Supplementary Information (SI) for RSC Sustainability.

Supporting Information

Life-Cycle Analysis of Microalgae-based Polyurethane Foams

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Number of pages: 31

Number of Figures: 9

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S1 Life cycle assessment (LCA) data

S1.1 GHG emissions of conventional counterparts for the biorefinery products

Table S1 presents the values of the GHG emissions, fossil energy, and water consumption used in the estimation of the impacts of conventional counterpart pathways in this study.

Table S1. Environmental impacts of conventional counterparts.[1]

Coproduct	GHG emissions	Fossil energy	Water consumption
Flexible PU	3.43 kg CO_2e/kg	72.4 MJ/kg	4.97 L/kg
Rigid PU	3.21 kg CO_2e/kg	69.2 MJ/kg	4.79 L/kg
Petroleum diesel	91.4 g CO_2e/MJ	1.18 MJ/MJ	0.083 L/MJ
Petroleum naphtha	92.9 g CO_2e/MJ	1.15 MJ/MJ	0.076 L/MJ
Electricity	0.47 kg CO_2e/kWh	5.91 MJ/kWh	2.23 L/kWh

S1.2 Life cycle inventory data of the biorefinery

This section presents the material and energy requirements obtained from the Aspen Plus modeling of the microalgae biorefinery. This information was obtained from previous reports[2–5] and is presented on a per hour and a per kg of product basis. The information on a per kg of PU foam was utilized for evaluation of the environmental impacts of Bio-PU and Bio-NIPU.

Table S2. Material and energy requirements for the cultivation of one kg of microalgae ash-free dry weight (AFDW).[2,3]

	Per hour of operation	Per kg microalgae AFDW
Process inputs		
Carbon dioxide (kg)	34,112	2.22
Ammonia (kg)	309	0.02
Diammonium phosphate (kg)	149	0.01
Process water input (Saline, kg)	511,527	33.29
Electricity (MJ)	32,569	2.12
Product		
Microalgae biomass AFDW (kg)	15,364	1

Table S3. Material and energy requirements of the microalgae biorefinery to produce Bio-PU.[2,4]

Basis	per hour of operation		per kg Bio-PU	
Route	Carboxylic acid (CA) intermediate	2,3-butanediol (BDO) intermediate	Carboxylic acid (CA) intermediate	2,3-butanediol (BDO) intermediate
Process inputs				
Feedstock				
Microalgae Biomass AFDW (kg)	15,987	15,987	4.45	4.45
Pretreatment				
Sulfuric acid (93%) (kg)	1,420	1,420	0.40	0.40
Ammonia (kg)	459	459	0.13	0.13

Lipid extraction and clean-up				
Hexane (kg)	84	84	0.02	0.02
Ethanol (kg)	34	34	0.01	0.01
Phosphoric acid (kg)	46	46	0.01	0.01
Silica (kg)	5	5	0.00	0.00
Clay (kg)	9	9	0.00	0.00
Carboxylic Acid Conversion				
Corn steep liquor (kg)	721	N.A.	0.20	N.A.
Diammonium phosphate (kg)	75	N.A.	0.02	N.A.
Hydrotalcite (kg)*	1	N.A.	2.8×10^{-4}	N.A.
Flocculant (kg)	64	N.A.	0.02	N.A.
Hexane (kg)	1	N.A.	0.00	N.A.
2,3-BDO Conversion				
Corn steep liquor (kg)	N.A.	107	N.A.	0.03
Diammonium phosphate (DAP, kg)	N.A.	13	N.A.	0.00
Hydrogen (kg)	N.A.	89	N.A.	0.02
Flocculant (kg)	N.A.	64	N.A.	0.02
Dehydration catalyst (kg)*	N.A.	0.07	N.A.	1.9×10^{-5}
Oligomerization catalyst (kg)*	N.A.	0.13	N.A.	3.6×10^{-5}
Final Fuel Upgrading (HDO/HI)				
Hydrogen (kg)	107	97	0.03	0.03
One step HDO/HI catalyst (1% Pt/SAPO-11, kg)*	0.23	0.25	6.4×10^{-5}	7.0×10^{-5}
Polyurethane Production				
Formic acid (kg)	347	347	0.10	0.10
Hydrogen peroxide (kg)	549	549	0.15	0.15
Nitrogen (kg)	52	52	0.01	0.01
Toluene diisocyanate (kg)	953	953	0.27	0.27
Diethanolamine (kg)	9	9	0.00	0.00
Surfactant (kg)	17	17	0.00	0.00
Tin catalyst (stannous octoate, kg)*	6	6	1.7×10^{-3}	1.7×10^{-3}
DABCO (1,4-diazabicyclo[2.2.2]octane, kg)*	3	3	8.3×10^{-4}	8.3×10^{-4}
Other Resource Consumption				
Supplemental natural gas (Combined, MJ)	44,502	60,342	12.39	16.79
Supplemental natural gas (fuel-only, MJ)	5,657	35,639	1.57	9.92
Supplemental natural gas (PU-only, MJ)	43,088	57,042	11.99	15.88
Process water (Combined, L)	47,913	54,538	13.34	15.18
Process water (fuel-only, L)	100	31,910	0.03	8.88
Process water (PU-only, L)	17,827	17,819	4.96	4.96
Process outputs				
CO2 Recycle				
CO2 (biogenic, kg)	9,090	8,981	2.53	2.50
CO2 (fossil, kg)	5,986	9,467	1.67	2.63
Products				
Diesel (MJ)	97,309	88,964	27.08	24.76
Naphtha (MJ)	40,265	51,410	11.21	14.31
Polyurethane (kg)	3,593	3,593	1.00	1.00
Electricity exported to grid (kWh)	5,045	5,846	1.40	1.63
Recovered streams				
AD Digestate cake - Bioavailable N (kg)	19	18	0.01	0.01

