

# Techno-economic Analysis and Life Cycle Assessment of Biomass-Derived Polyhydroxyurethane and Nonisocyanate Polythiourethane Production and Reprocessing

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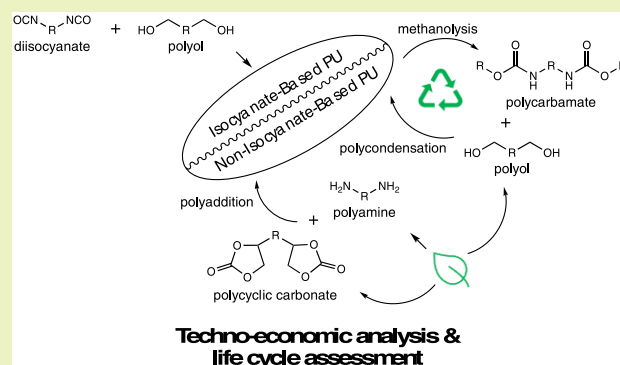
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**ABSTRACT:** Nonisocyanate polyurethanes (NIPUs) show promise as more sustainable alternatives to conventional isocyanate-based polyurethanes (PUs). In this study, polyhydroxyurethane (PHU) and nonisocyanate polythiourethane (NIPTU) production and reprocessing models inform the results of a techno-economic analysis and a life cycle assessment. The profitability of selling PHU and NIPTU is rationalized by identifying significant production costs, indicating that raw materials drive the costs of PHU and NIPTU production and reprocessing. After stepping along a path of process improvements, PHU and NIPTU can achieve minimum selling prices (MSPs) of 3.15 and 4.39 USD kg<sup>-1</sup>, respectively. Depolymerization yields need to be optimized, and polycondensation reactions need to be investigated for the reprocessing of NIPUs into secondary (2°) NIPUs. Of the NIPUs examined here, PHU has a low depolymerization yield and NIPTU has a high depolymerization yield. Fossil energy use, greenhouse gas (GHG) emissions, and water consumption are reported for the biobased production of PHU, NIPTU, 2° PHU, and 2° NIPTU and compared with baseline values for fossil-based PU production. There are options for reducing environmental impacts, which could make these pathways more sustainable. If barriers to implementation are overcome, 2° NIPUs can be manufactured at lower cost and environmental impacts than those of virgin NIPUs.

**KEYWORDS:** biopolymers, nonisocyanate polyurethanes, depolymerization, life cycle assessment, techno-economic analysis



## INTRODUCTION

The increasingly prevalent dangers of climate change and nonrenewable resource depletion are joined by the looming threat of plastic waste accumulation.<sup>1–5</sup> About 80% of global energy demand is from nonrenewable feedstocks, while 7–8% of global fossil fuels are used to provide energy and materials in the manufacturing of plastics.<sup>6–8</sup> Globally, annual plastics production continues to increase dramatically from 2 million tonnes in 1950 to around 438 million tonnes in 2017 with up to 99% of plastics made from fossil fuel-derived polymers.<sup>8</sup> Only around 30% of plastics produced since 1950 remain in use today. By 2050, over 1100 million tonnes of plastic will be produced annually if current trends continue.<sup>9,10</sup> To mitigate these issues, scientists and engineers continue to develop technologies to recycle plastics and use alternative resources in plastics production.<sup>11,12</sup>

Polyurethanes (PUs) are polymeric materials with versatile properties ranging in application from soft coatings and flexible foams to harder construction materials and rigid foams.<sup>13,14</sup> However, the production of PU involves monomers such as polyols and diisocyanates (DI), which deplete nonrenewable

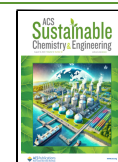
fossil fuel resources. In 2016, 2.9 million tonnes of polyurethane (PU) were produced in the United States at the expense of 1.1 million tonnes of crude oil and 1.1 million tonnes of natural gas.<sup>15</sup> With a 5.5% end-of-life recycling rate, PU is recycled at less than the average recycling rate of U.S. plastics in 2015.<sup>15,16</sup> The PU recycling rate is low for multiple reasons including the challenge and cost associated with collecting it and extracting it from products such as car seats and shoes along with achieving cost parity with virgin PU. Another challenge with today's technology for manufacturing PU is the use of isocyanates, which pose a human health hazard.<sup>17,18</sup> Accordingly, the U.S. Environmental Protection Agency (EPA) has considered a possible ban on consumer products containing uncured methylene diphenyl diisocyanate

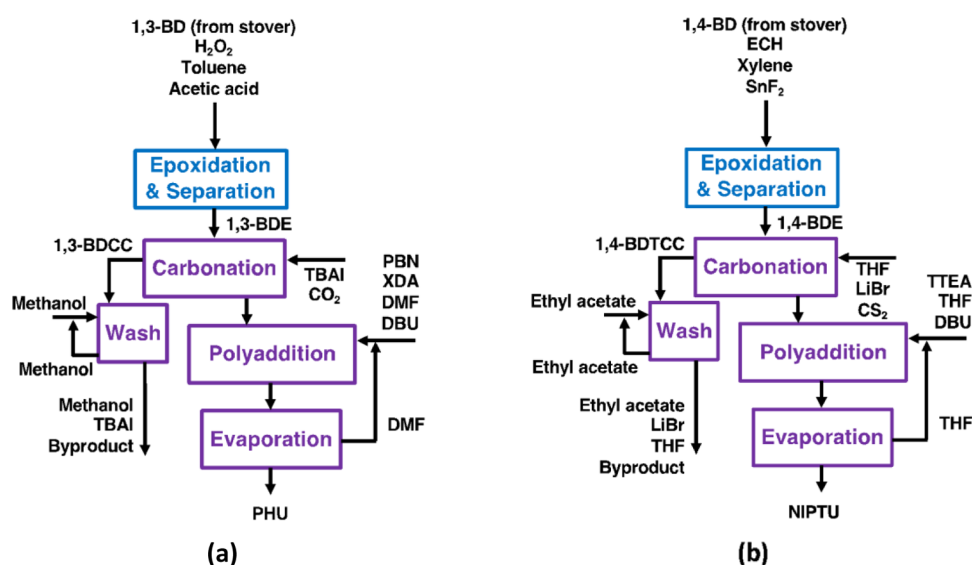
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**Figure 1.** Production process block flows: production processes for (a) PHU and (b) NIPTU. Blue blocks represent processes supported by data collected from the literature and patents. Purple blocks represent processes supported by data collected experimentally.

