

1 Techno-economic Analysis and Life Cycle  
2 Assessment of Biomass-Derived  
3 Polyhydroxyurethane and Non-Isocyanate  
4 Polythiourethane Production and Reprocessing

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4 ABSTRACT:

5 Non-isocyanate polyurethanes (NIPUs) show promise as more sustainable alternatives to  
6 conventional, isocyanate-based polyurethanes (PUs). In this study, polyhydroxyurethane (PHU)  
7 and non-isocyanate polythiourethane (NIPTU) production and reprocessing models inform the  
8 results of a techno-economic analysis and a life cycle assessment. The profitability of selling PHU  
9 and NIPTU is rationalized by identifying significant production costs, indicating that raw materials  
10 drive the costs of PHU and NIPTU production and reprocessing. After stepping along a path of  
11 process improvements, PHU and NIPTU can achieve minimum selling prices (MSPs) of 3.15 USD  
12 kg<sup>-1</sup> and 4.39 USD kg<sup>-1</sup>, respectively. Depolymerization yields need to be optimized and  
13 polycondensation reactions need to be investigated for the reprocessing of NIPUs into secondary  
14 (2°) NIPUs. Of the NIPUs examined here, PHU has a low depolymerization yield and NIPTU has  
15 a high depolymerization yield. Fossil energy use, greenhouse gas (GHG) emissions, and water  
16 consumption are reported for the bio-based production of PHU, NIPTU, 2° PHU, and 2° NIPTU  
17 and compared with baseline values for fossil-based PU production. There are options for reducing  
18 environmental impacts which could make these pathways more sustainable. If barriers to  
19 implementation are overcome, 2° NIPUs can be manufactured at lower cost and environmental  
20 impacts than virgin NIPUs.

21

## 1 INTRODUCTION:

2 The increasingly prevalent dangers of climate change and non-renewable resource depletion  
3 are joined by the looming threat of plastic waste accumulation.<sup>1-5</sup> About 80 % of global energy  
4 demand is from non-renewable feedstocks while 7-8 % of global fossil fuels are used to provide  
5 energy and materials in the manufacturing of plastics.<sup>6-8</sup> Globally, annual plastics production  
6 continues to increase dramatically from 2 million tonnes in 1950 to around 438 million tonnes in  
7 2017 with up to 99 % of plastics made from fossil fuel-derived polymers.<sup>8</sup> Only around 30 % of  
8 plastics produced since 1950 remain in use today. By 2050, over 1,100 million tonnes of plastic  
9 will be produced annually if current trends continue.<sup>9,10</sup> To mitigate these issues, scientists and  
10 engineers continue to develop technologies to recycle plastics and use alternative resources in  
11 plastics production.<sup>11,12</sup>

12 Polyurethanes (PUs) are polymeric materials with versatile properties ranging in application  
13 from soft coatings and flexible foams to harder construction materials and rigid foams.<sup>13,14</sup>  
14 However, the production of PU involves monomers such as polyols and diisocyanates (DI), which  
15 deplete nonrenewable fossil fuel resources. In 2016, 2.9 million tonnes of polyurethane (PU) were  
16 produced in the United States at the expense of 1.1 million tonnes of crude oil and 1.1 million  
17 tonnes of natural gas.<sup>15</sup> With a 5.5 % end-of-life recycling rate, PU is recycled at less than the  
18 average recycling rate of U.S. plastics in 2015.<sup>15,16</sup> Another challenge with today's technology for  
19 manufacturing PU is the use of isocyanates, which pose a human health hazard.<sup>17,18</sup> Accordingly,  
20 the U.S. Environmental Protection Agency (EPA) has begun to phase out their use in the synthesis  
21 of PU.<sup>19</sup> To enhance PU sustainability, it is necessary (1) to advance technologies for producing  
22 this material from bio-based feedstocks, (2) to expand methods for recycling PU monomers, and  
23 (3) to avoid the use of isocyanates in PU manufacturing.

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

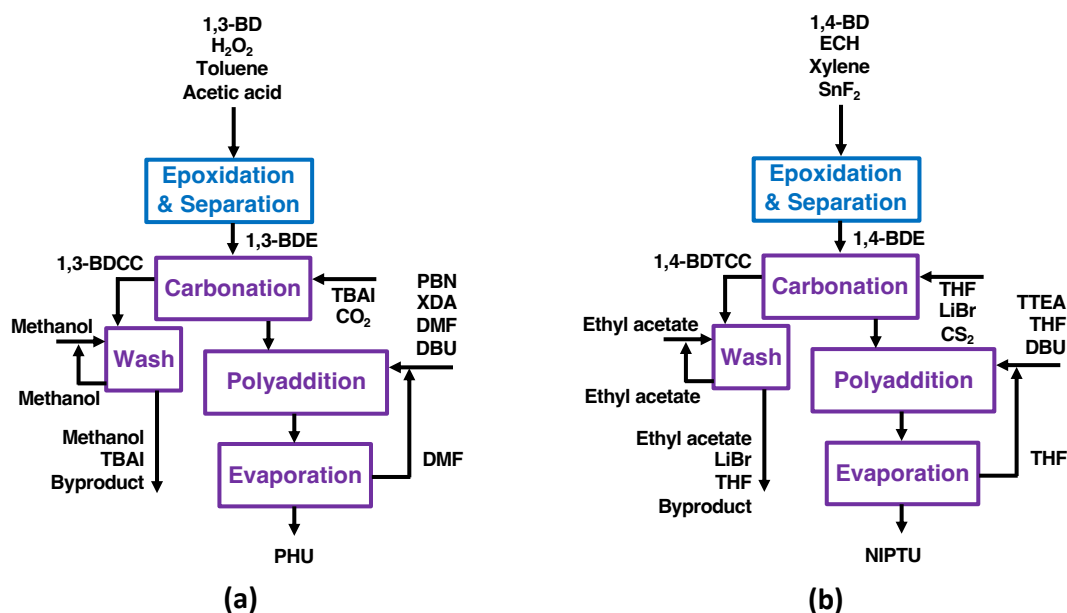
13 It is important to understand how shifts from manufacturing conventional PUs to  
14 manufacturing NIPUs may influence their cost and sustainability. We carried out techno-economic  
15 analysis (TEA) and life-cycle assessment (LCA) of four new NIPU production pathways: (1) a  
16 biomass-based PHU, (2) a 2° PHU via depolymerization, (3) a biomass-based NIPTU, and (4) a  
17 2° NIPTU via depolymerization. Using TEA, we compare the minimum selling prices (MSPs) of  
18 bio-based PHU, NIPTU, and 2° NIPUs with conventional PU market prices. We use LCA to  
19 compare greenhouse gas (GHG) emissions, fossil energy use, and water consumption of PHU,  
20 NIPTU, and 2° NIPUs to the same metrics for conventional PU. To date, PHU and NIPTU  
21 production routes have not been assessed for their cost competitiveness or environmental  
22 advantages. NIPU recovery has also not been evaluated from these perspectives. Accordingly, this