AD Effluent - Ammonia (kg)	233	228	0.06	0.06
AD Effluent - Diammonium phosphate (kg)	110	81	0.03	0.02
Recycled water (L)	105,285	107,533	29.30	29.93

* Considered negligible for the LCA

Table S4. Material and energy requirements of the microalgae biorefinery to produce Bio-NIPU.[2,5]

Basis	per hour of operation		per kg Bio-NIPU	
Route	Carboxylic acid (CA) intermediate	2,3-butanediol (BDO) intermediate	Carboxylic acid (CA) intermediate	2,3-butanediol (BDO) intermediate
Process inputs				
Feedstock				
Microalgae Biomass AFDW (kg)	15,987	15,987	3.52	3.52
Pretreatment				
Sulfuric acid (93%) (kg)	1,420	1,420	0.31	0.31
Ammonia (kg)	459	459	0.10	0.10
Lipid extraction and clean-up				
Hexane (kg)	84	84	0.02	0.02
Ethanol (kg)	34	34	0.01	0.01
Phosphoric acid (kg)	46	46	0.01	0.01
Silica (kg)	5	5	0.00	0.00
Clay (kg)	9	9	0.00	0.00
Carboxylic Acid Conversion				
Corn steep liquor (kg)	721	N.A.	0.16	N.A.
Diammonium phosphate (kg)	75	N.A.	0.02	N.A.
Hydrotalcite (kg)*	1	N.A.	2.2×10^{-4}	N.A.
Flocculant (kg)	64	N.A.	0.01	N.A.
Hexane (kg)	1	N.A.		N.A.
2,3-BDO Conversion				
Corn steep liquor (kg)	N.A.	107	N.A.	0.02
Diammonium phosphate (DAP, kg)	N.A.	13	N.A.	0.00
Hydrogen (kg)	N.A.	89	N.A.	0.02
Flocculant (kg)	N.A.	64	N.A.	0.01
Dehydration catalyst (kg)*	N.A.	0.07	N.A.	1.5×10^{-5}
Oligomerization catalyst (kg)*	N.A.	0.13	N.A.	2.9×10^{-5}
Final Fuel Upgrading (HDO/HI)				
Hydrogen (kg)	107	97	0.02	0.02
One step HDO/HI catalyst (1% Pt/SAPO-11, kg)*	0.23	0.25	5.1×10^{-5}	5.5×10^{-5}
Nonisocyanate polyurethane				
Toluene (kg)	54	54	0.01	0.01
Acetic Acid (kg)	461	461	0.10	0.10
Hydrogen peroxide (kg)	784	784	0.17	0.17
Nitrogen (kg)	50	50	0.01	0.01
Carbon dioxide (kg)	1,352	1,352	0.30	0.30
Tetrabutylammonium bromide (TBAB, kg)	247	247	0.05	0.05
Hexane Diamine (HMDA, kg)	936	936	0.21	0.21
Ammonium Bicarbonate (kg)	202	202	0.04	0.04
Citric Acid (kg)	98	98	0.02	0.02
Triazabicyclodecene (kg)*	12	12	2.6×10^{-3}	2.6×10^{-3}

Surfactant (kg)	20	20	4.4×10^{-3}	4.4×10^{-3}
Other Resource Consumption				
Supplemental natural gas (Combined, MJ)	44,502	60,342	9.79	13.28
Supplemental natural gas (fuel-only, MJ)	5,657	35,639	1.25	7.84
Supplemental natural gas (PU-only, MJ)	45,127	59,081	9.93	13.00
Process water (Combined, L)	47,913	54,538	10.55	12.00
Process water (fuel-only, L)	100	31,910	0.02	7.02
Process water (PU-only, L)	17,113	17,105	3.77	3.77
Process outputs				
CO2 Recycle				
CO2 (biogenic, kg)	9,766	9,657	2.20	2.18
CO2 (fossil, kg)	6,042	9,523	1.36	2.15
Products				
Diesel (MJ)	97,309	88,964	21.94	20.06
Naphtha (MJ)	40,265	51,410	9.08	11.59
Polyurethane (kg)	4,436	4,436	1.00	1.00
Electricity exported to grid (kWh)	3,377	4,178	0.76	0.94
Recovered streams				
AD Digestate cake - Bioavailable N (kg)	19	18	0.004	0.004
AD Effluent - Ammonia (kg)	233	228	0.05	0.05
AD Effluent - Diammonium phosphate (kg)	110	81	0.02	0.02
Recycled water (L)	105,285	107,533	23.74	24.24

* Considered negligible for the LCA

S2 Process-level approach information

Figure 1 in the main manuscript shows the process flow diagram utilized in the process-level approach calculations. As mentioned in the main manuscript this approach excluded the fuel processing stages and carried out a mass allocation for the intermediate products in each stage. The liquid hydrolysate and the free fatty acids were the intermediate streams that did not take part of the PU production pathway, as these are inputs for fuel processing. The residual biomass was considered a waste and was not included in the mass allocation factor estimations of the solvent extraction stage. The residual biomass was later processed through anaerobic digestion and combined heat and power (CHP). Ammonia and DAP were recycled to the cultivation stage and surplus electricity from CHP and digestate from AD were exported and assumed to displace grid electricity and calcium nitrate, respectively. The material and energy inputs involved with each stage are available in Table S5 and Table S6 for Bio-PU and Bio-NIPU, respectively.

