

Supporting Information

Assessment of Plant and Microalgal Oil Derived Non-isocyanate Polyurethane Products for Potential Commercialization

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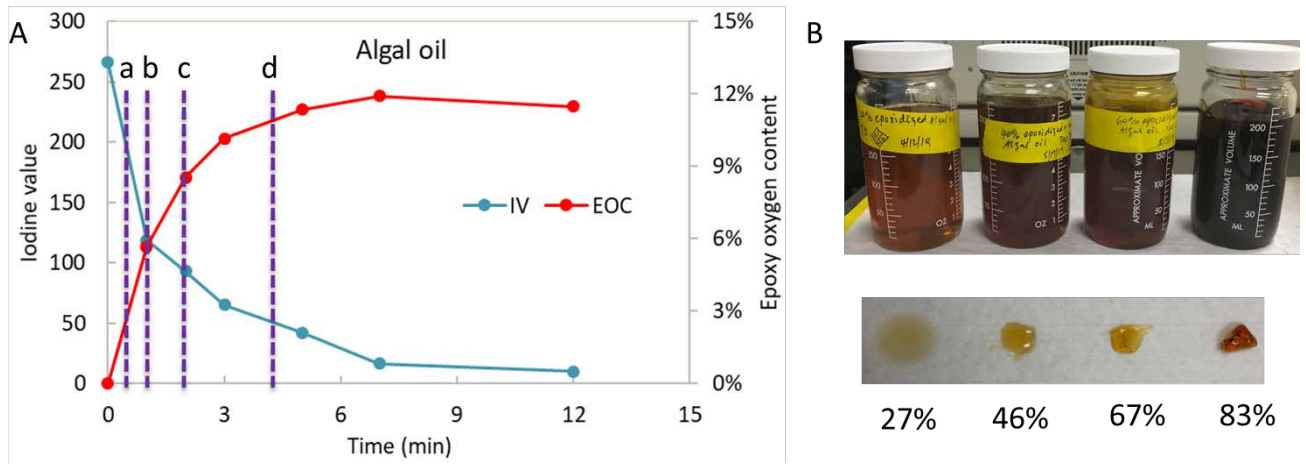


Figure S1. Epoxidation of algal oil (A), and partially carbonated algal oil (B)

a: epoxidation 0.5h (27% epoxy), b: epoxidation 1h (46% epoxy), c: epoxidation 2.5h (67% epoxy), d: epoxidation 4.5h (83% epoxy)