1 research represents an important step in evaluating the role of bio-based, recyclable NIPUs in the  
2 polymers market.

3 METHODS:

#### 4 **Process modeling**

5 Processes for PHU and NIPTU production are depicted in **Fig. 1(a)** and **Fig. 1(b)**, respectively.  
6 We modeled these processes in Aspen Plus V12 leveraging published models and experimental  
7 data.<sup>33-35</sup> Box colors in **Fig. 1** depict the origin of data. Blue boxes denote data derived from  
8 literature and patents.<sup>34,35</sup> Purple boxes indicate data arose from experiments.<sup>22,25-27,31</sup> Detailed  
9 process flow diagrams and stream summary tables are available in **Fig. S.1**, **Fig. S.2**, **Table S.1**,  
10 and **Table S.2** in the Supporting Information (SI). Biosynthesis of PHU begins with the  
11 epoxidation of 1,3-butadiene (1,3-BD) with two equivalents of hydrogen peroxide to form 1,3-  
12 butadiene diepoxide (1,3-BDE). Toluene and acetic acid are used as a solvent and an additive,



**Figure 1.** Production process block flows: production processes for (a) PHU and (b) NIPTU.

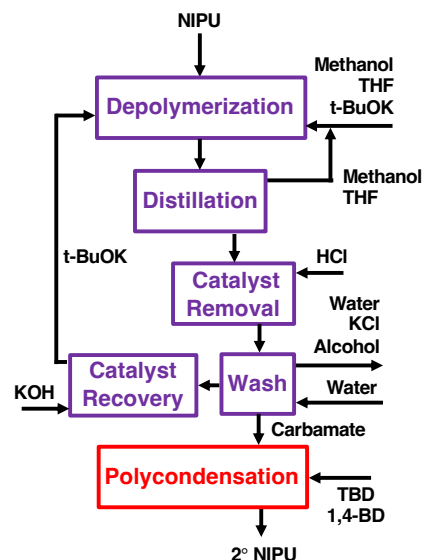
Blue blocks represent processes supported by data collected from literature and patents. Purple blocks represent processes supported by data collected experimentally.

1 respectively, for the epoxidation and separation steps. In the subsequent carbonation step, 1,3-BDE  
2 reacts with two equivalents of carbon dioxide using a tetrabutylammonium iodide (TBAI) catalyst  
3 affording 1,3-butadiene dicyclic carbonate (1,3-BDCC). Prior to polymerization, 1,3-BDCC is  
4 washed of residual catalyst. Polymerization of 1,3-BDCC with poly(butadiene-co-acrylonitrile)  
5 (PBN) and a p-xylylenediamine (XDA) chain extender is carried out using 1,8-  
6 diazabicyclo[5.4.0]undec-7-ene (DBU) as catalyst in dimethylformamide (DMF) solvent. PHU  
7 leaves the process after DMF is evaporated and recycled back to the polymerization step. **Fig.**  
8 **S.4(a)** contains a reaction flow diagram for the proposed PHU biosynthesis.

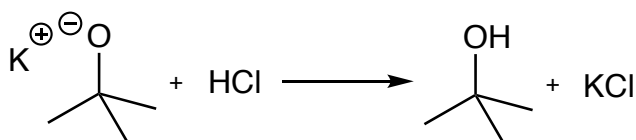
9 The biosynthesis of NIPTU begins with the substitution of the hydroxyl groups of 1,4-  
10 butanediol (1,4-BD) with two epichlorohydrin (ECH) molecules affording 1,4-butanediol  
11 diglycidyl ether (1,4-BDE). Xylene and tin difluoride are used as a solvent and an additive,  
12 respectively, for this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

20 A flow diagram for reprocessing used NIPU materials is depicted in **Fig. 2**. Purple boxes  
21 indicate process modeling relied on experimental data.<sup>22,25-27,31</sup> The downstream polycondensation  
22 step is depicted in red because the polycondensation reactions modeled here are yet to be tested  
23 experimentally, and they have not been fully investigated in the literature. Instead, the

1 polycondensation steps are modeled  
 2 stoichiometrically in Aspen Plus V12 based on  
 3 the general temperature profiles of carbamate  
 4 monomers polymerizing with diols using a TBD  
 5 catalyst.<sup>36-38</sup> This step was necessary to enable  
 6 consistent comparison with baseline polymers  
 7 and, although imperfect, allows for a general  
 8 understanding of relative cost and environmental  
 9 performance. A detailed process flow diagram  
 10 and a stream summary table for NIPU  
 11 reprocessing are located in **Fig. S.3** and **Table S.3**  
 12 of the SI, respectively. The methanolysis process  
 13 for carbamate monomer recovery is identical for  
 14 PHU and NIPTU. Used NIPU is chemically  
 15 depolymerized using a potassium tert-butoxide  
 16 catalyst (t-BuOK), THF solvent and methanol.  
 17 After methanol and THF are distilled and  
 18 recycled back to the depolymerization process, t-BuOK is neutralized using hydrochloric acid  
 19 producing tert-butanol (t-BuOH) and potassium chloride salt (**Scheme 1**).