Table S5. Material and energy inputs of the different stages in the process level approach per kg of Bio-PU.[2,4]

Stage	Pretreatment	Solid-liquid separation	Solvent extraction	Vacuum distillation	Polyurethane production	Anaerobic digestion
Process inputs						
Algae Biomass (DWAF) (kg)	4.449					
Sulfuric acid (93%) (kg)	0.395					
Ammonia (kg)	0.128					
Hexane (kg)			0.023			
Ethanol (kg)			0.009			
Phosphoric acid (oil cleanup) (kg)			0.013			
Silica (oil cleanup) (kg)			0.001			
Clay (oil cleanup) (kg)			0.003			
Formic acid (kg)					0.097	
Hydrogen peroxide (kg)					0.153	
Nitrogen (kg)					0.014	
Toluene diisocyanate (kg)					0.265	
Diethanolamine (kg)					0.003	
Surfactant (kg)					0.005	
Natural gas (MJ)	4.894		5.812	10.693	1.299	1.679
Water (L)	1.595	4.136	2.300	5.456	1.285	0.325
Process outputs						
Hydrolysate slurry (kg)	23.324					
Solids (kg)		14.874				
Liquids (kg)		17.278				
Lipids (kg)			1.270			
Residual biomass (kg)			13.653			
TAG (kg)				0.626		
FFA (kg)				0.550		
Polyurethane (kg)					1.000	
AD Digestate - Bioavailable N (kg)						0.005
AD Effluent - Ammonia (kg)						0.065
AD Effluent - Diammonium phosphate (kg)						0.031
Electricity exported to grid (MJ)						5.055
Recycled water (L)						29.303

CO_2 (biogenic, kg)						2.530
CO_2 (fossil, kg)						1.666

Table S6. Material and energy inputs of the different stages in the process level approach per kg of Bio-NIPU.[2,5]

Stage	Pretreatment	Solid-liquid separation	Solvent extraction	Vacuum distillation	Polyurethane production	Anaerobic digestion
Process inputs						
Algae Biomass (DWAF) (kg)	3.519					
Sulfuric acid (93%) (kg)	0.313					
Ammonia (kg)	0.101					
Hexane (kg)			0.018			
Ethanol (kg)			0.007			
Phosphoric acid (oil cleanup) (kg)			0.010			
Silica (oil cleanup) (kg)			0.001			
Clay (oil cleanup) (kg)			0.002			
Hydrogen peroxide (kg)					0.172	
Nitrogen (kg)					0.011	
Surfactant (kg)					0.004	
Toluene (kg)					0.012	
Acetic Acid (kg)					0.101	
Carbon dioxide (from flue gas capture, kg)					0.298	
TBAB (Tetrabutylammonium bromide, kg)					0.054	
Hexane Diamine (HMDA, kg)					0.206	
Ammonium Bicarbonate (kg)					0.045	
Citric acid (kg)					0.022	
Natural gas (MJ)	3.870		4.596	8.456	1.476	1.328
Water (L)	1.261	3.271	1.819	4.314	0.866	0.257
Process outputs						
Hydrolysate slurry (kg)	18.445					
Solids (kg)		11.762				
Liquids (kg)		13.664				
Lipids (kg)			1.004			
Residual biomass (kg)			10.797			
TAG (kg)				0.495		
FFA (kg)				0.435		
Polyurethane (kg)					1.000	

AD Digestate - Bioavailable N (kg)						0.004
AD Effluent - Ammonia (kg)						0.051
AD Effluent - Diammonium phosphate (kg)						0.024
Electricity exported to grid (MJ)						2.676
Recycle water (L)						23.173
CO2 (biogenic, kg)						2.149
CO2 (fossil, kg)						1.330

S3 Life cycle inventory data for chemicals used in the microalgae biorefinery

The majority of the chemicals utilized in the biorefinery were sourced from the GREET model.[1] The life cycle inventory data of any missing chemicals was obtained or developed from literature. Table S7 toTable S12 present the inventory data of those chemicals that were not available in GREET.

Table S7. Life cycle inventory data for 1 kg of ammonium bicarbonate.

Energy inputs	
Electricity	1.163 MJ
Material inputs	
Ammonia	0.227 kg
Carbon dioxide	0.586 kg

Table S8. Life cycle inventory data for 1 kg of toluene from naphtha cracking.[6]

Energy inputs	
Natural gas	0.077 MJ
Electricity	1.187 MJ
Material inputs	
Petroleum naphtha	1.000 kg

Table S9. Life cycle inventory data for 1 kg of hexane diamine.[7]

Energy inputs	
Natural gas	25.356 MJ
Electricity	1.656 MJ
Material inputs	
Butadiene	0.545 kg
Natural gas as feedstock	31.896 MJ
Phosphoric acid	0.005 kg
Ammonia	0.409 kg
Hydrogen	0.067 kg
Sodium sulfate	0.176 kg
Make-up water	67.144 L
Non-combustion emissions to air	
Carbon dioxide	0.616 kg

Table S10. Life cycle inventory data for 1 kg of tributyl amine.[8]

Energy inputs	
Natural gas	0.097 MJ
Material inputs	
Ammonia	0.092 kg
1-butanol	1.200 kg
Byproduct output	
Water	0.263 L

Table S11. Life cycle inventory data for 1 kg of 1-bromobutane.[9,10]

Energy inputs	
Natural gas	0.082 MJ
Material inputs	
1-butene	0.409 kg
Hydrogen bromide	0.590 kg

Table S12. Life cycle inventory data for 1 kg of tetrabutylammonium bromide.[8]

Energy inputs	
Electricity	0.649 MJ
Material inputs	
Tributylamine	0.575 kg
1-bromobutane	0.425 kg