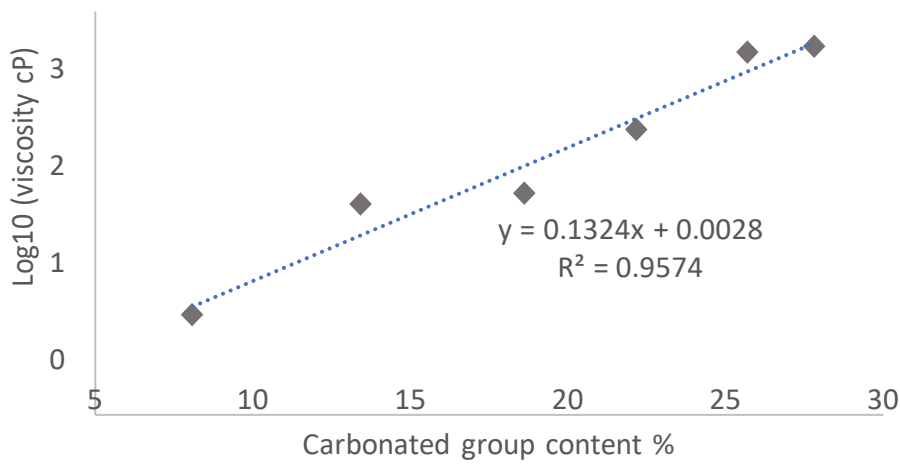


Figure S2. Impact of carbonated group content on viscosity

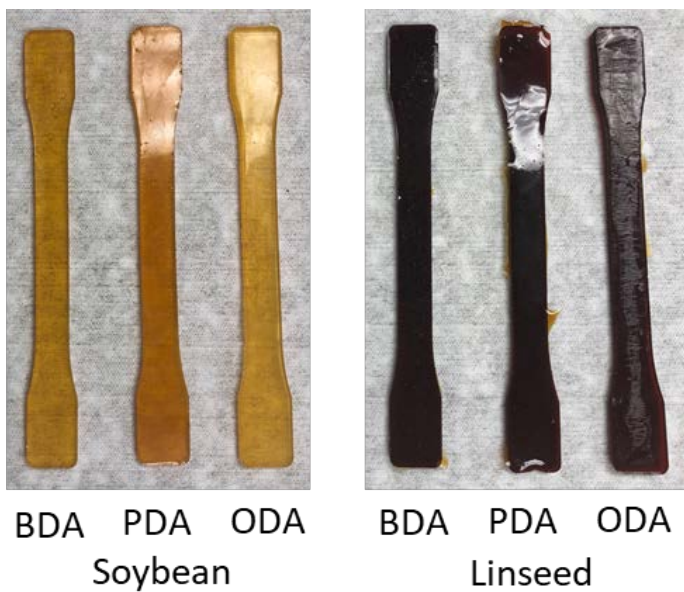


Figure S3. NIPU samples derived from soybean and linseed oil

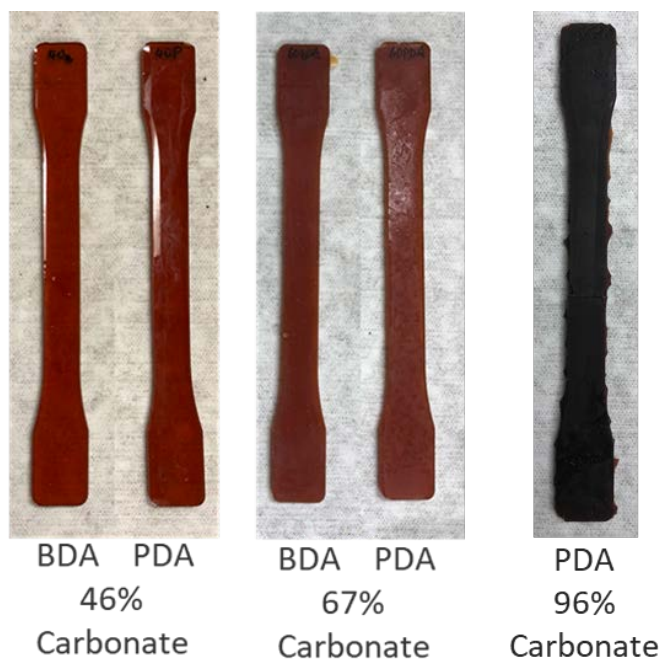


Figure S4. NIPU samples derived from algae oil (with different carbonate degree)

