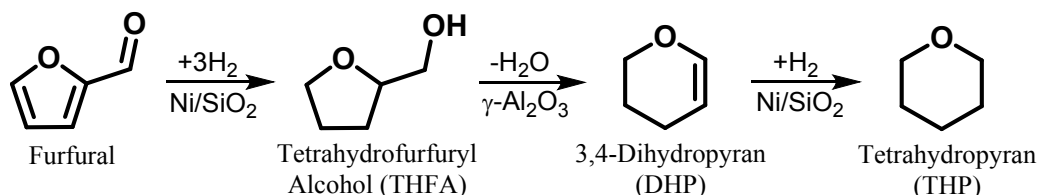
formation.¹⁴ DFT calculations show that this is due to higher energy barriers for both hydrogen abstraction from THP and subsequent molecular oxygen capture by the generated THP radical.¹⁵ The flash point, density, dielectric constant, dipole moment, and surface tension of THP are similar to those of MeTHF and THF. Owing to these favorable solvent properties, THP has been used to replace THF as the solvent for radical chain reactions, such as tributyltin hydride mediated reduction and cyclization (TTMSS).¹³ THP has also been used as the solvent for anionic polymerization of styrene,¹⁶ and α -methylstyrene.¹⁷ Another application of THP is in the form of organic electrolytes like lithium imide/THP for 4V lithium metal rechargeable batteries.¹⁸ Compared to other cyclic ether solvents, THP exhibited >95% Li cycling efficiency, >300 cycle life, and highest cathodic and anodic stability at high temperatures. Methyl THP has been successfully used as the solvent for organic reactions including radical, Grignard, Wittig, and organometallic reactions.¹⁹ In the pharmaceuticals industry, substituted THP compounds are used for their analgesic, anti-inflammatory, and cytotoxic activities.²⁰

Table 1. Solvent properties of tetrahydropyran, 2-methyltetrahydrofuran, tetrahydrofuran, and diethyl ether.

Solvent property	Tetrahydropyran	2-Methyl Tetrahydrofuran	Tetrahydrofuran	Diethyl ether
Structure				
Feedstock	Biomass (3,4-Dihydropyran)	Biomass (Furfural)	Petroleum (1,4-Butanediol)	Petroleum (Ethylene)
Molar mass (g/mol)	86.13	86.13	72.10	74.12
Boiling point (°C)	88.0	80.2	66.0	34.6
Melting point (°C)	-45	-136	-108.5	-116.3
Flash point (°C)	-16	-11	-14	-45
Viscosity (cP)	0.79	0.54	0.48	0.28
Density (g/cm ³)	0.88	0.85	0.88	0.71
Solubility in water (wt%)	8.57	14	Miscible	6.05
Dielectric constant	5.7	6.9	7.6	4.3
Dipole moment (D)	1.6	1.4	1.6	1.1
Surface tension (mN/m)	27.3	25.5	29.5	17
Peroxide formation (ppm at 3 h) ^{10,21}	None	>30	>100	>200

THP has been synthesized by dehydration of 1,5-pentanediol (1,5-PDO) over ZrO₂-ZnO but the selectivity is poor (54%).²² The market price of petroleum-based 1,5-PDO is also high (>\$5000/ton) since it is formed in low quantities as a byproduct of petroleum-based KA oil oxidation.²³ Unlike petroleum, lignocellulosic biomass is rich in five-carbon feedstock in the form of xylose – the second most abundant sugar in the world.²⁴ Xylose is dehydrated to produce furfural which is a major commodity chemical with a projected market volume of 400,000 tons by 2024.²⁵ Tetrahydrofurfuryl alcohol (THFA) is then synthesized in near quantitative yields from hydrogenation of furfural over Ni/SiO₂.²⁶ The patented “PyranDiol” technology that we developed is used to produce dihydropyran (DHP) from dehydration of THFA over γ -Al₂O₃ at 375°C, followed by hydration and hydrogenation reactions to produce 1,5-PDO.²⁷⁻²⁹ In this work, THP

production has been demonstrated from hydrogenation of DHP over Ni/SiO₂, as shown in **Scheme 1**. The intrinsic kinetics of this reaction have been identified, including apparent activation energies and reaction orders, and a Hougen-Watson kinetic model has been developed. The minimum selling price of THP and its variation with production volume and DHP feedstock price have been determined. Lastly, the use of THP as a solvent has been demonstrated using a combination of computational and experimental approaches. We hope to convince the readers that THP can become a low-cost biomass based renewable solvent in several promising applications.



Scheme 1. Reaction pathway for THP production from hydrogenation of furfural-derived DHP.

2. EXPERIMENTAL SECTION

2.1. Catalytic experiments

DHP hydrogenation to THP was carried out in a down-flow packed bed reactor. Ni/SiO₂ (0.1 g) was loaded into a stainless-steel reactor tube (316 SS, 15" length, 1/4" OD) and held in place by packing quartz wool and glass beads on both ends. The reactor tube was enclosed in an aluminum heating block with an embedded thermocouple and placed in a clamshell furnace (Thermo Scientific Lindberg Blue M). System pressure was maintained at 200 psig using a dome-loaded back pressure regulator (Equilibar) with Argon (Airgas, UHP grade) as the pilot fluid. At the start of each experiment, Ni/SiO₂ was reduced *in-situ* with 100 mL/min of H₂ (Airgas, UHP grade) at 500°C with 100°C/h ramp and 5 h hold. The furnace temperature was then reduced to 150°C and the feed, DHP (99%, Acros Organics), was pumped in at 0.1 mL/min using an HPLC pump (Eldex). H₂ co-feed was maintained at 100 mL/min for the duration of the reaction. For partial pressure experiments with THP co-feed, THP was purchased from Sigma-Aldrich (anhydrous, 99%). The products were collected in a stainless-steel vessel chilled with a circulating water/ethylene glycol solution maintained at -20°C to prevent losses to the gas phase. The reaction time on stream was measured from the time it took the reactor to reach the target temperature and pressure. Product samples were drawn every 3-6 hours, and the total reaction time was 24 h. The products were identified by gas chromatography-mass spectrometry (GC-MS) with a Shimadzu GCMS-QP2010 equipped with an RTX-VMS column and quadrupole MS and quantified using a Shimadzu GC 2010 with a flame ionization detector (GC-FID). The equations used to calculate the product yield, selectivity, flow rates, and ¹³C area enhancements are defined in **Eqs (1)-(2)**.

$$\text{Product rate} = \frac{\text{mmol}_{\text{product}}}{\text{h} \cdot g_{\text{catalyst}}} \quad (1)$$

$$\text{Product selectivity} = \frac{\text{mmol}_{\text{product}}}{\text{mmol}_{\text{total products}}} \quad (2)$$

2.2. Catalyst preparation and characterization

SiO₂ was purchased from Sigma-Aldrich and dried overnight in an air oven at 110 °C. Ni/SiO₂ catalysts containing 10 wt% Ni (labeled 10-Ni/SiO₂) were synthesized using incipient wetness impregnation of an aqueous solution of Ni(NO₃)₂·6H₂O (Sigma-Aldrich) onto SiO₂. Ni/SiO₂ catalysts containing 30 wt% Ni (labeled 30-Ni/SiO₂) were purchased from Clariant. All catalysts were dried overnight in an air oven again at 110°C, then calcined in a muffle furnace at 500°C for 10 h in an air atmosphere. Temperature-programmed reduction (TPR) and CO chemisorption of the catalyst were carried out using a Micrometrics