S4 Carbon balance in the biorefinery

The carbon balance determined the biogenic carbon content in the Bio-PU and Bio-NIPU. The carbon in microalgae TAG is formed from the CO_2 sequestered from pulverized coal plants. This uptake of CO_2 is the only carbon source considered during cultivation. Except for the CO_2 utilized in carbonation, all the additional reactants utilized in the PU synthesis stage were assumed to be obtained from fossil-carbon sources. The flow of the different reactants per kg of Bio-PU or Bio-NIPU (see Table S3 and Table S4) was multiplied by their corresponding carbon content (estimated from their chemical formula). The carbon content of the waste and vented streams (i.e., wastewater and CO_2 vented) was obtained from the Aspen Plus simulation. Carbon flows of solvents and other non-reacting materials were not included in the balance. Figure S1 shows the input and output carbon flows of the different stages involved in the conversion of TAG to PU. Carbon flows labeled as "uptake" indicate carbon sequestered from CO_2 from power plants, while those marked as "fossil" are associated to chemicals obtained from crude oil or natural gas. Only half of the amount of the CO_2 for carbonation is becoming part of the cyclic carbonates while the remaining 50% is vented to the atmosphere, with additional CO_2 produced during epoxidation.[5] To emphasize these features, the carbon flow from the CO_2 for carbonation flow is labeled as "captured for processing". Figure S1 indicates that the carbon uptake in Bio-PU and Bio-NIPU is estimated at 0.48 and 0.42 kg C/kg, respectively. These values are divided by the carbon content of CO_2 (0.27 kg C/kg) to calculate the carbon uptake credits of the PU, which resulted in 1.78 and 1.40 kg CO_2 e/kg of Bio-PU and Bio-NIPU respectively.

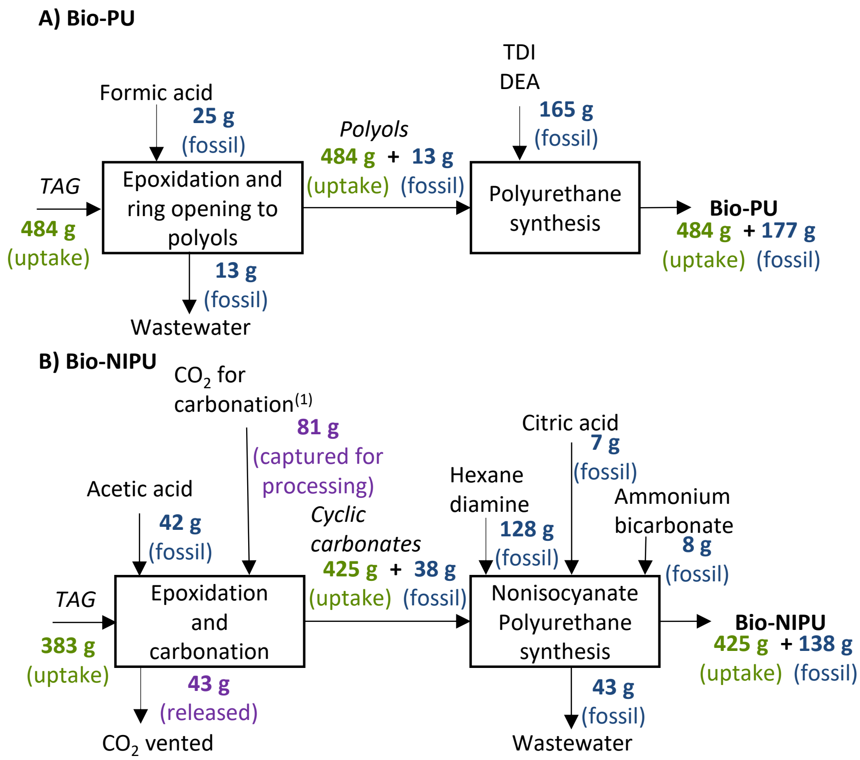

Figure S1. Carbon balance for one kg of microalgae-based PU foam of the two pathways analyzed: A) Production of Bio-PU and B) Production of Bio-NIPU. (1) Only half of the amount of CO_2 for carbonation is becoming part of cyclic carbonates. TAG: Triglycerides, TDI: Toluene diisocyanate, DEA: Diethanolamine, Bio-PU: Bio-based polyurethane, Bio-NIPU: Bio-based non-isocyanate polyurethane.

S5. Scenario analysis data

The comparison between the energy and material requirements for the CO_2 sourcing and microalgae cultivation is presented in Table S13 and Table S14, respectively. The data shown in the tables shows the expected reduction in the energy requirements in the futuristic projection.

Table S13. Comparison of the energy requirements for the sourcing of 1 kg of CO_2 in the 2022 state-of-technology (SOT) and the 2030 projection.[2,11]

Energy inputs	2022 SOT	2030 projection
Natural gas	2.244 MJ	0.689 MJ
Electricity	0.368 MJ	0.368 MJ

Table S14. Comparison of the material and energy requirements for the cultivation of 1 kg of AFDW *Scenedesmus* in the 2022 SOT and the 2030 projection.[2,11]

	2022 SOT	2030 projection
Energy inputs		
Electricity	2.120 MJ	1.312 MJ
Nutrient sources		
Ammonia	0.020 kg	0.020 kg
Diammonium phosphate	0.010 kg	0.010 kg
Carbon dioxide	2.220 kg	2.672 kg
Other materials		
Concrete	0.024 kg	0.017 kg
Steel	0.001 kg	0.001 kg
Plastic	0.005 kg	0.004 kg
Cast iron	0.003 kg	0.002 kg

The life cycle inventory data for the production of Bio-NIPU with pentane diamine is presented in Table S15 and Table S16 for the system and process level approaches, respectively.