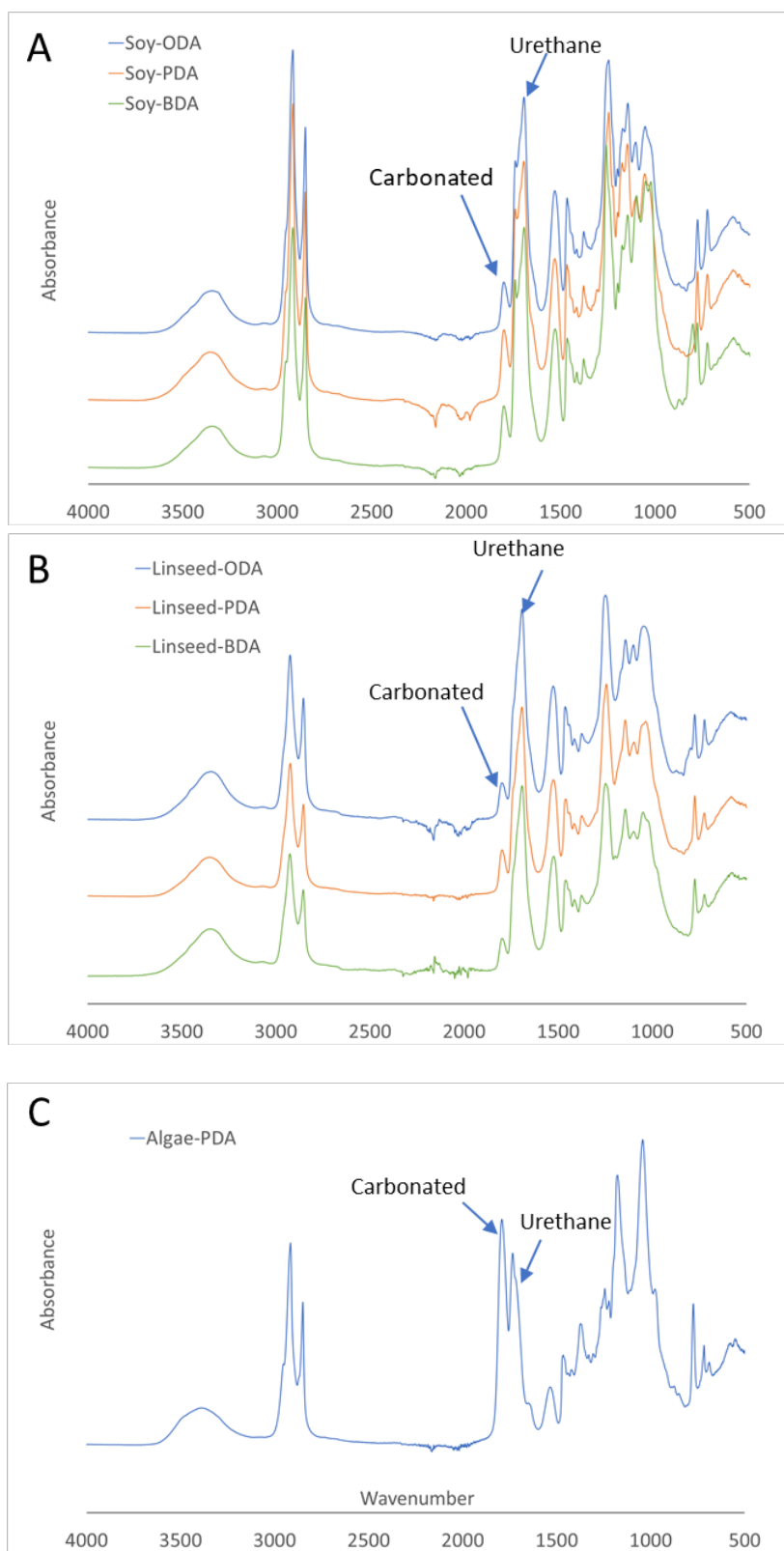


Figure S5. FTIR of NIPU resin samples (A) soybean; (B) linseed; (C) algae-PUFA

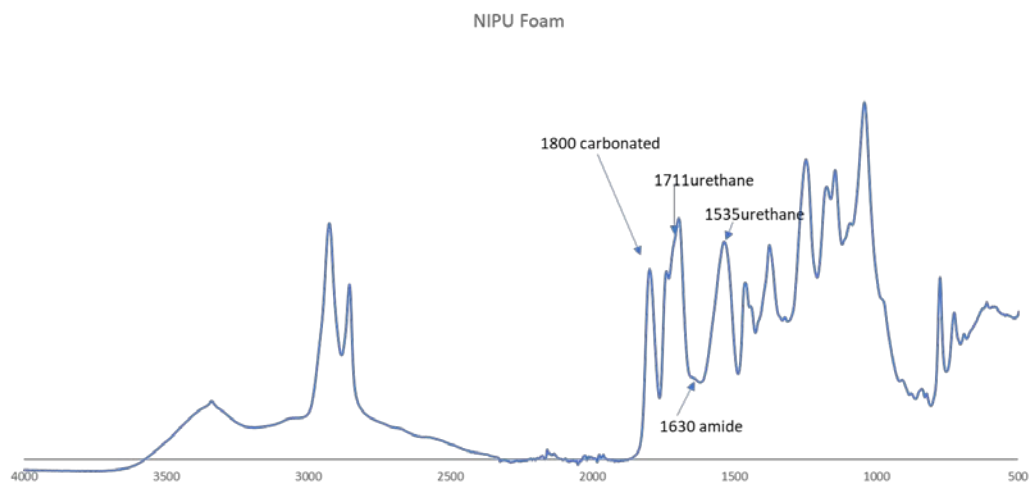


Figure S6. FTIR of NIPU foam derived from linseed oil

Table S1. Batch formula for NIPU foam samples.