(MDI) and toluene diisocyanate (TDI).<sup>19</sup> To enhance PU sustainability, it is necessary (1) to advance technologies for producing this material from biobased feedstocks, (2) to expand methods for recycling PU monomers, and (3) to investigate synthetic routes that avoid the use of isocyanates.

Progress exists on each of these three fronts. Polyhydroxyurethane (PHU) and nonisocyanate polythiourethane (NIPTU) are two types of nonisocyanate polyurethane (NIPU) materials that can be synthesized from biomass and reprocessed into secondary (2°) NIPU materials.<sup>20–27</sup> In addition, NIPU materials eliminate the need for toxic and potentially harmful diisocyanates.<sup>23,28,29</sup> For instance, catalytic coupling of epoxide residues with either carbon dioxide or carbon disulfide affords 5-membered cyclic carbonates or 5-membered cyclic dithiocarbonates, respectively. Subsequent ring-opening polyaddition with an amine affords PHU from the cyclic carbonates or NIPTU from the cyclic dithiocarbonates. Chemicals that can be derived from corn stover, including 1,3-butadiene or 1,4-butanediol,<sup>29,30</sup> are readily epoxidized through a reaction with hydrogen peroxide or an  $S_N2$  substitution with epichlorohydrin. Cyclic carbonate and dithiocarbonate moieties have also previously been derived from epoxidized plant seed oils for NIPU biosynthesis.<sup>31,32</sup>

It is important to understand how shifts from manufacturing conventional PUs to manufacturing NIPUs may influence their cost and sustainability. We carried out techno-economic analysis (TEA) and life cycle assessment (LCA) of four new NIPU production pathways: (1) a biomass-based PHU, (2) a 2° PHU via depolymerization, (3) a biomass-based NIPTU, and (4) a 2° NIPTU via depolymerization. Using TEA, we compare the minimum selling prices (MSPs) of biobased PHU, NIPTU, and 2° NIPUs with conventional PU market prices. We use LCA to compare greenhouse gas (GHG) emissions, fossil energy use, and water consumption of PHU, NIPTU, and 2° NIPUs to the same metrics for conventional PU. To date, PHU and NIPTU production routes have not been assessed for their cost competitiveness or environmental advantages. NIPU recovery has also not been evaluated from these perspectives. Accordingly, this research represents an

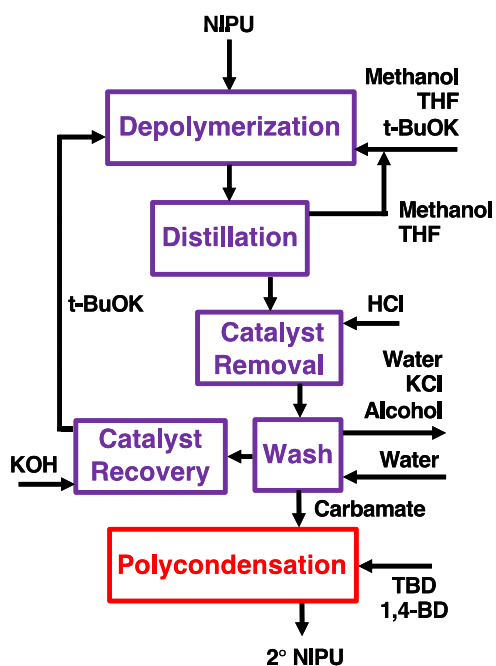
important step in evaluating the role of biobased, recyclable NIPUs in the polymers market.

## METHODS

**Process Modeling.** Processes for PHU and NIPTU production are depicted in Figure 1a,b, respectively. We modeled these processes in Aspen Plus V12 leveraging published models and experimental data.<sup>33–35</sup> Box colors in Figure 1 depict the origin of the data. Blue boxes denote data derived from literature and patents.<sup>34,35</sup> Purple boxes indicate data arose from experiments.<sup>22,25–27,31</sup> Detailed process flow diagrams and stream summary tables are available in Figures S.1, S.2, Tables S.1, and S.2 in the Supporting Information (SI). Biosynthesis of PHU begins with the epoxidation of 1,3-butadiene (1,3-BD) with 2 equiv of hydrogen peroxide to form 1,3-butadiene diepoxide (1,3-BDE). Toluene and acetic acid are used as solvents and additives, respectively, for the epoxidation and separation steps. In the subsequent carbonation step, 1,3-BDE reacts with 2 equiv of carbon dioxide using a tetrabutylammonium iodide (TBAI) catalyst affording 1,3-butadiene dicyclic carbonate (1,3-BDCC). Prior to polymerization, 1,3-BDCC is washed with residual catalyst. Polymerization of 1,3-BDCC with poly(butadiene-co-acrylonitrile) (PBN) and a *p*-xylylenediamine (XDA) chain extender is carried out using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a catalyst in dimethylformamide (DMF) solvent. PHU leaves the process after DMF is evaporated and recycled to the polymerization step. Figure S.4(a) contains a reaction flow diagram for the proposed PHU biosynthesis.