Table S15. Material and energy requirements of the microalgae biorefinery to produce Bio-NIPU using biobased pentane diamine.[2,5]

Basis	per hour of operation		per kg Bio-NIPU	
Route	Carboxylic acid (CA) intermediate	2,3-butanediol (BDO) intermediate	Carboxylic acid (CA) intermediate	2,3-butanediol (BDO) intermediate
Process inputs				
Feedstock				
Microalgae Biomass AFDW (kg)	15,987	15,987	3.60	3.60
Pretreatment				
Sulfuric acid (93%) (kg)	1,420	1,420	0.32	0.32
Ammonia (kg)	459	459	0.10	0.10
Lipid extraction and clean-up				
Hexane (kg)	84	84	0.02	0.02

Ethanol (kg)	34	34	0.01	0.01
Phosphoric acid (kg)	46	46	0.01	0.01
Silica (kg)	5	5	0.00	0.00
Clay (kg)	9	9	0.00	0.00
Carboxylic Acid Conversion				
Corn steep liquor (kg)	721	N.A.	0.16	N.A.
Diammonium phosphate (kg)	75	N.A.	0.02	N.A.
Hydrotalcite (kg)*	1	N.A.	2.3×10^{-4}	N.A.
Flocculant (kg)	64	N.A.	0.01	N.A.
Hexane (kg)	1	N.A.	2.3×10^{-4}	N.A.
2,3-BDO Conversion				
Corn steep liquor (kg)	N.A.	107	N.A.	0.02
Diammonium phosphate (DAP, kg)	N.A.	13	N.A.	0.00
Hydrogen (kg)	N.A.	89	N.A.	0.02
Flocculant (kg)	N.A.	64	N.A.	0.01
Dehydration catalyst (kg)*	N.A.	0.07	N.A.	1.6×10^{-5}
Oligomerization catalyst (kg)*	N.A.	0.13	N.A.	2.9×10^{-5}
Final Fuel Upgrading (HDO/HI)				
Hydrogen (kg)	107	97	0.02	0.02
One step HDO/HI catalyst (1% Pt/SAPO-11, kg)*	0.23	0.25	5.2×10^{-5}	5.6×10^{-5}
Nonisocyanate polyurethane				
Toluene (kg)	54	54	0.01	0.01
Acetic Acid (kg)	461	461	0.10	0.10
Hydrogen peroxide (kg)	784	784	0.18	0.18
Nitrogen (kg)	50	50	0.01	0.01
Carbon dioxide (kg)	1,352	1,352	0.30	0.30
Tetrabutylammonium bromide (TBAB, kg)	247	247	0.06	0.06
Biobased Pentane Diamine (kg)	828	828	0.19	0.19
Ammonium Bicarbonate (kg)	202	202	0.05	0.05
Citric Acid (kg)	98	98	0.02	0.02
Triazabicyclodecene (kg)*	12	12	2.7×10^{-3}	2.7×10^{-3}
Surfactant (kg)	20	20	4.5×10^{-3}	4.5×10^{-3}
Other Resource Consumption				
Supplemental natural gas (Combined, MJ)	44,502	60,342	10.03	13.60
Supplemental natural gas (fuel-only, MJ)	5,657	35,639	1.28	8.03
Supplemental natural gas (PU-only, MJ)	45,126	59,080	10.17	13.32
Process water (Combined, L)	47,913	54,538	10.80	12.30
Process water (fuel-only, L)	100	31,910	0.02	7.19
Process water (PU-only, L)	17,146	17,138	3.86	3.86
Process outputs				
CO2 Recycle				
CO2 (biogenic, kg)	9,766	9,657	2.15	2.13
CO2 (fossil, kg)	6,042	9,523	1.33	2.10
Products				
Diesel (MJ)	97,309	88,964	21.42	19.58
Naphtha (MJ)	40,265	51,410	8.86	11.32
Polyurethane (kg)	4,436	4,436	1.00	1.00
Electricity exported to grid (kWh)	3,377	4,178	0.74	0.92
Recovered streams				

AD Digestate cake - Bioavailable N (kg)	19	18	0.004	0.004
AD Effluent - Ammonia (kg)	233	228	0.05	0.05
AD Effluent - Diammonium phosphate (kg)	110	81	0.02	0.02
Recycled water (L)	105,285	107,533	23.17	23.67

* Considered negligible for the LCA

Table S16. Material and energy inputs of the different stages in the process level approach per kg of Bio-NIPU using pentane diamine.[2,5]

Stage	Pretreatment	Solid-liquid separation	Solvent extraction	Vacuum distillation	Polyurethane production	Anaerobic digestion
Process inputs						
Algae Biomass (DWAF) (kg)	3.604					
Sulfuric acid (93%) (kg)	0.320					
Ammonia (kg)	0.103					
Hexane (kg)			0.019			
Ethanol (kg)			0.008			
Phosphoric acid (oil cleanup) (kg)			0.010			
Silica (oil cleanup) (kg)			0.001			
Clay (oil cleanup) (kg)			0.002			
Hydrogen peroxide (kg)					0.177	
Nitrogen (kg)					0.011	
Surfactant (kg)					0.005	
Toluene (kg)					0.012	
Acetic Acid (kg)					0.104	
Carbon dioxide (from flue gas capture, kg)					0.305	
TBAB (Tetrabutylammonium bromide, kg)					0.056	
Biobased Pentane Diamine (kg)					0.187	
Ammonium Bicarbonate (kg)					0.046	
Citric acid (kg)					0.022	
Natural gas (MJ)	3.964		4.708	8.662	1.512	1.360
Water (L)	1.292	3.350	1.863	4.419	0.879	0.263
Process outputs						
Hydrolysate slurry (kg)	18.892					
Solids (kg)		12.048				
Liquids (kg)		13.995				
Lipids (kg)			1.029			
Residual biomass (kg)			11.059			
TAG (kg)				0.507		
FFA (kg)				0.445		

Polyurethane (kg)					1.000	
AD Digestate - Bioavailable N (kg)						0.004
AD Effluent - Ammonia (kg)						0.053
AD Effluent - Diammonium phosphate (kg)						0.025
Electricity exported to grid (MJ)						2.741
Recycled water (L)						23.736
CO2 (biogenic, kg)						2.202
CO2 (fossil, kg)						1.362

Additional information to perform the energy and market-value allocation is presented in Table S17 and Table S18, respectively.

Table S17. Energy content of the coproducts from the biorefinery.