Ingredient	weight (g)	Mole (mmol)
Carbonated linseed oil	79.3	67
Hexamethylene diamine	20.7	175
Citric Acid	2.67	14
Ammonium Bicarbonate	5.78	42
Triazabicyclodecene	0.3	2
Water	3.34	183
Vorasurf 5951	0.5	

Techno-economic Analysis

Selection of Plant Scale

For this analysis, a base-case scale of 2800 tons per year (TPY) of polyurethane foam product was chosen based on information obtained from an engineering subcontractor, Nexant;¹ this scale is also consistent with information on conventional polyurethane facilities from industrial databases. However, based on guidance from industry, larger polyurethane production facilities can reach capacities on the order of 100,000 TPY; thus, a range of scales is considered as a sensitivity (**Figure 6**). It should also be noted that capacity information for the largest foam production machines obtained from industry databases, suggests that foam production capacities on the order of 40,000 TPY from a single machine are possible, assuming a 24-hour operation and allowing for a 3 hour maintenance cycle every 8 hours. Although polyurethane plants do not typically operate on a 24-hour basis, this suggests that the economy of scale benefit could apply for foam production line sizes significantly larger than the identified base-scale. Above scales of 40,000 TPY, a scaling factor of one is assumed for foam production equipment.

Feedstock Selection

Based on the superior tensile strength results of the resins made from linseed oil (double bond number of 6.3), a generic triglyceride with a double bond number of 6 was chosen as a representative feedstock for the TEA model. Theoretically, this triglyceride feedstock could be vegetable or algal oil; however, the current costs for algal oil with high PUFA content are too high to be considered commercially relevant at this time, as these oils are produced for the nutraceutical market where the price and volumes are obstacles for NIPU production. However, it is possible that successful development of NIPU technology could provide incentives to expand the market for high PUFA algal oil and thus drive production volumes up and costs down.

Accordingly, a feedstock price associated with linseed oil (\$0.44/lb, a 5-year average of linseed oil price from industry databases) was chosen for the base case TEA. However, it should be emphasized that the results of this analysis do not directly translate to a NIPU facility that utilizes other lipids including those derived from algal biomass, since they would be associated with a different cost. For the purpose of determining impact of lipid cost on MPSP, a range of feedstock costs are considered in **Figure 6**.

Production of NIPU Foam

It should also be noted that discussions of TEA assume the production of a saleable flexible polyurethane foam. The exact end-use of this foam is not identified, given that foam properties can be tuned by specific process parameters such as conversion through epoxidation and carbonation. Additionally, profiles of triacyl-glyceride (TAG) that are fed into the process can affect foam properties. The end-uses for this foam could include flexible bedding foams, transportation, furniture, flooring underlay, packaging, and textiles, which in total account for approximately 1.3 MM tons per year of flexible polyurethane foam in the US market. The foam produced in this study demonstrates a proof-of-concept to produce foam with the potential to meet these end-uses, with potential for optimization of a

specific product. While the samples produced in this work would be generally classified as rigid foams, final product specifications could be tuned by varying process conditions or adding monomers with low carbonate density.

Process Summary and Assumptions – NIPU Plant

A block flow diagram for the modeled NIPU facility is shown in **Figure 1**. Process assumptions relevant to each area are given in **Tables S2, S3, and S4**. Unless otherwise noted, process variables are consistent with experimental conditions.

TAG with a double bond number of 6 is fed into the epoxidation reactor, along with the required reactants (pure hydrogen peroxide and glacial acetic acid), acidic heterogeneous catalyst (Amberlite IR-120), and a toluene solvent. The epoxidation reactor is a jacketed CSTR slurry reactor with a residence time of 9 hours. In the epoxidation reactor, the TAG reacts with peracetic acid (produced in situ by H₂O₂ and acetic acid) to form an epoxide. A toluene solvent is used to prevent ring opening, as is consistent with academic and patent literature for the epoxidation of fatty acids.^{2,3} Alternatively, epoxidation and ring opening can be achieved simultaneously in the presence of water to produce a polyol; in this case, this is an undesirable reaction and thus water content in the reactor must be minimized.