AutoChem II 2920 instrument equipped with an MKS Cirrus 2 quadrupole mass spectrometer. For the TPR, 100 mg of catalyst was loaded into a quartz tube and heated from 50 to 900°C at 10°C/min in 25 mL/min flow of 10% H₂/ Ar. **Figure S1** shows the temperature-programmed reduction (TPR) profile of 10-Ni/SiO₂. For CO chemisorption, 100 mg of catalyst was first reduced at 500°C for 4 h with a 10°C/min ramp in 10% H₂/Ar, then cooled to 50°C in He, followed by CO pulsing in 0.5 mL pulses. The surface Ni sites were measured assuming a stoichiometric factor of 1, i.e. one CO molecule chemisorbed on one Ni surface atom. N₂ physisorption of the catalyst was carried out using a Micromeritics ASAP 2020 instrument. Nickel content of the catalyst was measured using inductively coupled plasma - optical emission spectroscopy (ICP-OES) using a VISTA-MPX instrument. Thermogravimetric analysis (TGA) of the spent catalyst was carried out in a TA Instruments TGA Q500 V6 instrument. 10 mg of the catalyst was placed into a platinum pan, inserted into the instrument, then analyzed with 50 mL/min of the sample gas (N₂ or O₂) while heating from 25 to 600°C at 10°C/min.

2.3. Polymerization experiments

Polymerizations were performed in glass reactors inside an inert glovebox or on a Schlenk line. The monomer (THF or THP, or a 1:1 mixture of THF and THP) and catalyst (BF₃·Et₂O, CF₃SO₃H or Yb(OTf)₃) were added into the reactor. For the polymerization at -30°C, the reactor was placed in the glovebox freezer; for the polymerization at 0°C, the reactor was taken out of the glovebox and placed in a freezer with the temperature of 0°C; for the polymerization at 80°C, the reactor was taken out of the glovebox and placed in an oil bath with the temperature of 80°C. After a desired time, the polymerization was quenched by NaOH aqueous solution. The quenched mixture was then precipitated into cold methanol to remove the catalyst residue, and the obtained polymer was dried in a vacuum oven at room temperature overnight to a constant weight. The following polymer properties were determined: melting transition (T_m) temperature, glass transition (T_g) temperature, decomposition (T_d) temperature, weight-average molecular weight (M_w), number-average molecular weight (M_n), and dispersity index ($D = M_w/M_n$). The experimental details of polymer characterization have been summarized in the **Supplementary Information**.

2.4. Techno-economic analysis

The minimum selling price (MSP) of THP was estimated by a techno-economic analysis (TEA) to determine the economic feasibility of the THP production process. The THP production simulation model was developed in Aspen Plus (V12.0 Aspen Technology) based on the experimental data reported here. Equipment sizing and cost analysis for the corresponding equipment were estimated using Aspen Process Economic Analyzer (V12.0 Aspen Technology). **Figure 1** shows the process flow diagram for THP production from hydrogenation of DHP with 30-Ni/SiO₂ at 200°C. **Table S1** lists the temperature, pressure, and mass flow rate of each stream. DHP is pumped into the system via Stream 1 and heated up to 200°C. The H₂/DHP molar ratio in the inlet stream (Stream 2) to the catalytic reactor (R-1) is maintained at 34. The product stream from R-1 (Stream 3) is cooled from 200°C to 25°C, and then sent to the fractionating column (F-1). High purity product THP is collected from the bottom while unreacted H₂ and small amounts of DHP are removed from the top (Stream 4). 3 % of Stream 4 is purged, and the rest is recycled back to R-1. The H₂ makeup stream (Stream 6) is used to maintain a constant H₂/DHP molar ratio of 34 in R-1. The lifetime of the catalyst is assumed to be three months on stream. After three months, the reaction is stopped and the catalyst is regenerated, while the DHP is fed into a parallel reactor.

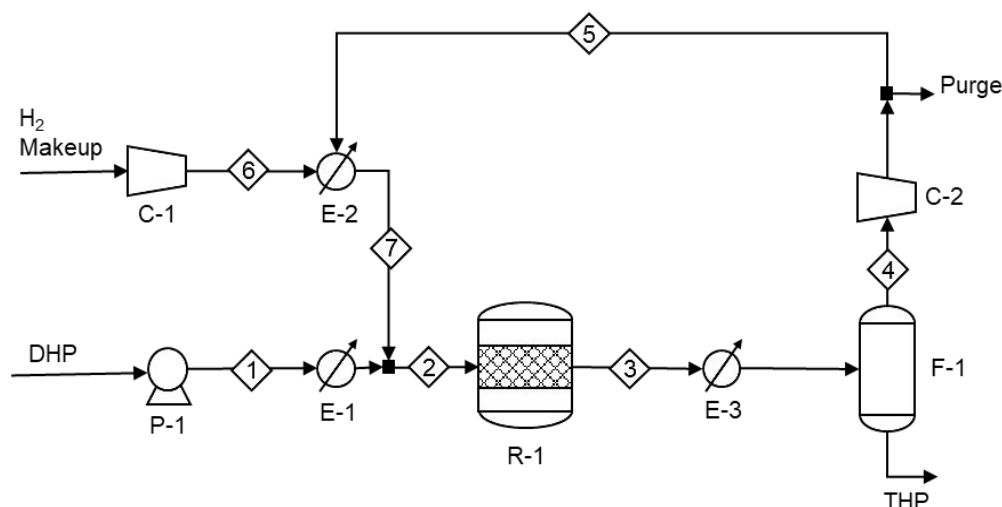


Figure 1. Process flow diagram for THP production from hydrogenation of DHP in a packed bed reactor. C: compressor, E: heat exchanger, F: flash column, P: pump, R: reactor.

2.5. Computational modeling of solvent properties

To investigate the potential applications of THP as a solvent, we employed a set of computational tools to identify similar solvents to THP and study the potential use of THP for polymer dissolution. These computational methods include the Conductor-like Screening Model for Real Solvents (COSMO-RS)^{30, 31} and classical molecular dynamics (MD) simulations. COSMO-RS can predict the thermodynamic properties of multicomponent systems based on quantum mechanical calculations and statistical thermodynamics methods.³² It represents each chemical compound by the probability distribution profile of the screening charge densities on the molecular surface, which is called the σ -profile. We quantified solvent similarity by calculating the Euclidean distance between the σ -profiles of two solvents. COSMO-RS solubility predictions were performed using the *COSMOtherm 19* software with the BP_TZVP_19 parameterization and pre-calculated COSMO files from the database COSMObase-1901-BP-TZVP.^{33, 34} **Figure 2** shows some examples of screening charge distributions of THP, THF, and a low density polyethylene (LDPE) oligomer. In previous work, we employed these tools to predict the solubility of 8 common polymers in 1,007 solvents at multiple temperatures.^{35, 36} This information was used to populate the polymer solubility database and to predict polymer solubility in THP and other solvents in this work. Further MD simulations of oligomer molecules in different solvents were performed to support the dissolution predictions. The details of the MD simulation setup have been summarized in the **Supplementary Information**.