Coproduct	Energy content	Source
Renewable diesel	42.79 MJ/kg	GREET[1]
Renewable naphtha	44.94 MJ/kg	GREET[1]
PU flexible foam	30.51 MJ/kg	Hasanzadeh et al.[12]
PU rigid foam	31.21 MJ/kg	Hasanzadeh et al.[12]

Table S18. Prices of the coproducts from the biorefinery.

Coproduct	Price	Source
Renewable fuels	2.50 USD/GGE*	Cai et al.[2]
Electricity	0.166 USD/kWh	U.S. Bureau of Labor Statistics[13]
PU foam	4.50 USD/kg	Cai et al.[2]

* For the estimations a conversion factor of 120 MJ per GGE was used.[1,14]

A synthetized description of the four coproduct treatment methods evaluated during this study is presented in Table S19 to improve clarity.

Table S19. Description of coproducts treatment methods used for the microalgae-based PU foam.

Method	Description
Hybrid method	Material and energy inputs allocation by mass to naphtha, diesel, and PU Credits from displacement grid electricity (allocated by mass to naphtha, diesel, and PU) Credits from displaced nitrogen (allocated by mass to naphtha, diesel, and PU)
Market-value allocation	Material and energy inputs allocation by market-value to naphtha, diesel, electricity, and PU Credits from displaced nitrogen (allocated by market-value to naphtha, diesel, electricity, and PU)

Energy allocation	Material and energy inputs allocation by energy to naphtha, diesel, electricity, and PU Credits from displaced nitrogen (allocated by energy to naphtha, diesel, electricity, and PU)
Displacement	Subtract the emissions of the co-products, assuming displacement of conventional counterparts **Naphtha:** Displaces conventional petroleum naphtha **Diesel:** Displaces conventional petroleum diesel **Electricity:** Displaces electricity from the average U.S. grid

S6. Additional results

S6.1 Analysis of additional indicators and scenarios

Figure S2 presents the results of GHG emissions with a breakdown of the emissions associated to the material and energy feedstocks. Figure S3 and Figure S4 show the results of the fossil energy and water consumption, respectively, that are discussed in the main manuscript. Figure S5 shows the breakdown of the GHG emission results by process stage but with the use of renewable electricity.

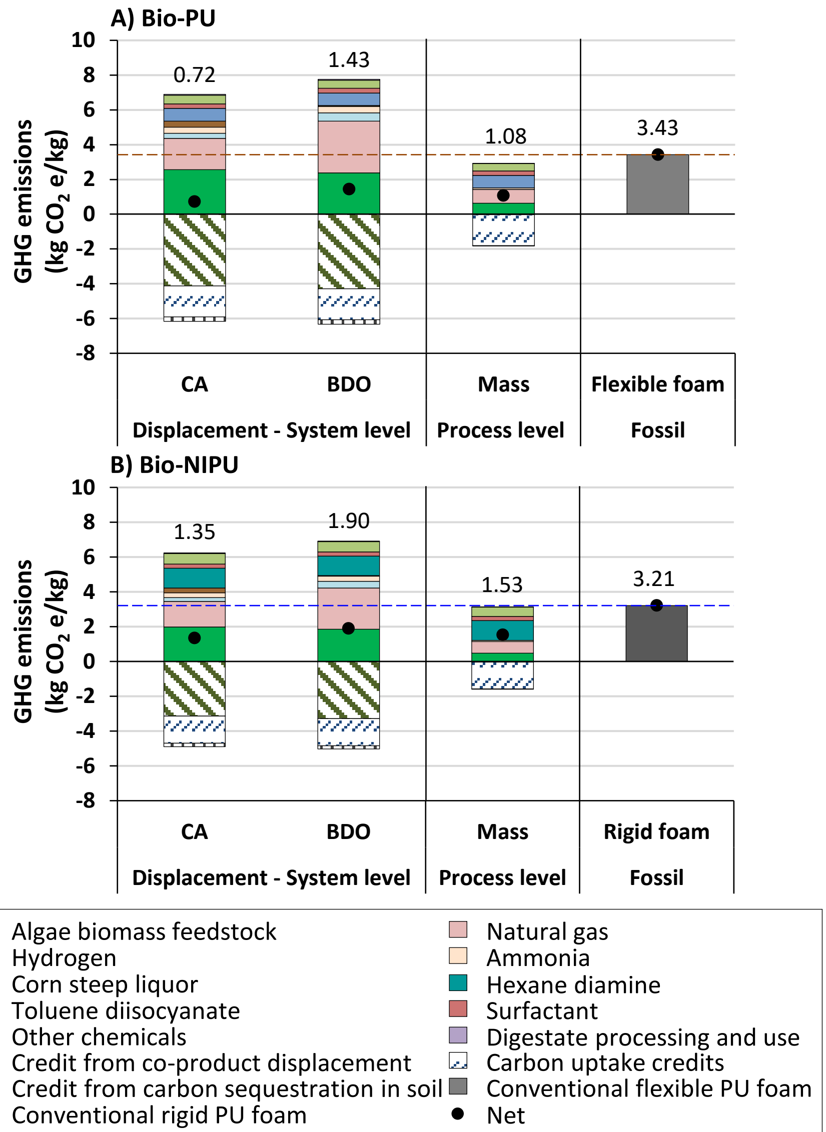

Figure S2. GHG emissions of the production of A) Bio-PU and B) Bio-NIPU with a breakdown of the emissions associated to material and energy inputs. The orange and blue dashed lines indicate the GHG emissions of conventional flexible and rigid PU foam, respectively. The credit from coproduct displacement comprises the avoided GHG emissions to produce conventional diesel and gasoline blendstock and generation of grid electricity.