The epoxidation reaction is assumed to proceed to 100% conversion. Full conversion is not necessarily required, though incomplete conversion could have an impact on final NIPU properties and decreased yields on a weight per weight of TAG feedstock basis. This assumption is deemed reasonable given that experimental results demonstrate the ability of a linseed oil-based resin to produce a functional NIPU product. This assumption is looked at in more detail in the sensitivity analysis section.

After epoxidation, the reactor effluent is washed with water to remove excess acetic acid and is subsequently filtered to recover the catalyst. The organic phase (toluene and epoxidized TAG) separates from the aqueous with minimal aqueous carryover; any residual water is removed by a molecular sieve dryer. The recovery of acetic acid, though achievable by various distillation strategies⁴, was determined not economically justifiable; therefore, the aqueous phase is sent to wastewater treatment. The organic phase, devoid of any water, is then flashed at 140°C to separate and recycle the majority of the toluene solvent before being placed in two sequential wiped-film evaporators (run at 140°C and 260°C, respectively, with both at mild vacuum) for removal of high-boiling volatiles, which can cause odors in the final product.

The epoxidized TAG is then cooled and sent to the carbonation reactor, which is modeled as a CO₂-sparged CSTR operating at 500 psig. It should be noted that literature suggests carbonation can be achieved at lower pressures on the order of 100-200 psig⁵; however, a modeled operating pressure of 500 psig was chosen to be consistent with the experimental conditions. A homogeneous catalyst, tetra-n-butylammonium bromide (TBAB), is also fed into the reactor. In the carbonation reactor, the CO₂ reacts with epoxide groups to produce 5-membered cyclic carbonate groups. Given that the reactor is constantly mixed, CO₂ in the headspace is also assumed to be available for reaction. A conversion of 100% of the epoxide groups is assumed, with 50% loss of CO₂ assumed out of the reactor vent. The carbonation commercial design varies from the experimental design in that a solvent (ethyl acetate) is

used to thin the oil for recovery after reaction, while the TEA process does not use a solvent. For an industrial process, it is assumed that this viscous liquid would be flowable with the help of a positive-displacement pump, which are designed to handle high-viscosity fluids. In addition to the successful solvent-free carbonation reaction demonstrated here, prior work by Doley and Dolui has shown successful solvent-free carbonation of epoxidized sunflower oil, which has a similar oil content to linseed oil.⁶

After reaction, the carbonated oil is washed with water to remove the water-soluble TBAB catalyst. For the sake of this analysis, it was assumed that the TBAB catalyst would be unrecoverable from the water phase. However, it may be that the TBAB could be recovered by ion exchange or simple evaporation of the water. This possibility is examined in the sensitivity analysis section and could result in savings of \$0.09/lb at a 90% recovery rate, but should be verified experimentally. Alternatively, other studies have looked at using a silica-supported heterogeneous catalyst to allow for easier recovery.⁷ Though the results were promising, the heterogeneous catalyst would require further improvement to match the activity of the homogeneous TBAB.

The carbonated resin is then sent to the NIPU foam production section, where, in the presence of a foaming agent, it polymerizes with a diamine to produce a foam product. The foam production section looks very similar to a conventional polyurethane foam production facility, which both consist of a raw material tank farm, a mixing and dosing section, a foaming section, and a manual cutting and handling section. Hexanediamine was chosen as a representative diamine for the model due to its common use as a reagent in the production of Nylon 6,6. Ammonium bicarbonate and citric acid are used as foaming agents. Additional reagents considered in the foaming section include a catalyst (Triazabicyclodecene, or TBD), surfactant (Vorasurf 5951), and water. In the foaming section, the ammonium bicarbonate reacts with citric acid to form triammonium citrate, CO₂, and water. Some of the ammonium bicarbonate also decomposes to form NH₃, CO₂, and water. It is assumed that 50% of the gaseous CO₂ and NH₃ are retained in the closed cells of the NIPU foam, and that 95% of the water is retained (resulting in a moisture content of <4% in the final product).