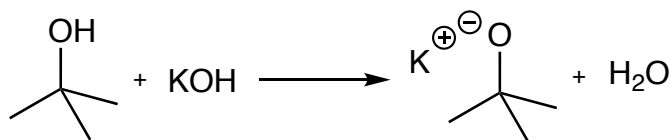


**Figure 2.** Monomer/NIPU recovery block flow: reprocessing of used PHU or NIPTU into 2° NIPUs. All NIPU recovery process flows are supported by data collected empirically. Blue blocks represent processes supported by data collected from literature and patents. Purple blocks represent processes supported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



**Scheme 1.** Catalyst removal: potassium tert-butoxide is neutralized with hydrochloric acid to afford tert-butanol and potassium chloride.

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



**Scheme 2.** Catalyst recovery: tert-butanol is reacted with potassium hydroxide to afford potassium tert-butoxide and water.

3 Recovered catalyst is recycled back to the depolymerization step. A reaction flow diagram of 2°  
 4 NIPU recovery from virgin PHU and NIPTU can be found in the SI (**Fig. S.5(a)** and **Fig. S.5(b)**,  
 5 respectively). Recovered carbamate monomer can be reprocessed into 2° NIPU via  
 6 polycondensation with 1,4-BD.<sup>36-38</sup> **Table 1.** List of assumptions: financial  
 7 Polycondensation is assumed to be facilitated assumptions used in TEA.  
 8 by a 1,5,7-triazabicyclo[4.4.0]dec-5-ene  
 9 (TBD) catalyst in a neat reaction.<sup>36</sup> **Table S.6**  
 10 documents the market values we adopted for  
 11 inputs to NIPU reprocessing.

## 12 Financial assumptions

13 Financial assumptions for the TEA are  
 14 listed in **Table 1**. We adopted a 30-year plant  
 15 life. Plant sizes vary; we chose a base case  
 16 capacity of 2540 tonne yr<sup>-1</sup>. Engineering,  
 17 procurement, and construction (EPC) lasts 24  
 18 weeks. EPC and startup phases together last  
 19 50 weeks. Working capital assets totaling 5 %  
 20 of the fixed capital investment (CI) are kept

**Table 1.** List of assumptions: financial assumptions used in TEA.

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

<sup>34</sup>Dong et al., 2021



1 at the plants. A straight-line method for calculating depreciation is implemented with salvage  
2 values for equipment set at 20 % of their original cost. We adopted a 20 % internal rate of return  
3 (IRR). Other assumed values including cost year of the USD, tax rate, and escalation rates can be  
4 found in **Table 1**.

## 5 **Life cycle inventory and impact categories**

6 Systems are compared based on three impact categories: fossil energy use, GHG emissions,  
7 and water consumption. We selected one tonne of NIPU or PU material as our functional unit. We  
8 carried out LCA using life cycle inventory data generated from Aspen Plus simulations and the  
9 Greenhouse gases, Regulated Emissions, and Energy use in Technologies (GREET) model (2021  
10 release).<sup>39</sup> Life cycle inventory data for PHU, NIPTU, and 2° NIPU are shown in **Table S.7**, **Table**  
11 **S.8**, and **Table S.9** of the SI. Life cycle inventory data for ECH, t-BuOK, XDA, TTEA, and SnCl<sub>2</sub>  
12 (**Table S.10**, **Table S.11**, **Table S.12**, **Table S.13**, and **Table S.14**, respectively) were not available  
13 through GREET and were obtained from literature, openLCA software, and patents.<sup>40-43</sup> Data for  
14 the epoxidation and separation steps of PHU and NIPTU production were obtained from the  
15 literature.<sup>34,35</sup> Empirical data were used in evaluating PHU and NIPTU production as well as  
16 carbamate monomer recovery processes.<sup>25,26</sup> Experimental data to inform material and energy  
17 flows for the polycondensation reactions modeled in this study is limited for 2° PHUs and absent  
18 for 2° NIPTUs. To enable a consistent comparison with baseline polymers, we modeled these  
19 reactions stoichiometrically in Aspen Plus V12 based on the general temperature ranges for  
20 polycondensation reactions between carbamates and 1,4-BD.<sup>36-38</sup> Baseline data for the fossil  
21 energy use, greenhouse gas (GHG) emissions, and water consumption of fossil-based PU foams  
22 were sourced from the GREET model.<sup>39</sup> While the baseline fossil-based PUs analyzed in our study  
23 are foams, the NIPU materials under examination are bulk materials. To make PU foams from