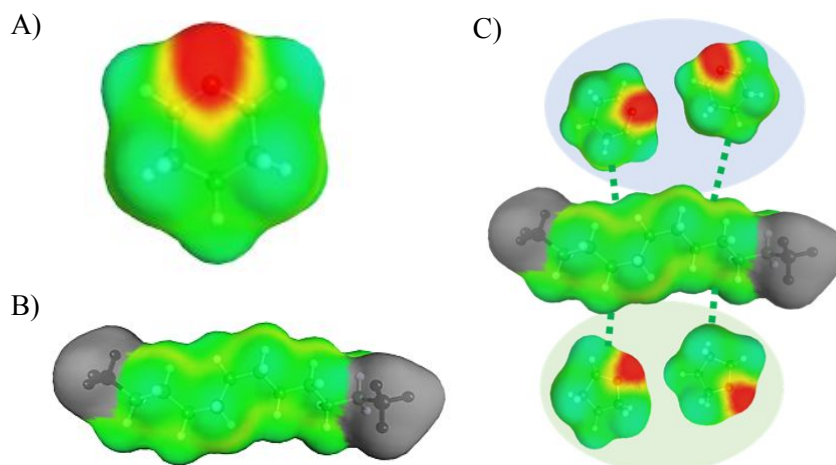


Figure 2. Screening charge distributions from COSMO-RS for: A) THP; B) LDPE oligomer; C) Intermolecular interactions of an LDPE oligomer with THP (top), and THF (bottom).

3. RESULTS AND DISCUSSIONS

3.1. DHP hydrogenation to THP over Ni/SiO₂

The thermodynamics of DHP hydrogenation to THP were evaluated using Aspen Plus prior to kinetic experiments. Since the over-hydrogenolysis of THP produces 1-pentanol as the side product, calculations for THP hydrogenation to 1-pentanol were also evaluated.³⁷ **Figure 3** shows the variation in ΔG_{rxn} and ΔH_{rxn} from 100 – 500°C at 200 psig. The ΔG_{rxn} of DHP hydrogenation to THP decreases in magnitude from -55 kJ/mol at 100°C to -1.4 kJ/mol at 500°C. THP hydrogenation to 1-pentanol is increasingly exergonic with rising temperatures, with the ΔG_{rxn} increasing from -100 kJ/mol at 100°C to -120 kJ/mol at 500°C. Both reactions are exothermic over the entire range of temperatures simulated. The ΔH_{rxn} of DHP hydrogenation to THP is -105 kJ/mol, while the ΔH_{rxn} of THP hydrogenation to 1-pentanol is less exothermic at -80 kJ/mol over the full temperature range. These calculations demonstrate that 1-pentanol is the thermodynamically favored product, especially at higher temperatures. The subsequent kinetic studies were conducted at lower temperatures between 150 – 200°C.

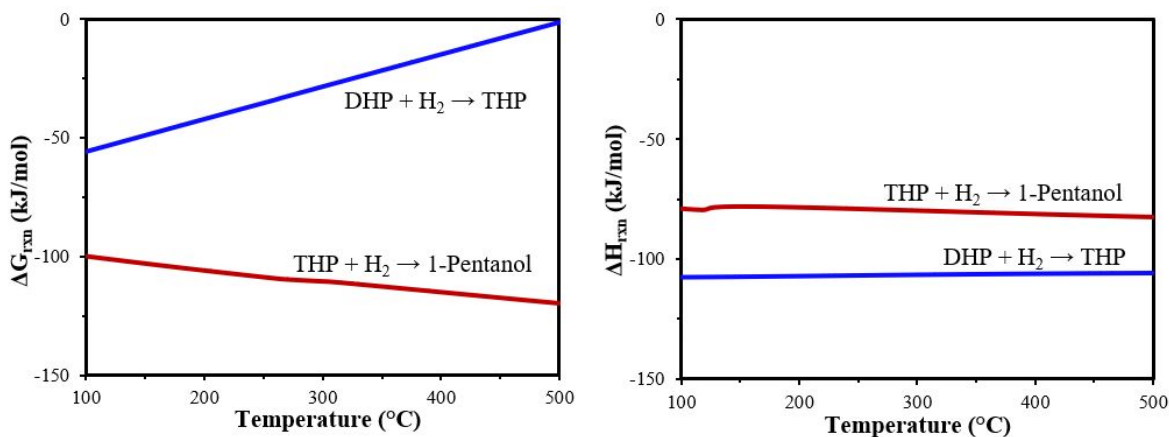


Figure 3. ΔG_{rxn} and ΔH_{rxn} for DHP hydrogenation to THP and over-hydrogenolysis of THP to 1-pentanol, as calculated from Aspen Plus. Simulation conditions: 200 psig, Peng-Robinson package.

The kinetics of THP formation was studied using a continuous flow reactor packed with Ni/SiO₂ catalysts. **Table 2** summarizes the changes in DHP conversion, THP production rate, 1-pentanol production rate, and THP selectivity with reaction temperatures (150, 180 and 200°C) and Ni loading of catalyst (10 and 30 wt%). DHP conversion and THP production rate at 150°C were negligible over SiO₂, indicating that any activity arises from the metallic Ni sites. Over 10-Ni/SiO₂, the DHP conversion increased five times from 3.5% at 150°C to 15.8% at 200°C. The corresponding THP production rate more than doubled from 104.1 mmol/h/g_{cat} at 150°C to 263.5 mmol/h/g_{cat} at 200°C. The 1-pentanol production rate also increased from 0.01 mmol/h/g_{cat} to 0.27 mmol/h/g_{cat} with rise in temperature, but the selectivity to THP remained >99.8%. This indicates that THP is the kinetically favored product, in contrast to the previous thermodynamic calculations. Over 30-Ni/SiO₂, DHP conversion increased from 80.2% at 150°C to 98.0% at 200°C, which is outside the kinetic regime. The highest rate of THP formation observed was 701 mmol/h/g_{cat} over 30-Ni/SiO₂ at 200°C. Despite operating at near complete conversion over 30-Ni/SiO₂, the 1-pentanol production rate remained <0.5 mmol/h and no other side products were observed by GC-MS. The conversion of DHP to THP was quantitative with >99.9% selectivity to THP over the range of temperatures and conversions studied, demonstrating that DHP hydrogenation over Ni/SiO₂ is a robust chemical pathway for production of high purity THP. The 10-Ni/SiO₂ catalyst was used for all kinetic studies that follow. The apparent activation energy, E_a, of THP production over 10-Ni/SiO₂ was 31.0 ± 0.1 kJ/mol, as seen from the Arrhenius plot in **Figure 4**. The E_a of 1-pentanol production was 91.1 kJ/mol, which was three times higher than the E_a of THP formation. The kinetic results of THP production further show that the unwanted over-hydrogenolysis of THP to 1-pentanol can be minimized by operating at lower reaction temperatures.

Table 2. DHP conversion, product STY and selectivity as a function of reaction temperature. Reaction conditions: 150 – 200°C, 200 psig, 0.1 g catalyst, 0.1 mL/min DHP, 100 mL/min H₂, 24 h.