Process Summary and Assumptions – Conventional PU Plant

For comparison, a conventional (isocyanate-based) polyurethane plant was also modeled. This TEA model was based on inputs from work with a subcontractor (Nexant). Briefly, it involves a one-pot epoxidation and ring opening step of the TAG feedstock to produce a polyol.¹ That polyol is then reacted with toluene di-isocyanate to produce flexible polyurethane foam. All costs and assumptions are identical to the NIPU plant where applicable, including raw material and utility costs, equipment costs (for the epoxidation and ring opening and foam production areas), personnel needs, and economic assumptions.

Equipment and Material Costs

The installed equipment costs for several areas are based on subcontractor inputs as described in the 2019 Algae Biorefinery Technical Report.¹ This is true for both the epoxidation and foam production areas; equipment costs for the carbonation section are based on information from Aspen Capital Cost

Estimator (ACCE) as well as other biorefinery analyses.^{8,9} It should be noted that the equipment costs for the epoxidation section were originally based on a “one-pot” epoxidation and ring opening reaction section; however, the process design for each are very similar, and the residence time for the one-pot reactor is slightly higher (roughly 12 hours for complete ring opening) than the 9 hours used in this study.¹⁰ Given the difficulty in accounting for this residence time disparity in the lumped equipment costs, no adjustment was made (meaning that the resulting epoxidation cost estimations err on the conservative side). The lumped installed cost also accounts for the wiped film evaporators, which would be used in both processes to eliminate high-boiling impurities. Therefore, it was deemed an appropriate approximation to use these costs for the epoxidation approach presented here. Likewise, the foam production line would be very similar to the conventional (isocyanate based) foam production; thus, those costs are assumed here. Given this similarity, further potential economic benefits could be realized from retrofitting an existing foam production facility for NIPUs. These benefits are considered in the sensitivity analysis.

Raw material costs are obtained from industry databases and prior works,^{9,11} and utility costs (low-pressure steam, cooling water, and wastewater treatment) are determined using correlations from literature.¹²

Economic Analysis Approach

The approach used in this economic analysis is consistent with prior works and will not be repeated in such detail here.⁹ Briefly, the mass and energy balance from the process model is utilized to size equipment based on various process parameters such as stream flows, temperatures, and pressures. These parameters are used in conjunction with a scaling factor to adjust equipment costs from their original costs. Raw material and utility requirements are determined from the process model. Direct and indirect costs are determined as factors of the total installed equipment costs (details shown in **Table S5**). Fixed costs (e.g., employee wages) are also considered and adjusted based on the size of the plant. Other fixed costs, such as maintenance, insurance, and taxes, are calculated as factors of capital cost. Finally, with the capital and operating expenditures of the process determined, a discounted cash flow calculation is performed with the assumptions listed in **Table S6**. This calculation accounts for all cash flows related to the construction and operation of the NIPU plant over a 30-year lifetime. Within this analysis, the selling price of NIPU (\$/lb) is determined such that it results in a net present value of 0 for the construction and operation of the plant.

Results: Sensitivity Analysis

A single-point sensitivity analysis on several key parameters of interest was performed to determine the impact of each parameter on process economics. Results of the sensitivity analysis are shown in **Figure S3**. As discussed, plant production capacity can have a dramatic effect on economics (**Figure 6**). To compare this effect to other parameters, NIPU production capacities of 1,000 and 10,000 TPY are considered; however, it is acknowledged that significantly higher capacities are likely possible for large commercial plants. When the NIPU production capacity is increased to 10,000 TPY, an MPSP of \$1.50/lb (a savings of \$0.67/lb) can be realized, relative to the base case at \$2.17/lb. Inversely, a production

capacity of 1,000 TPY is associated with a significantly higher MPSP of \$3.35/lb. A plant scale of roughly 3364 TPY (1.2x the base capacity) would correlate to an MPSP of \$2.04/lb, which is equivalent to a typical market price for conventional polyurethane foam.