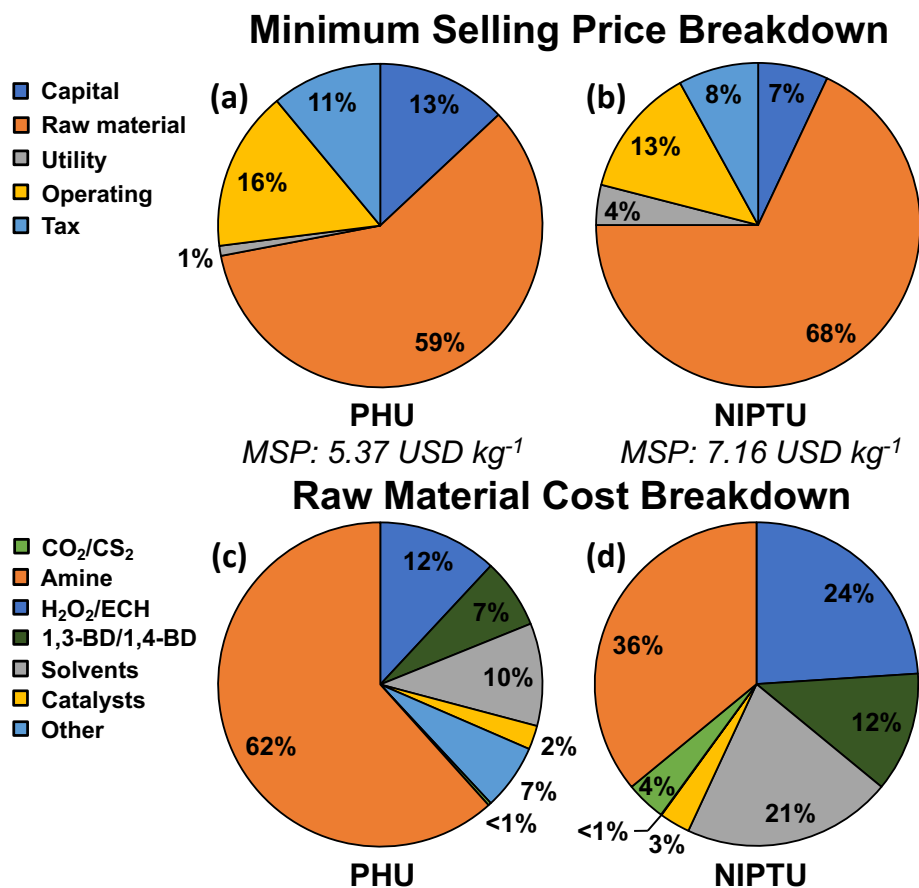
1 bulk materials, blowing agents are introduced to create a cellular structure. This process and the  
2 materials it consumes would add to the energy and emissions burdens of NIPU materials we are  
3 examining.<sup>44</sup> Blowing agent such as cyclopentane on average represent 8 % (*w/w*) of rigid and  
4 flexible PU foams.<sup>15</sup> We recognize this could increase fossil energy use and GHG emissions by  
5 approximately 6,000 MJ tonne<sup>-1</sup> and 214 kg CO<sub>2</sub> tonne<sup>-1</sup> after accounting for the use of  
6 cyclopentane as a blowing agent.<sup>44</sup> The Young's modulus and elongation at break properties of  
7 the NIPUs assessed here<sup>22,25-27</sup> are comparable to those same properties of traditional flexible  
8 foam materials.<sup>45</sup>

## 9 RESULTS AND DISCUSSION:

### 10 **Techno-economic analysis results**

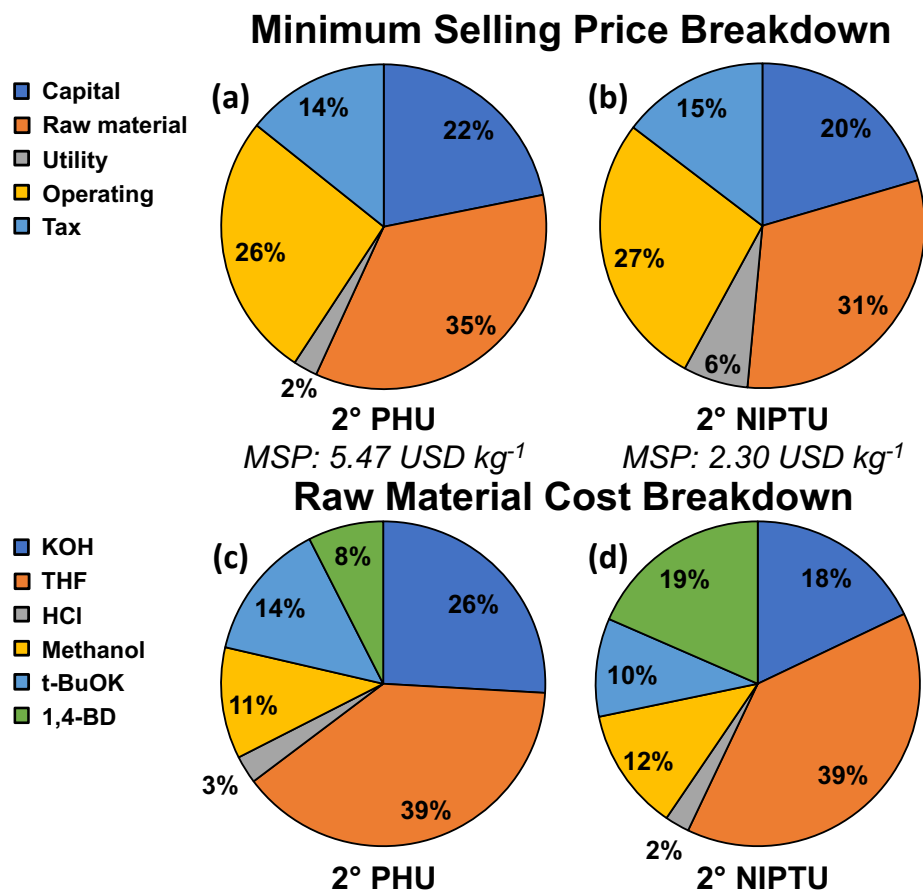
11 **Fig. 3(a)** and **Fig. 3(b)** report MSPs of bio-based PHU and NIPTU assuming a 20 % internal  
12 rate of return (IRR). The MSPs of PHU and NIPTU are 5.37 USD kg<sup>-1</sup> and 7.16 USD kg<sup>-1</sup>,  
13 respectively. In the production of PHU, raw materials are responsible for 59 % of total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