Catalyst	Reaction temperature (°C)	DHP Conversion (%)	THP rate (mmol/h/g _{cat})	1-Pentanol rate (mmol/h/g _{cat})	THP selectivity (%)
SiO ₂	150	0.05	0	0	N/A
10-Ni/SiO ₂	150	3.5	104.1	0.01	99.98
10-Ni/SiO ₂	180	9.5	191.3	0.19	99.89
10-Ni/SiO ₂	200	15.8	263.5	0.27	99.89
30-Ni/SiO ₂	150	80.2	618.1	0.43	99.94
30-Ni/SiO ₂	180	89.3	689.4	0.48	99.93
30-Ni/SiO ₂	200	98.0	701.0	0.49	99.93

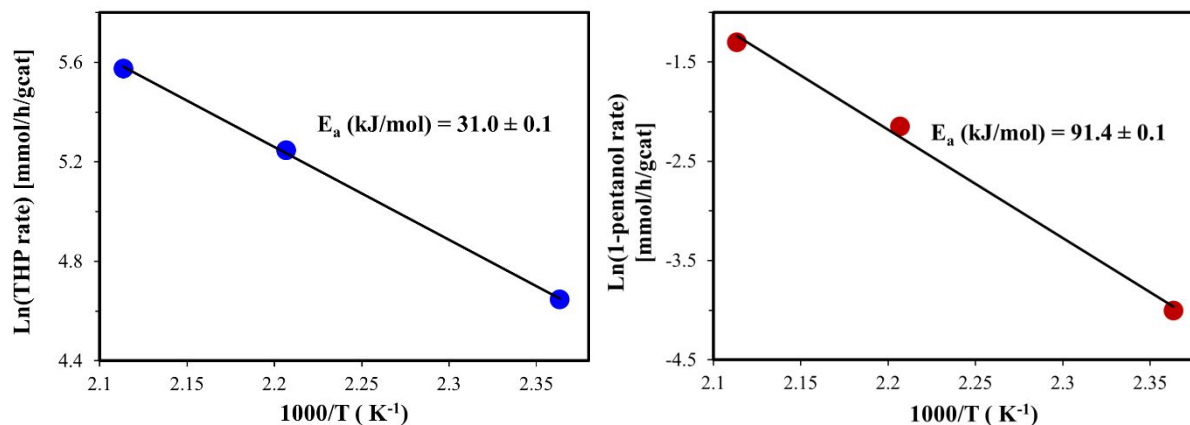


Figure 4. Arrhenius plots of THP rate and 1-pentanol rate during DHP hydrogenation to THP, with apparent activation energies listed. Reaction conditions: 150 – 200°C, 200 psig, 0.1 g 10-Ni/SiO₂, 0.1 mL/min DHP, 100 mL/min H₂, 24 h at each temperature, catalyst bed replaced when temperature varied.

3.2. Reaction orders of THP formation from partial pressure experiments

The reaction orders of DHP hydrogenation to THP with respect to the partial pressures of H₂, DHP, and THP are shown in the log-log plots of **Figure 5 (A-C)**. As the H₂ partial pressure was varied from 100 to 250 psig, the THP rate increased from 14.1 to 34.3 mmol/h/g_{cat}. The corresponding reaction order with respect to H₂ partial pressure was 2nd order, the highest observed reaction order. As the DHP partial pressure was increased from 5 to 20 psig, the rate of THP formation increased from 35.2 to 158.4 mmol/h, corresponding to a reaction order of 1 with respect to DHP partial pressure. When THP was co-fed at a partial pressure of 0.5 – 3.5 psig, the rate of THP formation decreased from 35.2 to 18.6 mmol/h. The corresponding reaction order of DHP hydrogenation was -0.3 with respect to THP partial pressure. The negative order dependence on THP partial pressure indicates the inhibitive effect of THP adsorption on catalyst activity.

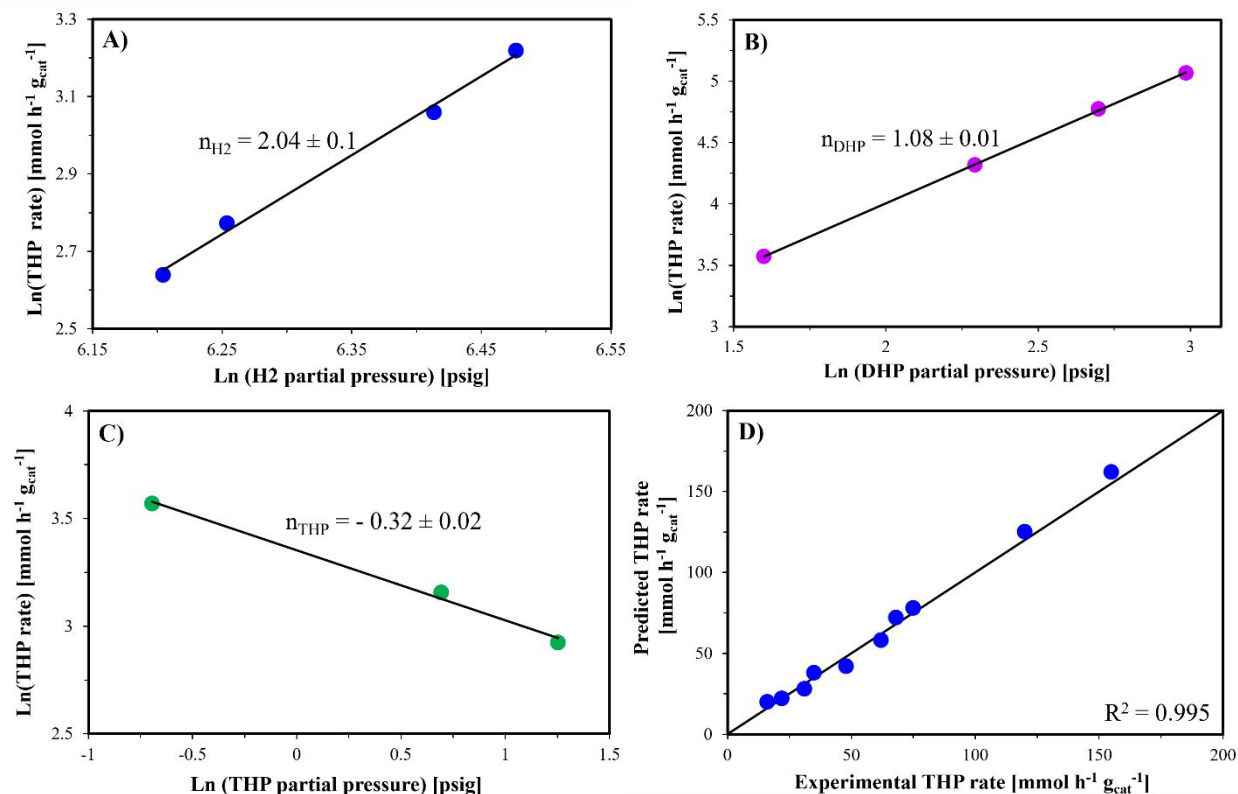


Figure 5. Log-log plots of THP production rate as a function of: (A) H₂ partial pressure; (B) DHP partial pressure; and (C) THP partial pressure. (D) Parity plot of predicted THP rate vs. experimental THP rate based on the kinetic model in Eq 7. Reaction conditions: 150°C, 200 psig, 0.1 g 10-Ni/SiO₂, 0.1 mL/min DHP, 100 mL/min H₂, 24 h at each condition.

3.3. Hougen-Watson kinetic model for DHP hydrogenation to THP

A kinetic model for DHP hydrogenation to THP was proposed using Hougen-Watson (HW) kinetics. The first step is the reversible adsorption of DHP onto the Ni/SiO₂ surface (Eq 3), and the second step is the dissociative adsorption of H₂ (Eq 4). This is followed by the surface reaction between adsorbed DHP and 2H to form THP (Eq 5). The last step is the desorption of the product THP (Eq 6). Vlachos *et al.* performed DFT calculations on the hydrogenation of dihydrofuran (DHF) to THF on Pd(111) catalysts and observed that the rate limiting step was the hydrogenation of DHF to trihydrofuran.³⁸ Similarly, experimental results for hydrogenation of DHP to THP in this work indicate the rate limiting step was likely the first hydrogenation of DHP to trihydropyran, the latter being an unobserved intermediate that rapidly hydrogenates to THP. The hydrogenation of DHP to trihydropyran and subsequent hydrogenation to THP have been considered as one step (Eq 5), which is assumed to be the rate limiting step with rate constant k_3 . All other steps (Eq 3, 4, and 6) are assumed to be in quasi-equilibrium with equilibrium rate constants K_1 , K_2 and K_4 . The HW kinetic model and the corresponding equation for the least squares error are displayed in Eq 7 and 8 respectively. The fitted rate constants are shown in Table 3 and the parity plot of predicted rate vs. experimental rate is shown in Figure 5-D. In previous work, a Hougen-Watson kinetic model for DHP production from THFA dehydration has been demonstrated in a similar manner.³⁹





$$r = \frac{k_3 K_1 P_{\text{DHP}} (K_2 P_{\text{H}_2})^2}{1 + K_1 P_{\text{DHP}} + \sqrt{K_2 P_{\text{H}_2}} + \frac{P_{\text{THP}}}{K_4}} \quad (7)$$

$$R^2 = 1 - \frac{\sum_{i=1}^n (r_{\text{experimental}} - r_{\text{model}})^2}{\sum_{i=1}^n r_{\text{experimental}}^2} \quad (8)$$

Table 3. Estimated kinetic parameters for DHP hydrogenation to THP over Ni/SiO₂ from the kinetic model shown in Eq 5.