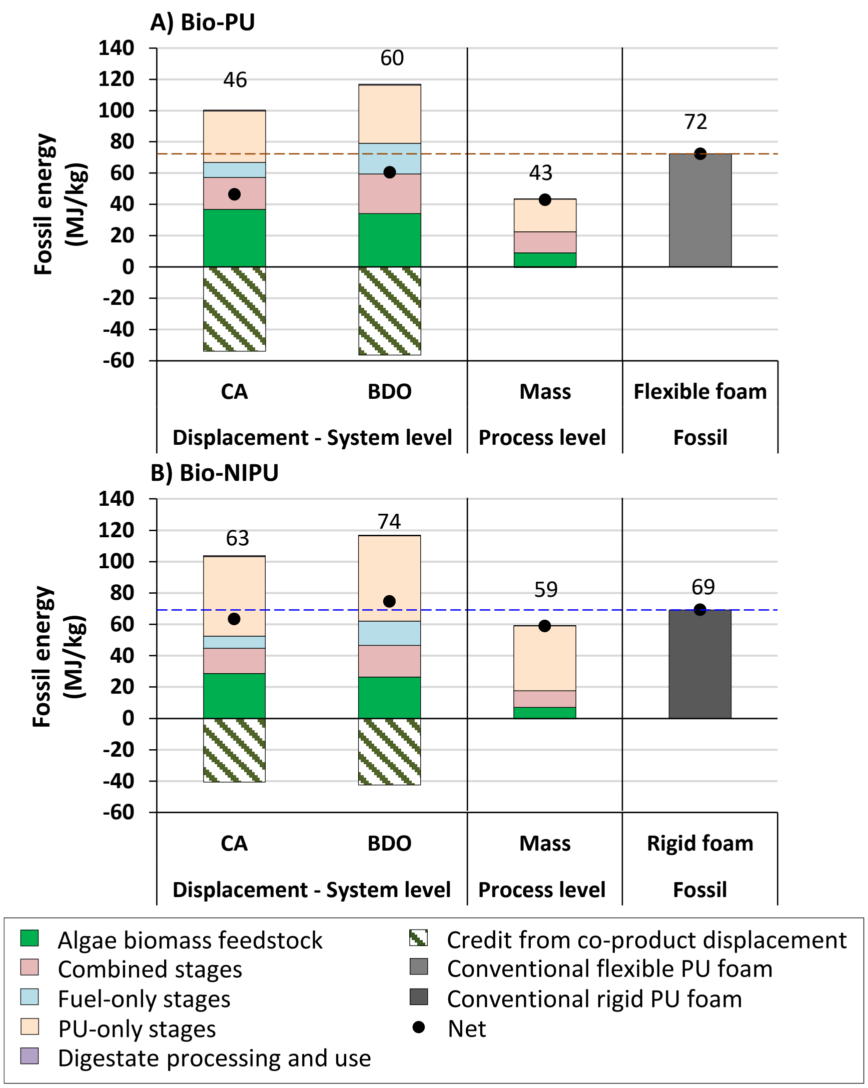

Figure S3. Fossil energy of the production of A) Bio-PU and B) Bio-NIPU. The orange and blue dashed lines indicate the GHG emissions of conventional flexible and rigid PU foam, respectively. The credit from coproduct displacement comprises the avoided fossil energy to produce conventional diesel and gasoline blendstock and generation of grid electricity.

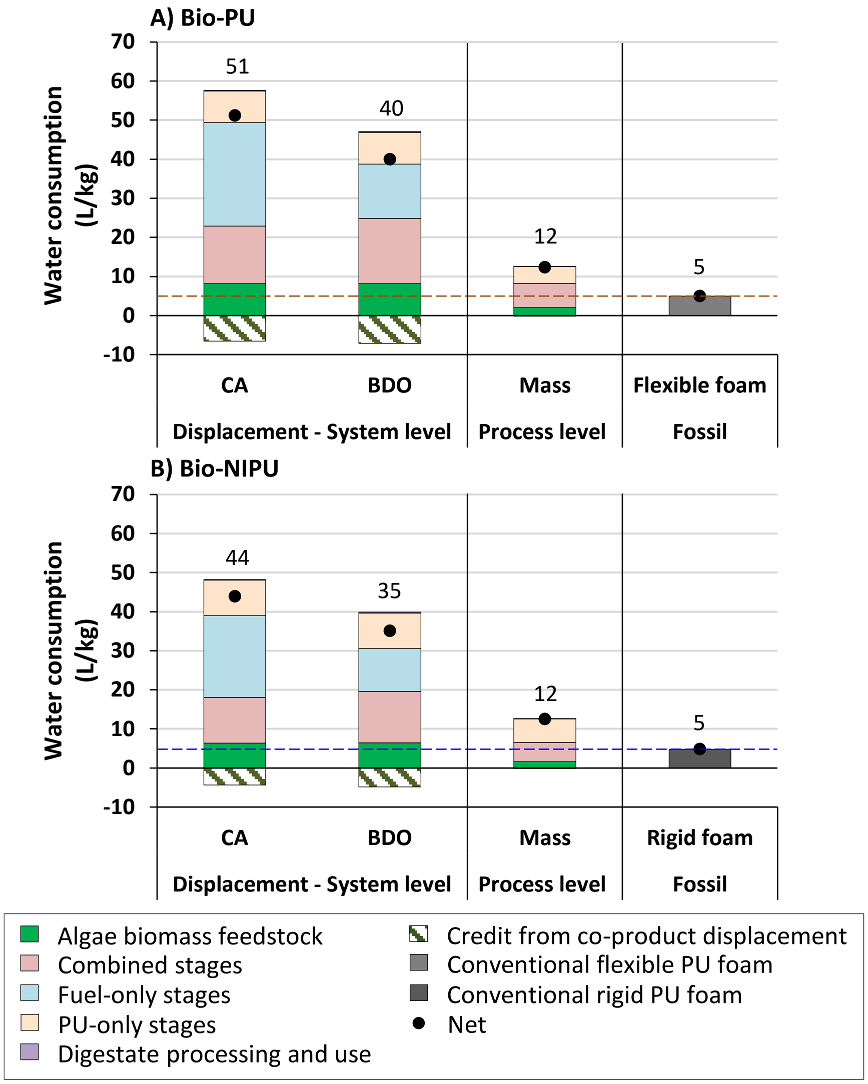

Figure S4. Water consumption of the production of A) Bio-PU and B) Bio-NIPU. The orange and blue dashed lines indicate the GHG emissions of conventional flexible and rigid PU foam, respectively. The credit from coproduct displacement comprises the avoided water consumption to produce conventional diesel and gasoline blendstock and generation of grid electricity.