22 We also assessed the commercial viability of NIPU reprocessing (**Fig. 4(a)** and **Fig. 4(b)**). The  
23 MSPs of 2° PHU and 2° NIPTU are 5.47 USD kg<sup>-1</sup> and 2.30 USD kg<sup>-1</sup>, respectively. In the recovery



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

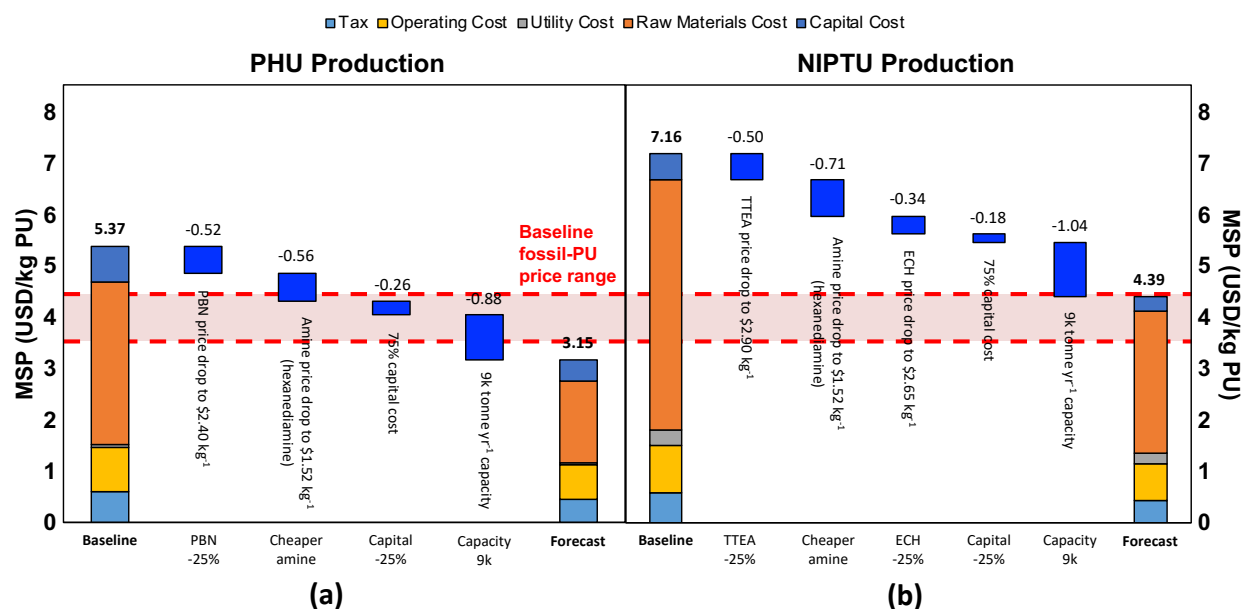
1 of 2° PHU, raw material purchases are 35 % of total process costs. Operating expenses (26 %) are  
 2 the next greatest contributor to total costs. The recovery of 2° NIPTU follow a similar trend in  
 3 major cost contributors with raw material still being the largest cost (31 % cost contribution). Cost  
 4 breakdowns of both processes (**Fig. 4(c)** and **Fig. 4(d)**) are very similar. The greatest raw material  
 5 cost is in the THF solvent (39 % of total raw material cost) followed by the cost of potassium  
 6 hydroxide (26 % and 18 % of raw material costs for 2° PHU and 2° NIPTU, respectively) used in  
 7 catalyst recovery.



**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.

1 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 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  
 3 than that of NIPTU, the prospect of reprocessing PHU is less economically feasible. The higher  
 4 cost of NIPTU production mainly arises from the comparatively high cost of NIPTU raw materials  
 5 (Table S.4 and Table S.5). The high cost of PHU reprocessing stems from its unfavorable 50 %  
 6 (mol/mol) depolymerization yield. The depolymerization yield of the NIPTU thiocarbamate

1 monomer recovery process is a favorable 94 % (mol/mol).<sup>25</sup> Note, while there are many unique  
 2 PHU and NIPTU materials studied in the literature,<sup>46-49</sup> these yields were empirically measured  
 3 for the particular NIPU materials investigated in this analysis. The low solubility of the  
 4 thiocarbamate monomer in THF solvent is beneficial as it shifts equilibrium toward monomer  
 5 recovery during depolymerization. Although the PHU and NIPTU samples used as examples in  
 6 this study are amorphous, we also note that differences in crystallinities of semi-crystalline PHUs  
 7 and NIPTUs may affect depolymerization yields. By improving the depolymerization solvent or  
 8 the other reagents used in PHU manufacturing and reprocessing, 2° NIPU recovery can be  
 9 improved thereby minimizing its MSP.