The biosynthesis of NIPTU begins with the substitution of the hydroxyl groups of 1,4-butanediol (1,4-BD) with two epichlorohydrin (ECH) molecules, affording 1,4-butanediol diglycidyl ether (1,4-BDE). Xylene and tin difluoride are used as a solvent and an additive, respectively, for this step. Next, 1,4-BDE couples with 2 equiv of carbon disulfide in the carbonation step. This step uses a lithium bromide catalyst in a tetrahydrofuran (THF) solvent and affords 1,4-butanediol dithiocyclic carbonate (1,4-BDTCC). Prior to polymerization, 1,4-BDTCC is washed with residual lithium bromide using ethyl acetate. Polymerization of 1,4-BDTCC with polyetheramine (TTEA) is carried out using DBU as a catalyst in THF solvent. NIPTU leaves the process after THF is evaporated and recycled back to the polymerization step. Figure S.4(b) is a reaction flow diagram for NIPTU biosynthesis. The assumed market values of individual feeds for PHU and NIPTU synthesis can be found in the SI (Tables S.4 and S.5).

A flow diagram for reprocessing used NIPU materials is depicted in Figure 2. Purple boxes indicate process modeling relied on



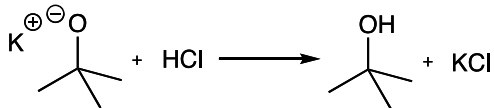
**Figure 2.** Monomer/NIPU recovery block flow: reprocessing of used PHU or NIPTU into 2° NIPUs. All NIPU recovery process flows are supported by data collected empirically. Blue blocks represent processes supported by data collected from literature and patents. Purple blocks represent processes supported by data collected experimentally.

experimental data.<sup>22,25–27,31</sup> The downstream polycondensation step is colored red because the polycondensation reactions modeled here are yet to be tested experimentally, and they have not been fully investigated in the literature. Instead, the polycondensation steps are modeled stoichiometrically in Aspen Plus V12 based on the general temperature profiles of carbamate monomers polymerizing with diols using a TBD catalyst.<sup>36–38</sup> This step was necessary to enable consistent comparison with baseline polymers and, although imperfect, allows for a general understanding of the relative cost and environmental performance. A detailed process flow diagram and a stream summary table for NIPU reprocessing are located in Figure S.3 and Table S.3 of the SI, respectively. The methanolysis process for carbamate monomer recovery is identical for PHU and NIPTU. Used NIPU is chemically depolymerized using a potassium *tert*-butoxide catalyst (*t*-BuOK), THF solvent, and methanol. After methanol and THF are distilled and recycled back to the depolymerization process, *t*-BuOK is neutralized using hydrochloric acid producing *tert*-butanol (*t*-BuOH) and potassium chloride salt (Scheme 1).

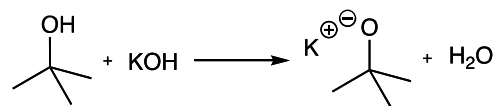
Next, a water-based wash step recovered carbamate, alcohol, and salt. Reacting *t*-BuOH with potassium hydroxide recovers the *t*-BuOK catalyst and 1 equiv of water (Scheme 2).

Recovered catalyst is recycled back to the depolymerization step. A reaction flow diagram of 2° NIPU recovery from virgin PHU and NIPTU can be found in the SI (Figure S.5(a,b), respectively).

### Scheme 1. Catalyst Removal: Potassium *tert*-Butoxide Is Neutralized with Hydrochloric Acid to Afford *tert*-Butanol and Potassium Chloride



### Scheme 2. Catalyst Recovery: *tert*-Butanol Is Reacted with Potassium Hydroxide to Afford Potassium *tert*-Butoxide and Water



Recovered carbamate monomer can be reprocessed into 2° NIPU via polycondensation with 1,4-BD.<sup>36–38</sup> Polycondensation is assumed to be facilitated by a 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) catalyst in a neat reaction.<sup>36</sup> Table S.6 documents the market values we adopted for inputs to NIPU reprocessing. Byproducts (e.g., methanol) were all present in less than 10% mass in Figures 1 and 2. Accordingly, we assigned all environmental burdens to the main products (PHU, NIPTU, and secondary NIPUs) in Figures 1 and 2. LCA results for these main products therefore represent a higher bound because we did not undertake coproduct allocation given the small mass shares of minor byproducts.

**Financial Assumptions.** Financial assumptions for the TEA are listed in Table 1. We adopted a 30 year plant life. Plant sizes vary; we

**Table 1.** List of Assumptions: Financial Assumptions Used in the TEA<sup>a,b</sup>

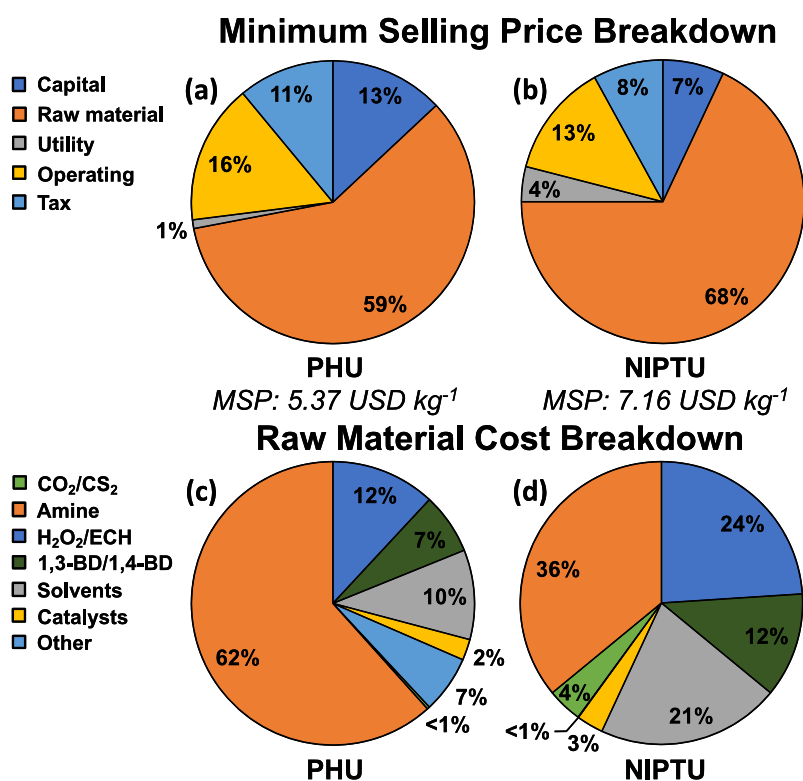
description	value	unit
plant life	30	yr
plant capacity	2540	tonne yr <sup>-1</sup>
cost year USD	2022	
internal rate of return	20	%
EPC duration	24	wk
EPC and startup duration	50	wk
working capital	5	% of CI
tax rate	40	%
salvage value	20	% of cost
depreciation method	straight line	
project capital escalation	5	% yr <sup>-1</sup>
products escalation	5	% yr <sup>-1</sup>
raw material escalation	3.5	% yr <sup>-1</sup>
labor escalation	3	% yr <sup>-1</sup>
utilities escalation	3	% yr <sup>-1</sup>