Catalyst	K ₁	K ₂	k ₃ [$\frac{\text{mmol}}{\text{h} \cdot \text{g}_{\text{cat}} \cdot (\text{psig})^3}$]	1/K ₄
10-Ni/SiO ₂	0.0127 ± 0.005	0.0225 ± 0.002	6.13 ± 0.3	0.11 ± 0.8

3.4. Ni/SiO₂ catalyst characterization and deactivation

The 10-Ni/SiO₂ catalyst was studied for 100 h time on stream (TOS), then regenerated with *in situ* calcination and reduction, and studied for another 30 h TOS. **Figure 6** shows the variation in THP rate with TOS for the fresh catalyst and regenerated catalyst. For the first 24 h, the rate of THP formation was nearly constant at 205 mmol/h/g_{cat} at a DHP conversion of 12%. The THP rate then decreased monotonically and reached 75 mmol/h/g_{cat} at 95 h TOS. The first-order deactivation rate constant for the catalyst was determined from the slope of the ln(THP rate) vs. TOS graph to be 0.012 h⁻¹. **Figure 7** shows the TGA curves for the fresh and spent catalyst (before and after the 100 h TOS run) from 0 – 600 °C in O₂ flow. The fresh catalyst had minimal loss in sample weight (< 5 wt%) while the spent catalyst had a 50 wt% loss in mass of sample. TGA was also carried out in N₂ flow and both the fresh and spent catalyst had negligible loss in sample weight. **Table 4** lists the catalyst characterization results of the fresh and spent 10-Ni/SiO₂ catalyst using N₂ physisorption, CO chemisorption and ICP-OES. The BET surface area of the catalyst decreased from 264 to 221 m²/g, while the t-plot micropore area decreased slightly by 37 to 32.5 m²/g, indicating pore blocking of the catalyst. Ni dispersion also decreased from 18.6% to 12.5%, indicating that Ni sites are sintering during the reaction. The Ni content of the catalyst did not change much, demonstrating that Ni leaching is not occurring. After regeneration by *in situ* calcination in 1% O₂/Ar at 400 °C and reduction in H₂ at 500 °C, the THP rate recovered to 200 mmol/h/g_{cat} (**Figure 6**). After 30 h TOS with the regenerated catalyst, the THP rate had decreased to 125 mmol/h/g_{cat}. The deactivation rate constant for the regenerated catalyst is 1.8 times higher at 0.022 h⁻¹. The TOS study shows that the catalyst deactivates due to coke deposition, pore blocking, and Ni sintering, but can be regenerated to achieve THP formation rates nearly as high as those of the fresh catalyst.

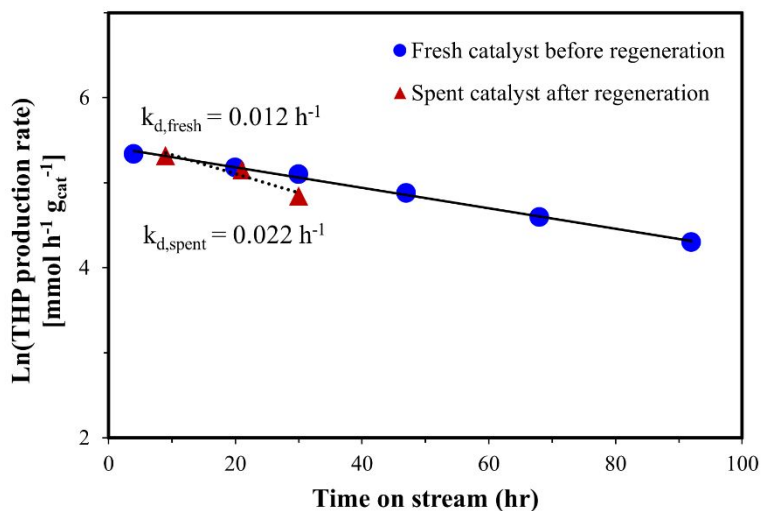


Figure 6. Variation in THP formation rate with reaction time on stream (TOS). Reaction conditions: 150°C, 200 psig, 0.1 g 10-Ni/SiO₂, 0.1 mL/min DHP, 100 mL/min H₂, 100 h. Catalyst regenerated *in situ* by calcination with 100 mL/min of 1% O₂/Ar at 400 °C followed by reduction with 100 mL/min H₂ at 500 °C, then reaction continued for another 30 h.

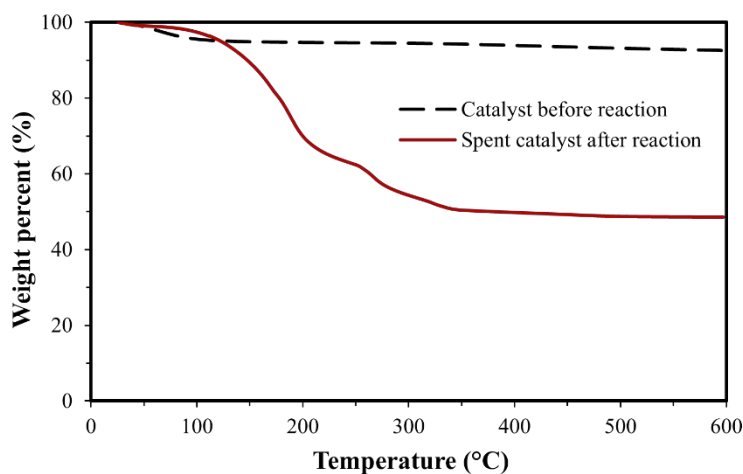


Figure 7. Thermogravimetric analysis (TGA) of fresh and spent 10-Ni/SiO₂, i.e., before and after 100 h TOS reaction. Experimental conditions: 20 – 600°C at 10°C/min in 50 mL/min O₂ flow.

Table 4. Characterization of fresh and spent 10-Ni/SiO₂ catalyst, i.e. before and after 100 h TOS reaction, using N₂ physisorption, CO chemisorption, and ICP-OES.