The potential benefit of retrofitting an existing polyurethane foam production facility was also examined. Given that foam production technology would not differ significantly from an isocyanate-based operation, it is likely that much of the equipment could be retrofitted to meet NIPU production needs. It was assumed that this retrofitting would result in a 75% reduction in installed equipment costs for the foam production plant, and a 100% reduction in the cost for the polyurethane foam warehouse. The resulting MPSP of \$1.90/lb (a reduction of \$0.27/lb from the baseline MPSP) showed that retrofitting is another potential pathway for meeting polyurethane market price targets.

Total installed cost also had a significant impact on MPSP. When varied by a factor of 25% in either direction, MPSP saw a net change of \$0.19/lb in each case. This range of values for installed costs is meant to address potential inaccuracies for equipment cost estimations, especially reactors, since the specifications here are done at a fairly high level. Though significant, this impact is overshadowed by the dramatic implications plant scales can have on process economics.

Several assumptions made in the model were tested to determine the possible impacts if those assumptions were not valid. For example, 100% conversion was assumed in each step of the process, as opposed to experimentally observed conversion of 87% and 95% in epoxidation and carbonation, respectively (usually >99% carbonation conversion was achieved). To check these assumptions, conservative experimental conversions were used in a sensitivity case. This resulted in an MPSP of \$2.27/lb, an increase of \$0.10/lb, which can be attributed to a lower production rate for the same amount of raw materials (given incomplete conversion). This additional cost could potentially be reduced by reducing the relative amounts of reactants, assuming the same conversions could be achieved. However, it should be noted that any product quality effects resulting from the incomplete conversion are not captured here.

In the base case, the catalyst for the carbonation reaction (TBAB) was assumed to be unrecoverable from the water after washing. Given a relatively low price of TBAB, this loss of catalyst could be acceptable. However, if 90% of the catalyst was recovered and recycled, this would result in a net MPSP benefit of \$0.09/lb. Recovery on this order may be possible by ion exchange or simple evaporation. Similar savings would be seen if a heterogeneous (solid) catalyst with a similar activity was used, assuming that the solid catalyst could be easily recoverable from the carbonated oil.

Another sensitivity case was run using butanediamine as the NIPU cross-linker, rather than the hexanediamine used in the base case. Butanediamine or other alternative diamines may be chosen as a cross-linker based on more desirable final product properties. Since costing information was not available for butanediamine, the hexanediamine price (\$0.69/lb) was maintained. This case resulted in an increase of \$0.07/lb to the MPSP, resulting from a lower mass contribution of the diamine to the final product. Though not insignificant, this shows the flexibility of the process to switch to various diamines, based on what is desired for final NIPU product performance. Separately, the diamine price in the base case was varied by 25% in either direction. This did not have a significant effect on MPSP (net impact on MPSP was \$0.04 /lb for each).

Table S2. TEA process parameters for epoxidation.

Parameter	TEA Model Value
Temperature	65°C
Residence Time	9 hours
Catalyst	Ion exchange resin (Amberlite IR-120)
Catalyst loading	0.25 w/w oil
Solvent	Toluene
Solvent: TAG weight ratio	0.5
Mole ratio H ₂ O ₂ : acetic acid: double bond	1.5: 0.5: 1
Conversion	100%*

*compared to an experimental conversion of 87%

Table S3. TEA process parameters for carbonation.

Parameter	TEA Model Value
Reactor Design	CSTR with CO ₂ sparge
Temperature	140°C
Pressure	140-500 psi (500 psi experimental)
Residence Time	23 hours
Catalyst	TBAB
Catalyst loading	0.05 mol/mol epoxy group
Solvent	None
Conversion	100%*
CO ₂ Utilization	50%

*compared to an experimental conversion of 95%

Table S4. TEA process parameters for foam processing.

Parameter	TEA Model Value
Facility Design	(1) Raw material tank farm (2) Mixing/dosing (3) Foaming (4) Cutting & handling
Diamine loading	0.5 mol/mol carbonate group
Foaming agents	Ammonium bicarbonate, citric acid (set to match experimental loadings in Table S1)
Other chemicals	TBD, surfactant, water (set to match experimental loadings shown in Table S1)
Conversion of carbonated TAG	100%
Temperature	80°C

Table S5. Direct and indirect cost factors for TEA model.