<sup>a</sup>Aspen Process Economic Analyzer, default values for the U.S.<sup>33</sup>

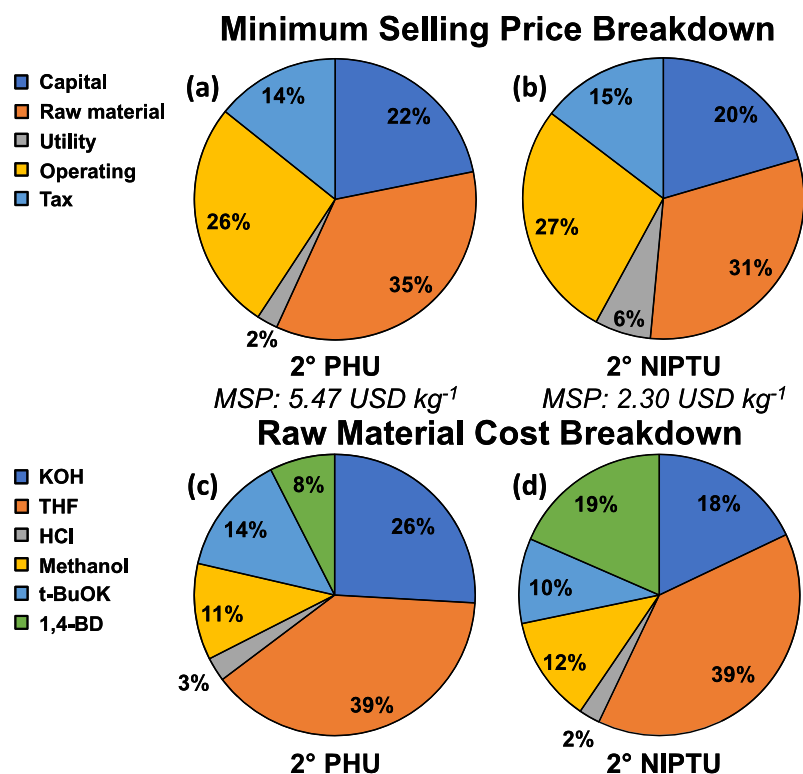
<sup>b</sup>Dong et al.<sup>34</sup>

chose a base case capacity of 2540 tonne yr<sup>-1</sup>. Engineering, procurement, and construction (EPC) last 24 weeks. EPC and startup phases together last 50 weeks. Working capital assets totaling 5% of the fixed capital investment (CI) are kept at the plants. A straight-line method for calculating depreciation is implemented with salvage values for equipment set at 20% of its original cost. We adopted a 20% internal rate of return (IRR). Other assumed values including cost year of the USD, tax rate, and escalation rates can be found in Table 1.

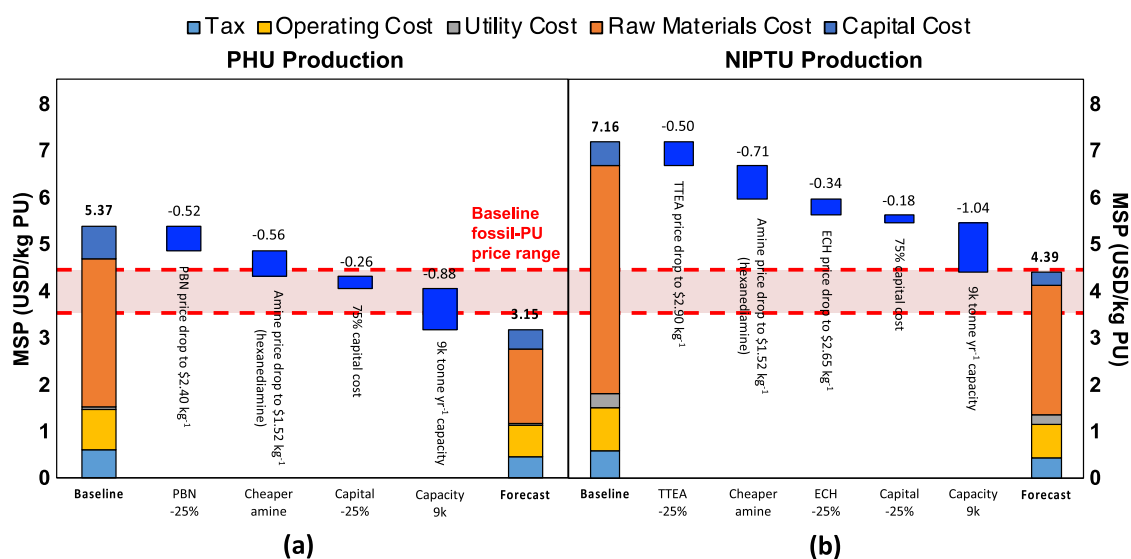
**Life Cycle Inventory and Impact Categories.** Systems are compared based on three impact categories: fossil energy use, GHG emissions, and water consumption. We selected one tonne of NIPU or PU material as our functional unit. We carried out LCA using life cycle inventory data generated from Aspen Plus simulations and the Greenhouse gases, Regulated Emissions, and Energy use in Technologies (GREET) model (2021 release).<sup>39</sup> Life cycle inventory data for PHU, NIPTU, and 2° NIPU are shown in Tables S.7–S.9 of the SI. Life cycle inventory data for ECH, *t*-BuOK, XDA, TTEA, and SnCl<sub>2</sub> (Tables S.10–S.14, respectively) were not available through GREET and were obtained from literature, openLCA software, and patents.<sup>40–43</sup> Data for the epoxidation and separation steps of PHU and NIPTU production were obtained from the literature.<sup>34,35</sup>



**Figure 3.** Cost breakdowns for PHU and NIPTU: minimum selling prices (MSPs) of NIPTU realized in (a) for the PHU production process and (b) for the NIPTU production process. Major raw material cost contributors are itemized for (c) the PHU production process and (d) the NIPTU production process.