Property	Fresh 10-Ni/SiO ₂	Spent 10-Ni/SiO ₂
BET surface area (m ² /g)	264	221
t-Plot micropore area (m ² /g)	37	32.5
CO uptake (μmol/g _{cat})	85	76
Ni dispersion (Ni _{surface} /Ni _{bulk})	18.6	12.5
Ni amount (wt%) ^b	10.2	9.8

3.5. Inertness of THP to polymerization

A critical property of solvents is their chemical stability at harsh reaction conditions. THF has a ring strain energy (RSE) of 6.9 kcal/mol, but THP has a much lower RSE of 2.0 kcal/mol.⁴⁰⁻⁴² Five-membered cyclic ethers such as THF and MeTHF are susceptible to ring-opening polymerization (ROP) to form polyethers as undesired side products, especially in the presence of acidic catalysts or reagents.⁴³ We hypothesized that six-membered THP would be more resistant to ROP due to its negligible ring strain. To demonstrate the superior chemical stability of THP as a solvent, we compared the polymerization behavior of THF and THP under identical conditions. **Table 5** shows the differences in polymerization of THF and THP using different strongly acidic catalysts ($\text{BF}_3 \cdot \text{Et}_2\text{O}$ and $\text{CF}_3\text{SO}_3\text{H}$), monomer/catalyst molar ratios (100/10 and 100/1), and temperatures (0, 23, and 80°C). While THF polymerization was observed at all conditions tested, THP remained intact with 0% conversion at all conditions. With 10 mol% $\text{BF}_3 \cdot \text{Et}_2\text{O}$, 43% conversion of THF was achieved in 24 h to afford poly(THF), with $M_n = 37.3$ kg/mol and relatively narrow dispersity (D) = 1.17. A similar THF conversion of 45% was achieved with $\text{CF}_3\text{SO}_3\text{H}$, but the resulting poly(THF) has a much lower $M_n = 1.6$ kg mol⁻¹ and broader $D = 1.58$. When the catalyst loading was decreased to 1 mol%, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ achieved only 7% THF conversion after 24 h but $\text{CF}_3\text{SO}_3\text{H}$ achieved 77% THF conversion after 24 h, affording poly(THF) with $M_n = 24.8$ kg mol⁻¹ and $D = 1.13$. Poly(THF) formation and lack of poly(THP) formation was verified using ¹H NMR (**Figure S2**). Poly(THF) was observed to be a semi-crystalline material with a melting-transition temperature (T_m) of 30°C, as determined by DSC (**Figure S3**).

Table 5. Polymerization of THF and THP with varying catalysts, monomer to catalyst ratios, and temperatures. ^a

Catalyst	[Monomer]/[Cat]	T (°C)	Conversion (%) ^b	
			THF	THP
$\text{BF}_3 \cdot \text{Et}_2\text{O}$	100/10	0	43	0
$\text{CF}_3\text{SO}_3\text{H}$	100/10	0	45	0
$\text{BF}_3 \cdot \text{Et}_2\text{O}$	100/1	0	7	0
$\text{CF}_3\text{SO}_3\text{H}$	100/1	0	77	0
$\text{CF}_3\text{SO}_3\text{H}$	100/10	23	17	0
$\text{Yb}(\text{OTf})_3$	100/1	80	--	0

^aConditions: Polymerization was conducted in bulk monomer for 1 day with THF, and for 3 days with THP. ^bMonomer conversion was determined by ¹H NMR spectra.

The inability to polymerize THP under homopolymerization conditions demonstrated the inert nature of THP to ring opening. However, in some cases, a low ring strain monomer can be incorporated into polymer chains by copolymerization with a high ring strain comonomer.^{44, 45} Therefore, the copolymerization of THP (low ring strain) and THF (high ring strain) was further explored. The results are shown in **Table 6**, which indicated that only THF was selectively polymerized (**Figure S5**), while THP polymerization was still not observed. Specifically, 30% THF was converted to poly(THF) at 0°C with $[\text{THF}]/[\text{THP}]/[\text{BF}_3 \cdot \text{Et}_2\text{O}] = 100/100/10$ after 3 days. The corresponding M_n and D of the poly(THF) were 34.5 kg/mol and 1.16, respectively. Similarly, THF conversion was 21% and 13% at 0°C and -30°C, respectively, with $[\text{THF}]/[\text{THP}]/[\text{CF}_3\text{SO}_3\text{H}] = 100/100/10$ after 3 days, but THP conversion was still 0%. The separated poly(THF) was confirmed by ¹H NMR (**Figure S2**) and characterized using DSC and TGA (**Figure S3**). These copolymerization results further confirmed the inertness of THP towards

polymerization. Overall, the above extensive polymerization and copolymerization studies under various conditions demonstrated that THP is highly stable under conditions that THF is readily polymerized. This non-polymerizability, coupled with its biorenewability and higher boiling point, confirms our hypothesis of THP being a more stable solvent than THF or MeTHF.

Table 6. Copolymerization of THF and THP with varying catalysts and temperatures. ^a

Catalyst	[THF]/[THP]/[Cat]	T (°C)	Conversion (%) ^b	
			THF	THP
BF ₃ ·Et ₂ O	100/100/10	0	30	0
CF ₃ SO ₃ H	100/100/10	0	21	0
CF ₃ SO ₃ H	100/100/10	-30	13	0

^aConditions: Polymerization was conducted in bulk monomer for 3 days.

^bMonomer conversion was determined by ¹H NMR spectra.

3.6. Technoeconomic analysis of THP production

In previous work, we have shown that 1,5-PDO can be manufactured at a minimum selling price (MSP) of \$1,973/ton when the furfural feedstock costs \$1,000/ton and the 1,5-PDO production volume is 37,000 ton/yr.⁴⁶ An extensive technoeconomic analysis of furfural production from lignocellulosic biomass fractionation has also been carried out in the past.⁴⁷ High purity DHP is produced as an intermediate during 1,5-PDO production at an MSP of \$1,478/ton and production volume of 16,300 ton/yr. Using these values, the minimum selling price (MSP) of THP produced from hydrogenation of DHP with 30-Ni/SiO₂ has been assessed. The process flow diagram is shown in **Figure 1**, and **Table S1** lists the corresponding temperature, pressure, and mass balance of each stream. The reaction data for the DHP production from THP was taken from the high conversion data (last entry in **Table 2**). **Tables S2-4** summarize the economic parameters and assumptions for a commercial THP production unit, including plant operating hours, capital costs, variable operating costs, and fixed operating costs. Based on this analysis, THP can be produced at an MSP of \$1,812/ton and production volume of 16,185 ton/yr when the DHP feedstock price is \$1,478/ton and feed rate is 16,300 ton/yr. The corresponding purity of THP in the product stream is 97.8%. **Figure 8** shows the price of DHP feedstock is the main cost driver of the THP production process, constituting 81.5% of the total required cost.

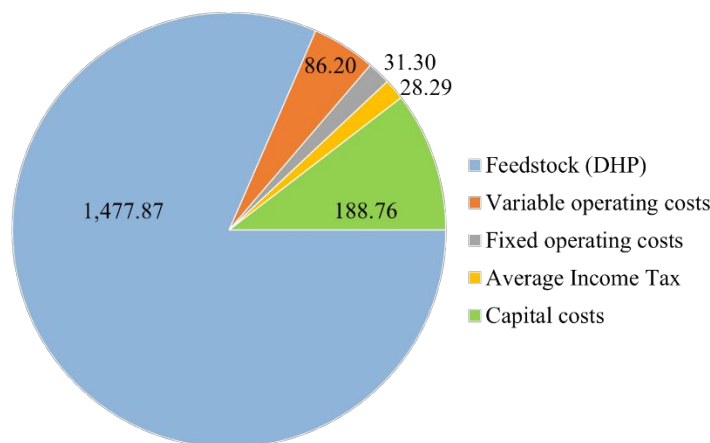


Figure 8. Minimum selling price (\$/ton) breakdown for production of THP from hydrogenation of DHP over 30-Ni/SiO₂ in a packed bed reactor at a DHP feed rate of 16,300 ton/yr.