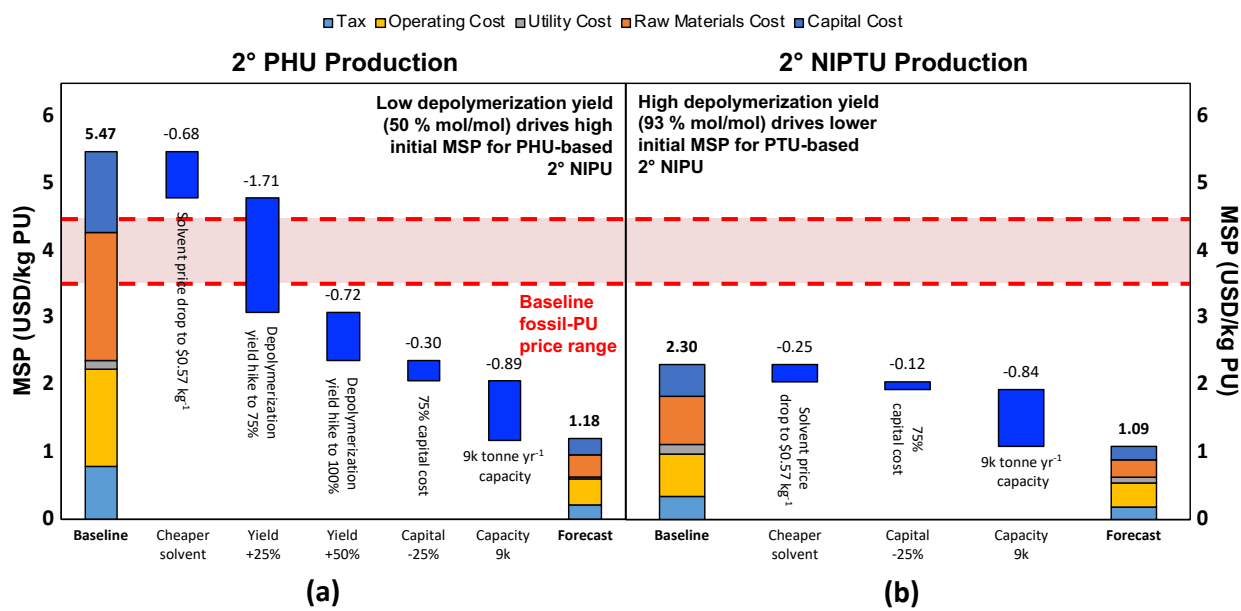


**Figure 5.** Cumulative abatement of costs of PHU and NIPTU production: waterfall plot analysis with MSPs of NIPU production in (a) process for PHU production and (b) process for NIPTU production. Red shaded area reflects range of baseline PU prices.

10 As a next step in our analysis, we compared the above-described MSPs with baseline PU  
 11 flexible foam prices of 3.53 – 4.49 USD kg<sup>-1</sup> (highlighted in red in **Fig. 5**).<sup>49</sup> We considered how  
 12 MSPs of PHU and NIPTU might change with changes to selected critical parameters in the TEA

1 (Fig. 5(a) and Fig. 5(b), respectively). The individual sensitivities of key variables in the  
2 production of NIPUs can be found in the SI (Fig. S.6(a)). The outlined process improvements  
3 bring the MSPs of bio-based NIPUs to levels comparable with the MSPs of fossil-based flexible  
4 PUs. With respect to PHU (Fig. 5(a)), a 0.52 USD kg<sup>-1</sup> drop in MSP results from a 25 % drop in  
5 PBN cost. In a separate TEA study, hexanediamine is adopted as a model compound for pricing  
6 amines (1.52 USD kg<sup>-1</sup>). If the cost of amine feeds in PHU production drop to the price of  
7 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  
8 in increase in production capacity were also examined, with capacity being the most influential  
9 variable in this analysis. An 0.88 USD kg<sup>-1</sup> drop in MSP results from raising production capacity  
10 to 9,000 tonne PHU yr<sup>-1</sup>. Thereby, it is shown how reductions in amine costs, reductions in capital  
11 cost, and increases in plant production capacity can bring the MSP of PHU below the range of  
12 fossil-based flexible PU MSPs. Cumulatively, these changes reduce the MSP of PHU to 1.18 USD  
13 kg<sup>-1</sup> and well below baseline costs.

14 With respect to NIPTU (Fig. 5(b)), a 0.50 USD kg<sup>-1</sup> drop in MSP results from a 25 % drop in  
15 TTEA cost. If the amine selling price drops to a comparable level to hexanediamine, the MSP of  
16 NIPTU drops a further 0.71 USD kg<sup>-1</sup>.<sup>35</sup> We also considered how variations of 25 % in ECH price  
17 and capital would affect the MSP of NIPTU. However, the most influential factor in reducing costs  
18 was once again production capacity. A 1.04 USD kg<sup>-1</sup> drop in MSP results from raising production  
19 capacity to 9,000 tonne NIPTU yr<sup>-1</sup>. After reductions in the price of amines, reductions in the price  
20 of ECH, reductions in capital costs, and increases in plant production capacity the MSP of NIPTU  
21 (4.39 USD kg<sup>-1</sup>) falls within the range of baseline PU MSPs. An even lower NIPTU MSP might  
22 be achievable with further increases in plant capacity or lower material costs.