**Figure 4.** Cost breakdowns for PHU and NIPTU monomer: minimum selling prices of carbamate monomers realized in (a) the PHU monomer recovery process and (b) the NIPTU monomer recovery process. Major raw material cost contributors are itemized for (c) the PHU monomer recovery process and (d) the NIPTU monomer recovery process.



**Figure 5.** Cumulative abatement of costs of PHU and NIPTU production: waterfall plot analysis with MSPs of NIPU production in the (a) process for PHU production and (b) process for NIPTU production. Red shaded area reflects range of baseline PU prices.

Empirical data were used in evaluating PHU and NIPTU production as well as carbamate monomer recovery processes.<sup>25,26</sup> Experimental data to inform material and energy flows for the polycondensation reactions modeled in this study are limited for 2° PHUs and absent for 2° NIPTUs. To enable a consistent comparison with baseline polymers, we modeled these reactions stoichiometrically in Aspen Plus V12 based on the general temperature ranges for polycondensation reactions between carbamates and 1,4-BD.<sup>36–38</sup> Baseline data for the fossil energy use, greenhouse gas (GHG) emissions, and water consumption of fossil-based PU foams were sourced from the GREET model.<sup>39</sup> While the baseline fossil-based PUs analyzed in our study are foams, the NIPU materials under examination are bulk materials. To make PU foams from bulk materials, blowing agents are introduced to create a cellular structure. This process and the materials it consumes would add to the energy and emissions burdens of NIPU materials we are examining.<sup>44</sup> Blowing agents such as cyclopentane on average represent 8% (w/w) of rigid and flexible PU foams.<sup>15</sup> We recognize this could increase fossil energy use and GHG emissions by approximately 6000 MJ tonne<sup>-1</sup> and 214 kg CO<sub>2</sub> tonne<sup>-1</sup> after accounting for the use of cyclopentane as a blowing agent.<sup>44</sup> Young's modulus and elongation at break properties of the NIPUs assessed here<sup>22,25–27</sup> are comparable to those same properties of traditional flexible foam materials.<sup>45</sup>

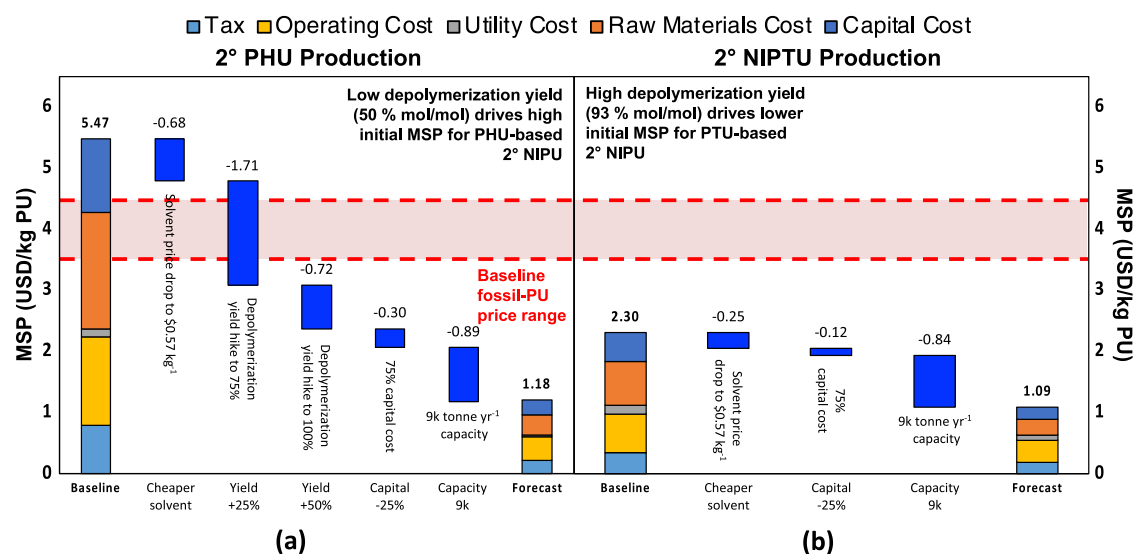
## RESULTS AND DISCUSSION

**Techno-economic Analysis Results.** Figure 3a,b reports MSPs of biobased PHU and NIPTU assuming a 20% internal rate of return (IRR). The MSPs of PHU and NIPTU are 5.37 and 7.16 USD kg<sup>-1</sup>, respectively. In the production of PHU, raw materials are responsible for 59% of the total costs. Operating expenses (16%) are the next highest contributor. Raw material costs account for 68% of the total costs in the production of NIPTU, 9% higher than the cost contributions of raw materials in PHU production. Operating expenses (13%) are again the next highest cost contributor. Raw materials drive total costs and are further broken down with respect to all material feeds to the PHU and NIPTU processes (Figure 3c,d). Amines dominate the raw material costs. In the PHU system, PBN is responsible for 62% of the raw material cost. The TTEA amine accounts for 36% of the NIPTU raw material costs. The cost of the epoxidizing agents, hydrogen peroxide, and ECH, followed by the cost of solvents are the next largest material costs.