We also conducted a sensitivity analysis for the THP production process as a function of DHP feedstock price (\$1,000–3,500/ton) and plant production volume (3,000–18,000 ton/yr). With new technologies enabling cheaper production of furfural, the price of DHP is expected to drop below \$1,478/ton. The results in **Figure 9** demonstrate that the MSP of THP is \$1,200–1,400/ton when the DHP feedstock costs \$1,000/ton, enabling THP manufacturing to be competitive with the commercial market price of petroleum-derived THF (\$900–1,400/ton). When the DHP feedstock price increases from \$1,000/ton to \$3,500/ton, the MSP of THP also rises from \$1,200/ton to >\$3,000/ton. On the other hand, the MSP of THP does not change much with the THP production volume for a given DHP feedstock price, decreasing by only \$300–400/ton when the THP production volume expands from 3,000 ton/yr to 80,000 ton/yr. This demonstrates that THP is economically competitive with THF manufacturing when the price of DHP is <\$1,200/ton over a wide range of production volumes.

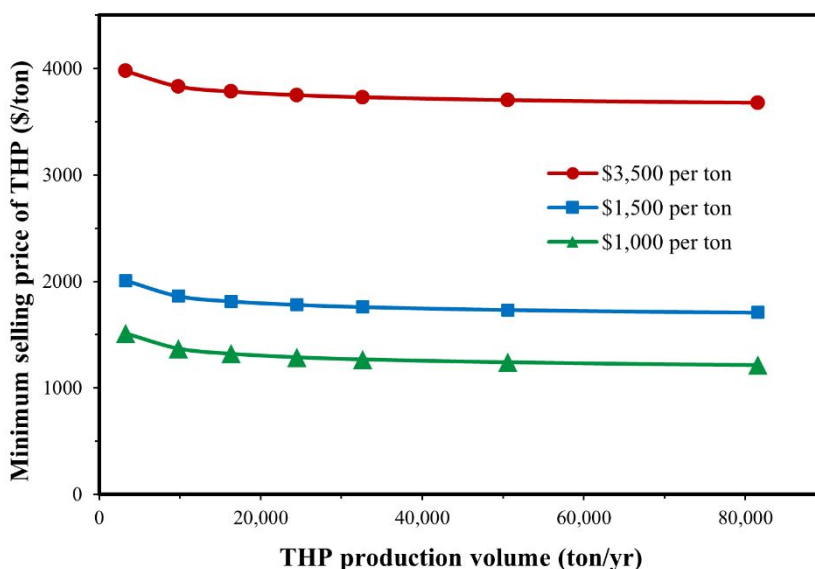


Figure 9. Minimum selling price of THP as a function of THP production volume for three different DHP feedstock prices.

3.7. Computational modeling of solvent properties of THP

A major challenge with commercialization of new biobased solvents like THP is the identification of potential applications. Using COSMO-RS to model the σ -profiles of THP and other industrially used solvents, we can determine which solvents are most similar to THP and then attempt to replace them with THP.³⁵ This approach measures similarity based on the chemical properties of solvents as opposed to their functional groups alone. We calculated the Euclidean distances between the THP and 1,008 other solvents and defined a solvent's similarity score to be its distance to THP normalized by the average distance of all solvents to THP. The lower the score, the higher the similarity. **Figure 10** compares the σ -profiles of THP with THF and dichloromethane (DCM). THF and THP have highly similar σ -profiles, leading to a small Euclidean distance between these profiles and a similarity score of 0.25 for THF. On the other hand, DCM has a very different σ -profile with a high similarity score of 78.8, identifying it as a dissimilar solvent of THP.

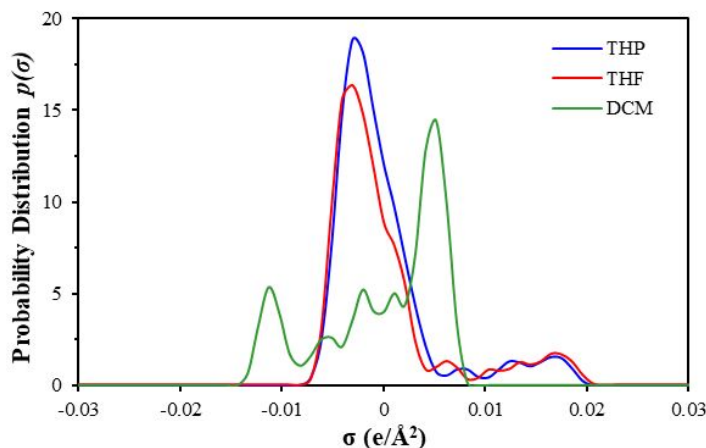


Figure 10. σ -profiles of THP, THF, and dichloromethane (DCM) as predicted from COSMO-RS. The similarity rankings of THF and DCM corresponding to THP are 0.4% and 78.8%, respectively.

Table 7 lists the 10 most similar solvents to THP and their corresponding similarity scores, with 2-methyltetrahydrofuran (MeTHF), diethyl ether, tetrahydrothiopyran, and THF in the top 4. We have also added 2,5-dimethyltetrahydrofuran⁴⁸ and 2,2,5,5-tetramethyltetrahydrofuran¹⁰ to the list as they are homologous compounds of THF and can be biomass-derived. However, their chemical properties are not as similar to THP, as evidenced by their higher similarity scores. Likewise, 1,4-dioxane ($C_4H_8O_2$) may appear to have a similar structure to THP, but it has a similarity score of 22.78, imparting it with very different properties. Our results also demonstrate why quantitative tools like COSMO-RS are required to assess solvent similarity, since general chemical intuition based on structures, molecular sizes or elemental compositions can be incorrect. Computational modeling also enables us to predict the dissolution of various polymers in a given solvent, which is critical for paint formulations, drug delivery, membrane science, and plastic recycling. **Table 7** lists the computationally predicted solubilities of 8 common polymers in THP and the solvents mentioned above. The polymers include: ethylene vinyl alcohol (EVOH), low density polyethylene (LDPE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), and two polyamides (PA): nylon-6 and nylon-66. Note that the temperature at which the solubility is predicted is determined by the boiling point of the solvent. Based on the predicted solubilities, THP could serve as a good solvent (defined as solubility in excess of 3g/100g solution) for LDPE, PP, PS and PVC, and as a poor solvent for EVOH, PET, nylon 6 and nylon 66. THP could serve as an alternative to other solvents, especially MeTHF, THF, dimethyl THF, and cyclopentyl methyl ether, which have similar predicted solubilities for almost all polymers listed. These values could be used as input parameters in process modeling and techno-economic analyses to study the costs and benefits of using THP as an alternative solvent.

Table 7. Solubility predictions of 8 polymers in THP, the top 10 solvents most similar to THP, and two homologous compounds of THF. The similarity scores and boiling points of the solvents have also been listed.