**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 range of baseline PU prices.

1 Improvements to PHU and NIPTU reprocessing can similarly lower the MSPs of 2° PHU and  
 2 2° NIPTU (**Fig. 6(a)** and **Fig. 6(b)**). The individual sensitivities of key variables in the reprocessing  
 3 of NIPUs can be found in the SI (**Fig. S.6(b)**). For example (**Fig. 6(a)**), if the solvent price dropped  
 4 to levels comparable to the price of dichloromethane ( $0.57 \text{ USD kg}^{-1}$ ),<sup>50</sup> PHU MSP drops by 0.68  
 5  $\text{USD kg}^{-1}$ . As mentioned previously, improving depolymerization yield would greatly benefit the  
 6 MSP of 2° PHU. From a baseline depolymerization yield of 50 % (mol/mol), a 25 % (mol/mol)  
 7 improvement in yield results in a 1.71  $\text{USD kg}^{-1}$  drop in MSP for 2° PHU. Reaching a 100 %  
 8 (mol/mol) depolymerization yield results in a further 0.72  $\text{USD kg}^{-1}$  drop in MSP. A 25 % drop in  
 9 capital cost and in increase in production capacity were also examined. Capacity increases are the  
 10 second most influential variable behind depolymerization yield. A drop in MSP of 0.89  $\text{USD kg}^{-1}$   
 11 results from raising production capacity to 9,000 tonne 2° PHU  $\text{yr}^{-1}$ . Altogether, the MSP of  
 12 reprocessed PHU could be significantly lower than the MSP for fossil-based flexible PU and virgin

1 PHU if process improvements occur. Most importantly, improvements in the depolymerization  
2 yields of PHU must be achieved. Testing other depolymerization solvents or other types of PHU  
3 with different characteristic crystallinities or monomers hold promise to increase yield. Overall,  
4 the improvements we considered result in a MSP of 1.18 USD kg<sup>-1</sup> for 2° PHU, which is well  
5 below baseline costs.

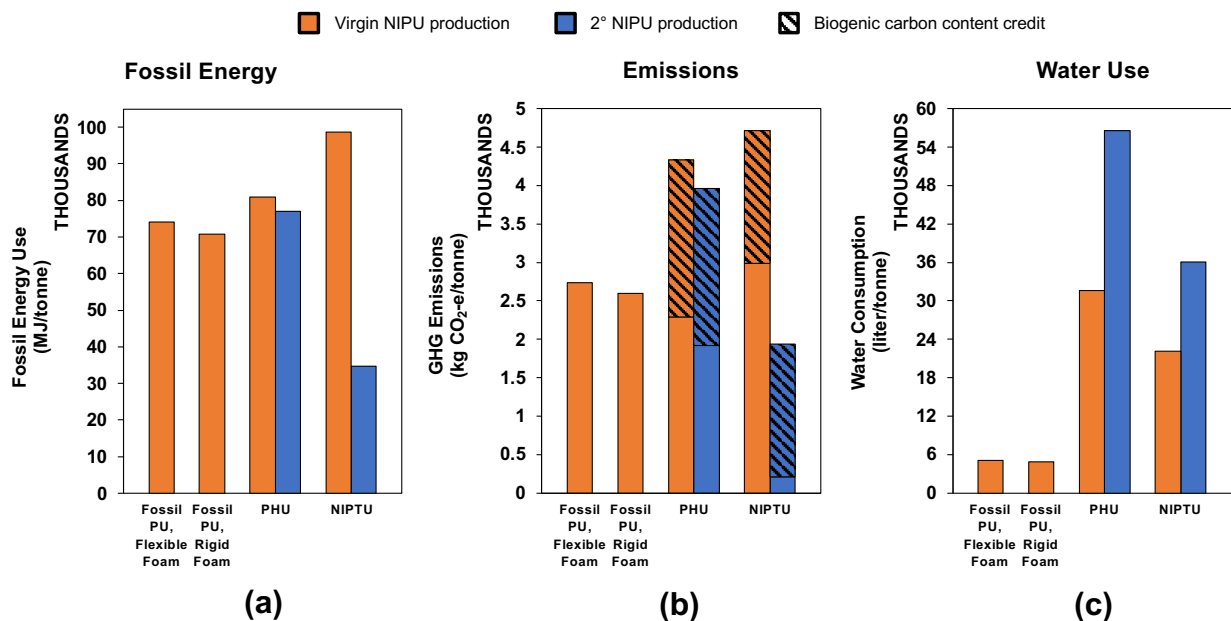
6 With respect to 2° NIPTU recovery (**Fig. 6(b)**), if the price of solvent dropped to 0.57 USD  
7 kg<sup>-1</sup> (comparable to the price of dichloromethane)<sup>50</sup> MSP drops by 0.25 USD kg<sup>-1</sup>. The NIPTU  
8 recovery process is also least sensitive to changes in capital cost. Production capacity was once  
9 again a highly influential cost variable. An 0.84 USD kg<sup>-1</sup> drop in MSP results from raising  
10 production capacity to 9,000 tonne NIPTU monomer yr<sup>-1</sup>. Although the MSP of 2° NIPTU was  
11 already below baseline costs, the aforementioned improvements could further reduce the MSP of  
12 2° NIPTU. After incremental decreases in solvent price, decreases in capital cost, and increases in  
13 NIPTU monomer production capacity, a final NIPTU monomer MSP of 1.08 USD kg<sup>-1</sup> is  
14 achievable.

15 The MSPs of PHU, NIPTU, 2° PHU, and 2° NIPTU were initially determined to be 5.37 USD  
16 kg<sup>-1</sup>, 7.16 USD kg<sup>-1</sup>, 5.47 USD kg<sup>-1</sup>, and 2.30 USD kg<sup>-1</sup>, respectively. After stepping along a path  
17 of cost abatement strategies, the following MSPs can be achieved (percentage reduction in price  
18 shown within parentheses): 3.15 USD kg<sup>-1</sup> (-41 %) for PHU, 4.39 USD kg<sup>-1</sup> (-39 %) for NIPTU,  
19 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  
20 results demonstrate that cost-competitive NIPUs and 2° NIPUs are possible, especially if research  
21 and development efforts focus on improving yields and exploring low-cost solvents and amines  
22 when applicable. Furthermore, designing plants with capacities that take advantage of economies  
23 of scale also benefit the commercial viability of these polymers.