We also assessed the commercial viability of NIPU reprocessing (Figure 4a,b). The MSPs of 2° PHU and 2° NIPTU are 5.47 and 2.30 USD kg<sup>-1</sup>, respectively. In the recovery of 2° PHU, raw material purchases represent 35% of total process costs. Operating expenses (26%) are the next greatest contributor to the total costs. The recovery of 2° NIPTU follows a similar trend in major cost contributors with raw material still being the largest cost (31% cost contribution). The cost breakdowns of both processes (Figure 4c,d) are very similar. The greatest raw material cost is in the THF solvent (39% of total raw material cost) followed by the cost of potassium hydroxide (26 and 18% of raw material costs for 2° PHU and 2° NIPTU, respectively) used in catalyst recovery.

A trend is seen in the MSPs of virgin PHU (5.37 USD kg<sup>-1</sup>), virgin NIPTU (7.16 USD kg<sup>-1</sup>), 2° PHU (5.47 USD kg<sup>-1</sup>), and 2° NIPTU (2.30 USD kg<sup>-1</sup>). While the MSP of PHU is 29% lower than that of NIPTU, the prospect of reprocessing PHU is less economically feasible. The higher cost of NIPTU production mainly arises from the comparatively high cost of NIPTU raw materials (Tables S.4 and S.5). The high cost of PHU reprocessing stems from its unfavorable 50% (mol/mol) depolymerization yield. The depolymerization yield of the NIPTU thiocarbamate monomer recovery process is a favorable 94% (mol/mol).<sup>25</sup> Note while there are many unique PHU and NIPTU materials studied in the literature,<sup>46–49</sup> these yields were empirically measured for the particular NIPU materials investigated in this analysis. The low solubility of the thiocarbamate monomer in THF solvent is beneficial, as it shifts equilibrium toward monomer recovery during depolymerization. Although the PHU and NIPTU samples used as examples in this study are amorphous, we also note that differences in crystallinities of semicrystalline PHUs and NIPTUs may affect depolymerization yields. By improving the depolymerization solvent or the other reagents used in PHU manufacturing and reprocessing, 2° NIPU recovery can be improved, thereby minimizing its MSP.

As a next step in our analysis, we compared the above-described MSPs with baseline PU flexible foam prices of 3.53–4.49 USD kg<sup>-1</sup> (highlighted in red in Figure 5).<sup>49</sup> We



**Figure 6.** Cumulative abatement of costs of PHU and NIPTU reprocessing: waterfall plot analysis with MSPs of (a) 2° PHU and (b) 2° NIPTU. Red shaded area reflects the range of baseline PU prices.

considered how MSPs of PHU and NIPTU might change with changes to selected critical parameters in TEA (Figure 5a,b, respectively). The individual sensitivities of key variables in the production of NIPUs can be found in the SI (Figure S.6(a)). The outlined process improvements bring the MSPs of biobased NIPUs to levels comparable with the MSPs of fossil-based flexible PUs. With respect to PHU (Figure 5a), a 0.52 USD kg<sup>-1</sup> drop in MSP results from a 25% drop in PBN cost. In a separate TEA study, hexanediamine is adopted as a model compound for pricing amines (1.52 USD kg<sup>-1</sup>). If the cost of amine feeds in PHU production drops to the price of hexanediamine, the MSP of PHU drops a further 0.56 USD kg<sup>-1</sup>.<sup>38</sup> A 25% drop in capital cost and an increase in production capacity were also examined, with capacity being the most influential variable in this analysis. An 0.88 USD kg<sup>-1</sup> drop in MSP results from raising production capacity to 9000 tonne PHU yr<sup>-1</sup>. Thereby, it is shown how reductions in amine costs, reductions in capital cost, and increases in plant production capacity can bring the MSP of PHU below the range of fossil-based flexible PU MSPs. Cumulatively, these changes reduce the MSP of PHU to 1.18 USD kg<sup>-1</sup> and are well below baseline costs.

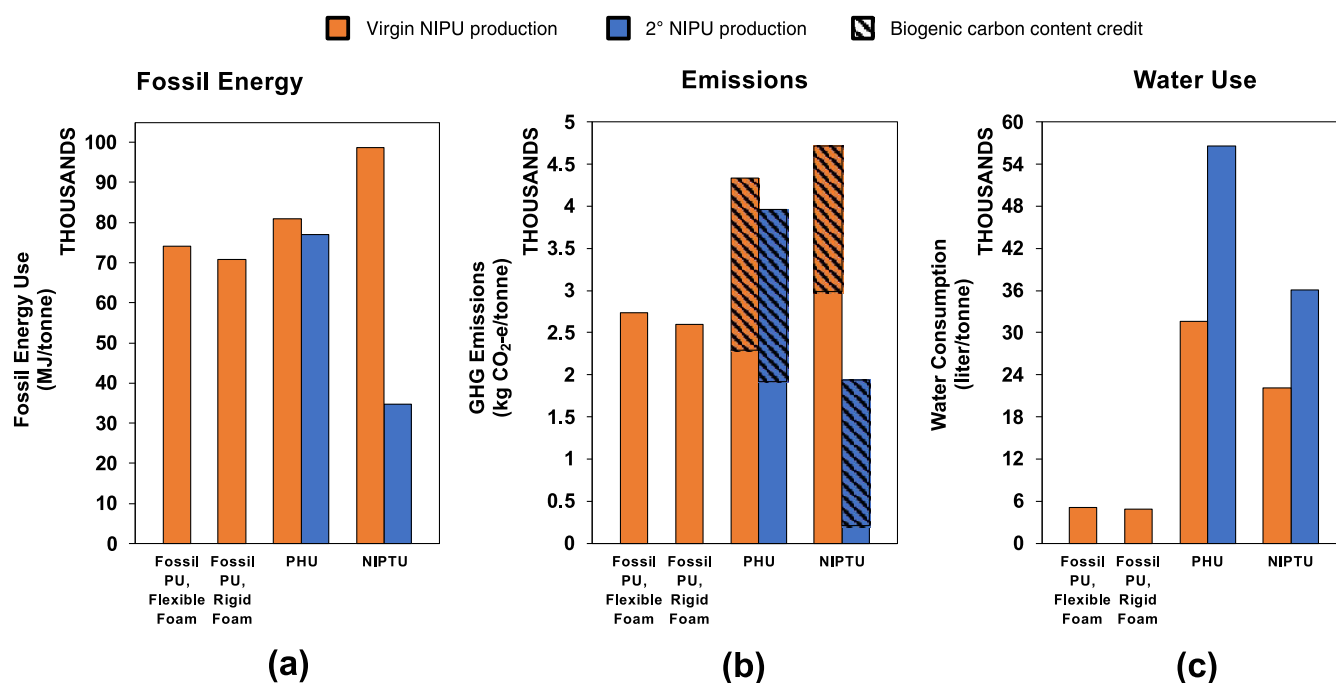
With respect to NIPTU (Figure 5b), a 0.50 USD kg<sup>-1</sup> decrease in MSP results from a 25% drop in TTEA cost. If the amine selling price drops to a comparable level to hexanediamine, the MSP of NIPTU drops a further 0.71 USD kg<sup>-1</sup>.<sup>35</sup> We also considered how variations of 25% in ECH price and capital would affect the MSP of NIPTU. However, the most influential factor in reducing costs was once again the production capacity. A 1.04 USD kg<sup>-1</sup> drop in MSP results from raising production capacity to 9000 tonne NIPTU yr<sup>-1</sup>. After reductions in the price of amines, reductions in the price of ECH, reductions in capital costs, and increases in plant production capacity, the MSP of NIPTU (4.39 USD kg<sup>-1</sup>) falls within the range of baseline PU MSPs. An even lower NIPTU MSP might be achievable with further increases in plant capacity or lower material costs.