Solvent	Similarity Score ^a	T ^b (°C)	Polymer solubility predictions (g polymer / 100g solution)							
			EVOH	LDPE	PET	PP	PS	PVC	Nylon-6	Nylon-66
THP	0.00	87.0	1.1	7.3	0.8	20.9	33.7	17.9	0.7	0.3

2-Methyl tetrahydrofuran	0.14	77.0	0.5	3.9	0.4	15.1	28.1	14.6	0.4	0.2
Diethyl Ether	0.21	33.5	0.0	0.2	0.0	4.4	10.8	4.0	0.0	0.0
Tetrahydrothiopyran	0.24	120.0	1.3	39.8	5.4	40.3	46.7	26.0	2.5	0.8
Tetrahydrofuran	0.25	64.0	0.9	1.7	0.8	10.1	31.3	19.1	0.4	0.2
Pyrrolidine	0.27	85.5	19.2	5.7	2.8	15.0	32.2	22.4	2.1	1.2
Dimethyl Ethanolamine	0.27	120.0	17.9	38.5	7.6	37.7	50.3	34.8	6.0	2.9
Methyl Ethyl Ether	0.28	6.4	0.0	0.0	0.0	1.3	9.4	4.2	0.0	0.0
1-Butanol	0.28	116.7	10.1	18.4	0.4	12.4	9.2	10.2	5.4	2.4
Cycloheptanone	0.28	120.0	8.3	30.1	3.9	27.2	41.7	27.9	3.2	1.4
Cyclopentyl Methyl Ether	0.29	105.0	0.9	19.6	0.6	31.3	33.6	14.6	0.8	0.3
2,5-Dimethyl tetrahydrofuran ^c	0.33	89.0	0.6	7.7	0.3	20.0	26.1	12.3	0.4	0.1
2,2,5,5-Tetramethyl tetrahydrofuran ^c	0.67	111.0	1.6	22.3	0.4	29.1	26.2	12.1	0.7	0.2

^a Similarity score calculated from normalized Euclidean distance between solvent and THP from COSMO-RS. ^b Temperature of simulation is $\sim 1^\circ\text{C}$ lower than boiling point of solvent. ^c Homologous compounds of THF.

3.8. Applications of THP for upcycling of mixed plastics

We recently developed a solvent-targeted recovery and precipitation (STRAP) process to recycle components from multilayer plastic films.⁴⁹ The STRAP process selectively dissolves constituent polymers through a series of solvent washes, each designed to dissolve only a single polymer component. The solubility data in **Table 7** indicate that THP has potential application as a selective solvent for STRAP processes of many plastic materials. For example, it could be used to selectively dissolve PP from PP/EVOH/PA mixture, which is the composition of an Amcor packaging film⁵⁰; dissolve PS from PS/PET, an UltiDent sealing film⁵¹; or PVC from PVC/EVOH, a Desu plastic sheet.⁵² These proposed applications are based on commercial products and demonstrate the applicability of THP to possible recycling processes. THP could also be used to replace hazardous solvents in existing STRAP processes. For example, we recently reported a STRAP process in which toluene is used as a selective solvent to dissolve LDPE from a LDPE/EVOH/PET mixture.⁵³ The predicted solubilities in **Table 7** indicate that THP should also dissolve LDPE but not EVOH or PET, and thus could be an alternative selective solvent to toluene. We performed MD simulations to further support the prediction that THP is a good solvent for an LDPE oligomer ($\text{C}_{40}\text{H}_{82}$), as shown in **Figure 11**. We also calculated the radius of gyration (R_g) and the solvent accessible surface area (SASA) of the oligomer molecule from the MD trajectories to evaluate the tendency of the oligomer to collapse into a folded conformation (indicative of poor solvent behavior) or extend into an elongated conformation (indicative of good solvent behavior).^{54, 55} **Figure S4** shows the oligomer's R_g -SASA distributions in THP and water. The oligomer molecule in water mostly obtains small values of R_g and SASA, indicating a preference for folded conformations. In THP, however, the oligomer tends to have large R_g and SASA, indicating elongated conformations. Since water is a poor solvent for LDPE, the different behavior of the oligomer chain in THP indicates that it is a good solvent in agreement with COSMO-RS predictions.

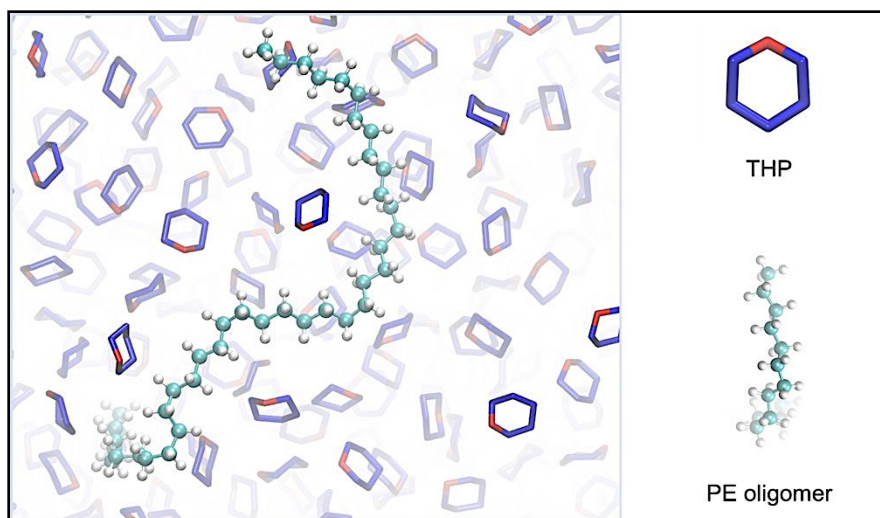


Figure 11. MD simulation of an LDPE oligomer in solution of THP.

CONCLUSIONS

Tetrahydropyran (THP) is a green solvent that does not form peroxides, offers excellent solvent properties, and is an economically competitive replacement for tetrahydrofuran (THF). In this work, we have demonstrated a new pathway to produce biobased THP from hydrogenation of furfural-derived 3,4-dihydropyran (DHP) over Ni/SiO₂ catalysts in a packed bed reactor. The selectivity to THP was >99.8% at a carbon balance of ~100% over a wide range of DHP conversions and temperatures with 1-pentanol as the only detected side product. Kinetic experiments with 10-Ni/SiO₂ show that the apparent activation energy of THP and 1-pentanol formation is 31 kJ/mol and 91 kJ/mol, respectively, indicating that THP is the kinetically favored product. THP formation has been observed to be 2nd order with respect to H₂ partial pressure and 1st order with respect to DHP partial pressure. Addition of a THP co-feed is inhibitive to THP formation, leading to a -0.3 reaction order with respect to THP partial pressure. A rate law expression for THP formation has been determined using Hougen-Watson kinetics. A time on stream study was performed to quantify a first-order deactivation rate constant of 0.012 h⁻¹ for 10-Ni/SiO₂ over 100 h. TGA analysis on the fresh and spent catalyst in O₂ flow showed a 50 wt% loss in sample weight of the spent catalyst, indicating that coke formation is a major factor in catalyst deactivation. THP was shown to have beneficial solvent properties including resistance to ring opening polymerization over a variety of catalysts and conditions that caused THF to polymerize. A techno-economic analysis determined that the MSP of THP can be competitive with the THF market price (\$900 - 1,400/ton) at a DHP feedstock cost of \$1,000/ton and a DHP feed rate of 16,300 ton/yr. Lastly, COSMO-RS and MD simulations were used to model the solvent properties of THP, compare it to 1007 other solvents, and predict the solubilities of 8 common plastics. THP can be used to replace THF, MeTHF, dimethyl THF, and cyclopentyl methyl ether as the solvent to dissolve PE, PP, PS and PVC, and can be used for upcycling multilayer waste plastics through selective dissolution.

AUTHOR CONTRIBUTIONS

Investigation, Formal Analysis, and Writing (Original Draft): RGD, MSK, PZ, ZL, CX. Writing (Reviewing and Editing), Supervision, and Funding Acquisition: KJB, DJM, EXC, RCV and GWH. The final manuscript has been read and approved by all authors.

CONFLICT OF INTEREST

The authors declare the following competing financial interest(s): GWH, KJB, and DJM have a financial interest in Pyran which is commercializing the technology to produce biomass-based C₅ chemicals from furfural.

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