## 1 Life cycle analysis results

2 In the LCA, the environmental impacts of each system are reported for the life cycle impact  
3 categories of fossil energy use (**Fig. 7(a)**), GHG emissions (**Fig. 7(b)**), and water consumption  
4 (**Fig. 7(c)**). The fossil energy uses of each operation of every process are tallied and juxtaposed  
5 with baseline fossil-based flexible and rigid PU fossil energy usage (**Fig. 7(a)**). The fossil energy  
6 input per tonne of PHU production is 9.3 % and 14.3 % greater than the fossil energy input required  
7 per tonne of flexible and rigid fossil-based PU foam, respectively. The fossil energy input per  
8 tonne of NIPTU production is 33.1 % and 39.2 % greater than the fossil energy input required per  
9 tonne of flexible and rigid fossil-based PU foam production, respectively. Fossil energy use per  
10 tonne of reprocessed NIPU is also tallied (blue bars in **Fig. 7(a)**) and shown to require less fossil  
11 energy than the fossil energy required per tonne of virgin NIPU produced. Reprocessed NIPU from



**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 production of PU flexible and rigid foams. Orange bars are representative of PU/NIPU production and blue bars are representative of NIPU reprocessing.

1 PHU requires 4.7 % less fossil energy than manufacturing virgin PHU, and reprocessed NIPU  
2 from NIPTU requires 64.8 % less fossil energy than manufacturing virgin NIPTU. Fossil energy  
3 consumption associated with material feeds and energy demands to NIPU production can be found  
4 in **Fig. S.7**.

5 GHG emissions associated with fossil-based PU production as well as PHU and NIPTU  
6 production are also tallied (**Fig. 7(b)**). Percentage differences in GHG emissions, not considering  
7 biogenic content, are larger than the differences observed in fossil energy inputs to fossil-based  
8 PU versus virgin NIPU. This is because fossil energy only includes fossil-based energy input, and  
9 not total energy, whereas GHG emissions encompass total process emissions. The emissions per  
10 tonne of PHU production, after considering a biogenic emissions credit, is 16.1 % and 11.5 %  
11 lower than the emissions generated per tonne of fossil-based flexible and rigid PU foam  
12 production, respectively. The emissions generated per tonne of NIPTU production, including the  
13 biogenic emissions credit, is 9.4 % and 15.4 % greater than the emissions generated per tonne of  
14 fossil-based flexible and rigid PU foam production, respectively. Emissions per tonne of NIPU  
15 reprocessed from PHU and NIPTU are depicted as blue bars in **Fig. 7(b)**. Note that biogenic  
16 contents of 2° NIPUs are repetitively depicted for reference, and care should be taken not to double  
17 count biogenic emission credits. Regardless of biogenic credit considerations, 2° NIPTU has lower  
18 GHG emissions than virgin NIPTU production.

19 Water consumptions were tallied and compared (**Fig. 7(c)**). The water consumption from  
20 producing flexible and rigid PU foam from fossil fuels are shown in the first two columns. Water  
21 consumption per tonne of PHU production is 6.2 and 6.5 times greater than water consumption per  
22 tonne of fossil fuel-based flexible and rigid PU foam production, respectively. Water consumption  
23 per tonne of NIPTU production is 4.3 and 4.5 times greater than the water consumption per tonne

1 of fossil fuel-based flexible and rigid foam production, respectively. Unlike the impact categories  
2 of fossil energy use and emissions, the water consumption associated with reprocessing both NIPU  
3 materials is considerably greater than the water consumption associated with virgin NIPU  
4 production. This is because the use of water as a solvent during the depolymerization process  
5 makes it inherently water demanding.

6 Virgin PHU and NIPTU production has higher fossil energy use and water consumption than  
7 baseline values. After accounting for biogenic carbon credits, PHU and NIPTU have lower and  
8 higher GHG emissions, respectively, than baseline emissions. The fossil energy use per tonne of  
9 2° NIPUs is consistently lower than the fossil energy use per tonne of both virgin PHU and NIPTU  
10 production. In fact, the fossil energy use per tonne of NIPU recovered from NIPTU is at least 51  
11 % lower than the fossil energy consumption per tonne of virgin PU foam produced from fossil  
12 fuels. Without considering biogenic emission credits, the emissions per tonne of 2° NIPTU is at  
13 least 25 % lower than baseline emissions. Higher fossil energy use and GHG emissions for 2° PHU  
14 than 2° NIPTU production is again primarily driven by low depolymerization yields.

15 Aside from improving depolymerization yield, high fossil energy use for virgin NIPU  
16 production can possibly be addressed by identifying energy intensive material inputs. A  
17 breakdown of the fossil energy demands from the inputs to PHU and NIPTU production is in the  
18 SI (**Fig. S.7**). Material process inputs drive fossil energy demands for both NIPU production  
19 processes. The ammoxidation conversion in XDA production was 53 % in the base case for PHU  
20 production. If these conversions improved to 80 % and biomethanol was used rather than fossil-  
21 based methanol in PHU production, a 33 % reduction in the fossil energy use can be  
22 realized.<sup>39,42,51,52</sup> These improvements alone would reduce fossil energy use for PHU below  
23 baseline values. Analysis of the GREET model output for NIPTU production showed that xylene

1 accounted for 16 % of the fossil energy consumption from all material feeds (**Fig. S.7(b)** and **Fig.**  
2 **S.7(d)**). Recycling xylene can result in an almost 16 % reduction in the fossil energy use of NIPTU  
3 production.

#### 4 CONCLUSION

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

#### 18 SUPPORTING INFORMATION

19 The SI contains process flow diagrams, sensitivity diagrams, supplementary raw material  
20 energy use data, and tabulated market value data.

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22

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