Improvements to PHU and NIPTU reprocessing can similarly lower the MSPs of 2° PHU and 2° NIPTU (Figure 6a,b). The individual sensitivities of key variables in the reprocessing of NIPUs can be found in the SI (Figure S.6(b)).

For example (Figure 6a), if the solvent price dropped to levels comparable to the price of dichloromethane (0.57 USD kg<sup>-1</sup>),<sup>50</sup> PHU MSP drops by 0.68 USD kg<sup>-1</sup>. As mentioned previously, improving depolymerization yield would greatly benefit the MSP of 2° PHU. From a baseline depolymerization yield of 50% (mol/mol), a 25% (mol/mol) improvement in yield results in a 1.71 USD kg<sup>-1</sup> drop in MSP for 2° PHU. Reaching a 100% (mol/mol) depolymerization yield results in a further 0.72 USD kg<sup>-1</sup> drop in MSP. A 25% drop in capital cost and an increase in production capacity were also examined. Capacity increases are the second most influential variable behind the depolymerization yield. A drop in MSP of 0.89 USD kg<sup>-1</sup> results from raising production capacity to 9000 tonne 2° PHU yr<sup>-1</sup>. Altogether, the MSP of reprocessed PHU could be significantly lower than the MSP for fossil-based flexible PU and virgin PHU if process improvements occur. Most importantly, improvements in the depolymerization yields of PHU must be achieved. Testing other depolymerization solvents or other types of PHU with different characteristic crystallinities or monomers holds promise to increase yield. Overall, the improvements we considered result in an MSP of 1.18 USD kg<sup>-1</sup> for 2° PHU, which is well below baseline costs.

With respect to 2° NIPTU recovery (Figure 6b), if the price of solvent dropped to 0.57 USD kg<sup>-1</sup> (comparable to the price of dichloromethane)<sup>50</sup> MSP drops by 0.25 USD kg<sup>-1</sup>. The NIPTU recovery process is also least sensitive to changes in the capital cost. Production capacity is once again a highly influential cost variable. An 0.84 USD kg<sup>-1</sup> drop in MSP results from raising production capacity to 9000 tonne NIPTU monomer yr<sup>-1</sup>. Although the MSP of 2° NIPTU was already below baseline costs, the aforementioned improvements could further reduce the MSP of 2° NIPTU. After incremental decreases in solvent price, decreases in capital cost, and increases in NIPTU monomer production capacity, a final NIPTU monomer MSP of 1.08 USD kg<sup>-1</sup> is achievable.

The MSPs of PHU, NIPTU, 2° PHU, and 2° NIPTU were initially determined to be 5.37, 7.16, 5.47, and 2.30 USD kg<sup>-1</sup>, respectively. After stepping along a path of cost abatement strategies, the following MSPs can be achieved (percentage reduction in price shown within parentheses): 3.15 USD kg<sup>-1</sup>



**Figure 7.** Life cycle impacts: (a) fossil energy consumption, (b) GHG emissions, and (c) water consumption impacts of NIPU production and reprocessing. Impacts for PHU and NIPTU production are compared to the production of PU flexible and rigid foams. Orange bars are representative of PU/NIPU production, and blue bars are representative of NIPU reprocessing.

(−41%) for PHU, 4.39 USD kg<sup>−1</sup> (−39%) for NIPTU, 1.18 USD kg<sup>−1</sup> (−78%) 2° PHU, and 1.08 USD kg<sup>−1</sup> (−53%) 2° NIPTU. Taken together, the TEA results demonstrate that cost-competitive NIPUs and 2° NIPUs are possible, especially if research and development efforts focus on improving yields and exploring low-cost solvents and amines when applicable. Furthermore, designing plants with capacities that take advantage of economies of scale also benefits the commercial viability of these polymers.