Cost type	Parameter	TEA Model Value
Direct	Polyurethane warehouse	Sized independently to allow for foam storage, in addition to normal warehouse cost
Direct	General warehouse	4% of ISBL ^a
Direct	Site development	9% of ISBL ^a
Direct	Additional Piping	4.5% of ISBL ^a
Indirect	Prorateable Expenses	10% of TDC ^b
Indirect	Field Expenses	10% of TDC ^b
Indirect	Home Office & Construction Fee	20% of TDC ^b
Indirect	Project Contingency	10% of TDC ^b
Indirect	Other Costs (Start-Up, Permits, etc.)	10% of TDC ^b

^aISBL = "Inside Boundary Limits," includes installed cost for all non-utility plant equipment

^bTDC = "Total Direct Costs," sum of all installed costs plus other direct costs

Table S6. Financial assumptions for TEA model.

Parameter	TEA Model Value
Plant life	30 years
Plant throughput	2,800 US tons per year (TPY) NIPU
Cost year dollar	2016\$s
Capacity Factor	90%
Discount rate	10%
General plant depreciation	MACR
General plant recovery period	7 years
Steam plant depreciation	MACR
Steam plant recovery period	20 years
Federal tax rate	21%
Financing	40% equity
Loan terms	10-year loan at 8% APR
Construction period	3 years
First 12 months' expenditures	8%
Next 12 months' expenditures	60%
Last 12 months' expenditures	32%
Working capital	5% of fixed capital investment
Start-up time	6 months
Revenues during start-up	50%
Variable costs during start-up	75%

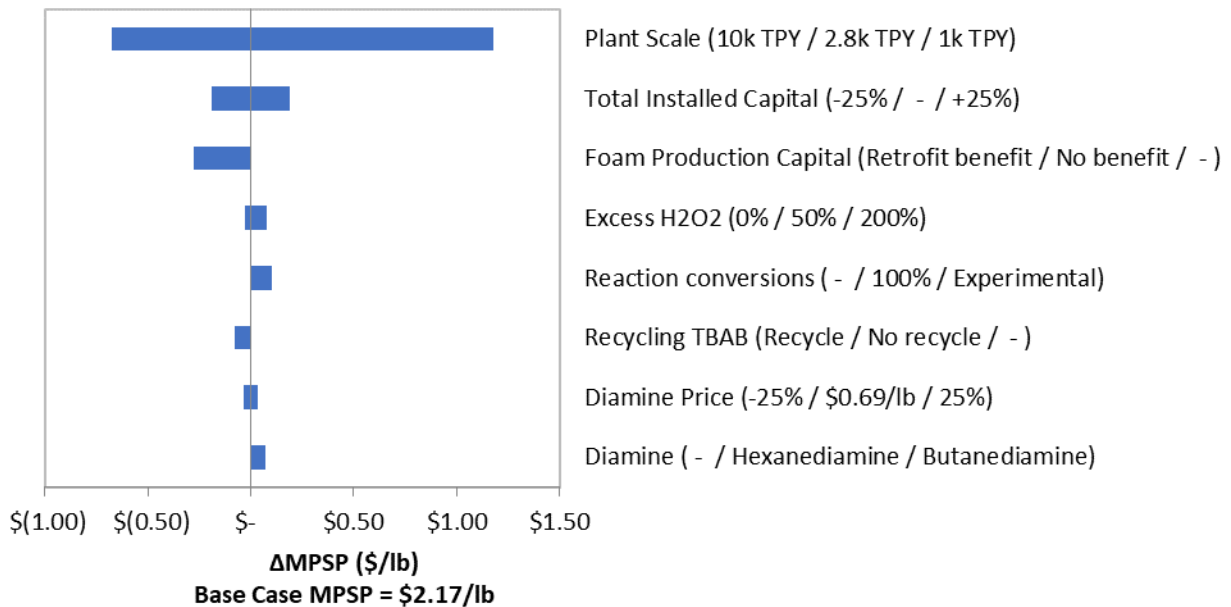


Figure S7. Single-point sensitivity analysis results for the TEA model. Variables in the parenthesis are associated with the lowest MPSP, the base case value, and the highest MPSP, respectively.

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