**Life Cycle Analysis Results.** We computed life cycle impact results for fossil energy use (Figure 7a), GHG emissions (Figure 7b), and water consumption (Figure 7c). The fossil energy use of each process is tallied. This sum is compared with baseline fossil-based flexible and rigid PU fossil energy usage (Figure 7a). The fossil energy input per tonne of PHU production (80,900 MJ tonne<sup>−1</sup>) is 9.3 and 14.3% greater than the fossil energy input required per tonne of flexible and rigid fossil-based PU foam, respectively. The fossil energy input per tonne of NIPTU production (98,600 MJ tonne<sup>−1</sup>) is 33.1 and 39.2% greater than the fossil energy input required per tonne of flexible and rigid fossil-based PU foam production, respectively. Fossil energy use per tonne of reprocessed NIPU is also tallied (blue bars in Figure 7a) and shown to require less fossil energy than the fossil energy required per tonne of virgin NIPU produced. Reprocessed NIPU from PHU requires 4.7% less fossil energy than manufacturing virgin PHU, and reprocessed NIPU from NIPTU requires 64.8% less fossil energy than manufacturing virgin NIPTU. Fossil energy consumption associated with material feeds and energy demands to NIPU production can be found in Figure S.7.

We report GHG emissions associated with fossil-based PU production as well as PHU and NIPTU production (Figure 7b). Percentage differences in GHG emissions, not considering biogenic content, are larger than the differences observed in fossil energy inputs to fossil-based PU versus virgin NIPU.

This is because fossil energy only includes fossil-based energy input and not total energy, whereas GHG emissions encompass total process emissions. The emissions per tonne of PHU production, after considering a biogenic emissions credit (2,290 kg of CO<sub>2</sub>-e tonne<sup>−1</sup>), are 16.1 and 11.5% lower than the emissions generated per tonne of fossil-based flexible and rigid PU foam production, respectively. The emissions generated per tonne of NIPTU production, including the biogenic emissions credit (2990 kg of CO<sub>2</sub>-e tonne<sup>−1</sup>), are 9.4 and 15.4% greater than the emissions generated per tonne of fossil-based flexible and rigid PU foam production, respectively. Emissions per tonne of NIPU reprocessed from PHU and NIPTU are depicted as blue bars in Figure 7b. Note that biogenic contents of 2° NIPUs are repetitively depicted for reference, and care should be taken not to double count biogenic emission credits. Regardless of biogenic credit considerations, 2° NIPTU has lower GHG emissions than virgin NIPTU production.

We also report water consumption associated with fossil-based PU, PHU, and NIPTU production (Figure 7c). The water consumption from producing flexible and rigid PU foam from fossil fuels is shown in the first two columns. Water consumption per tonne of PHU production (31,600 L tonne<sup>−1</sup>) is 6.2 and 6.5 times greater than water consumption per tonne of fossil fuel-based flexible and rigid PU foam production, respectively. Water consumption per tonne of NIPTU production (22,100 L tonne<sup>−1</sup>) is 4.3 and 4.5 times greater than the water consumption per tonne of fossil fuel-based flexible and rigid foam production, respectively. Unlike the impact categories of fossil energy use and emissions, the water consumption associated with reprocessing both NIPU materials is considerably greater than the water consumption associated with virgin NIPU production. This is because the use of water as a solvent during the depolymerization process makes it inherently water demanding.

Virgin PHU and NIPTU production has higher fossil energy use and water consumption than baseline values. After accounting for biogenic carbon credits, PHU and NIPTU have lower and higher GHG emissions, respectively, than baseline emissions. The fossil energy use per tonne of 2° NIPUs is consistently lower than the fossil energy use per tonne of both virgin PHU and NIPTU production. In fact, the fossil energy use per tonne of NIPU recovered from NIPTU is at least 51% lower than the fossil energy consumption per tonne of virgin PU foam produced from fossil fuels. Without considering biogenic emission credits, the emissions per tonne of 2° NIPTU are at least 25% lower than baseline emissions. Higher fossil energy use and GHG emissions for 2° PHU than 2° NIPTU production are again primarily driven by low depolymerization yields.

Aside from improving the depolymerization yield, high fossil energy use for virgin NIPU production can possibly be addressed by identifying energy-intensive material inputs. A breakdown of the fossil energy demands from the inputs to PHU and NIPTU production is in the SI (Figure S.7). Material process inputs drive fossil energy demands for both NIPU and NPPU production processes. We therefore explored LCA results' sensitivity to key material input parameters. For example, the ammoxidation conversion in XDA production was 53% in the base case for PHU production. If these conversions improved to 80% and biomethanol was used rather than fossil-based methanol in PHU production, a 33% reduction in the fossil energy use can be realized.<sup>39,42,51,52</sup> These improvements alone would reduce fossil energy use for PHU to below baseline values. In addition, analysis of the GREET model output for NIPTU production showed that xylene accounted for 16% of the fossil energy consumption from all material feeds (Figure S.7(b,d)). Recycling xylene can result in almost 16% reduction in the fossil energy use of NIPTU production.

## CONCLUSIONS

The need to address climate change, fossil fuel depletion, and plastic waste accumulation has driven the exploration of sustainable alternatives to PU production. Overall, this research contributes to ongoing efforts to promote environmentally conscious practices and investigate isocyanate-free methods in the plastics industry. The TEA results outlined how PHU and NIPTU production processes can achieve MSPs below and within, respectively, a baseline price range of fossil-based PU foam. We re-emphasize that conclusions regarding 2° NIPUs greatly depend on improving NIPU depolymerization yields and further investigating polycondensation chemistry needed to polymerize carbamate monomers with polyols. However, upon overcoming these barriers, we project that reprocessing NIPUs is more economically competitive than producing virgin NIPUs. Another barrier to implementing 2° NIPU recovery processes is the need to stockpile used NIPUs before recycling can become an option. Biomass-derived, reprocessable NIPUs have the potential to reduce GHG emissions and conserve fossil energy. Water consumption is identified as an area where NIPU production and reprocessing have harsher environmental impacts.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.4c04046>.

Process flow diagrams; sensitivity diagrams; supporting raw material energy use data; and tabulated market value data (PDF)

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### Notes

The authors declare no competing financial interest.

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