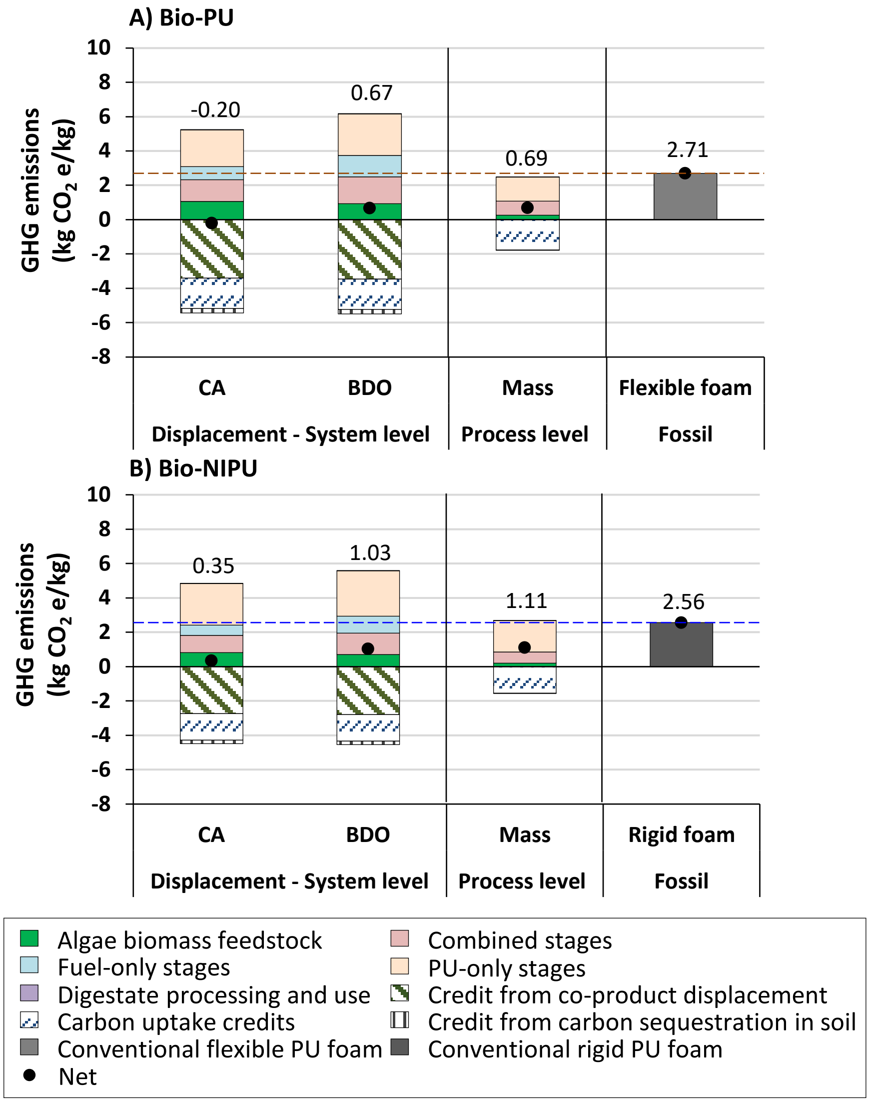

Figure S5. GHG emissions of the production of A) Bio-PU and B) Bio-NIPU under the use of renewable electricity (wind power). The orange and blue dashed lines indicate the GHG emissions of conventional flexible and rigid PU foam, respectively. The credit from coproduct displacement comprises the avoided GHG emissions to produce conventional diesel and gasoline blendstock.

S6.2 GHG emissions of fuels produced from the microalgae biorefinery

An alternative analysis was conducted to estimate the GHG emissions in a different context when viewing fuels as the main product and PU/NIPU as the coproduct in the microalgae biorefinery. This analysis followed the system-level approach described in section 2.1.1.1 of the main manuscript, incorporating not only the GHG emissions estimated through displacement but also mass and market-value allocation methods. The functional unit used was one megajoule (MJ) of fuel. Since renewable diesel and naphtha follow the same conversion pathway, they are treated as a single product, with the same allocation factors applied in the distribution of the GHG emissions between the other coproducts: PU and electricity. After estimating the GHG emissions for the combined fuel, they are disaggregated using an energy allocation factor. However, as the results are reported per MJ of fuel, the emissions for both renewable diesel and naphtha are numerically similar, and thus both are reported through a single value as renewable fuels.

The GHG emissions from renewable fuels produced in the microalgae biorefinery under different coproduct treatment methods are shown in Figure S6. The GHG emissions ranged between 23.9 to 84.5 g CO_2e/MJ. Similarly, to what was observed with Bio-PU and Bio-NIPU results, the GHG emissions associated with the CA route were lower than those of the BDO route, due to the higher natural gas and chemical requirements of the latter. Moreover, fuels derived by a biorefinery producing Bio-PU showed lower GHG emissions than those from a Bio-NIPU biorefinery, except under the market allocation approach which brought fuel GHG emissions for Bio-NIPU co-production lower than those for Bio-PU due to allocating a higher GHG fraction to the more valuable coproduct. Although the Bio-NIPU biorefinery had lower GHG emissions from feedstock requirements and more coproduct displacement than the Bio-PU biorefinery, the higher GHG emissions of the conversion process led to the overall higher GHG emissions of renewable diesel in the Bio-NIPU route.

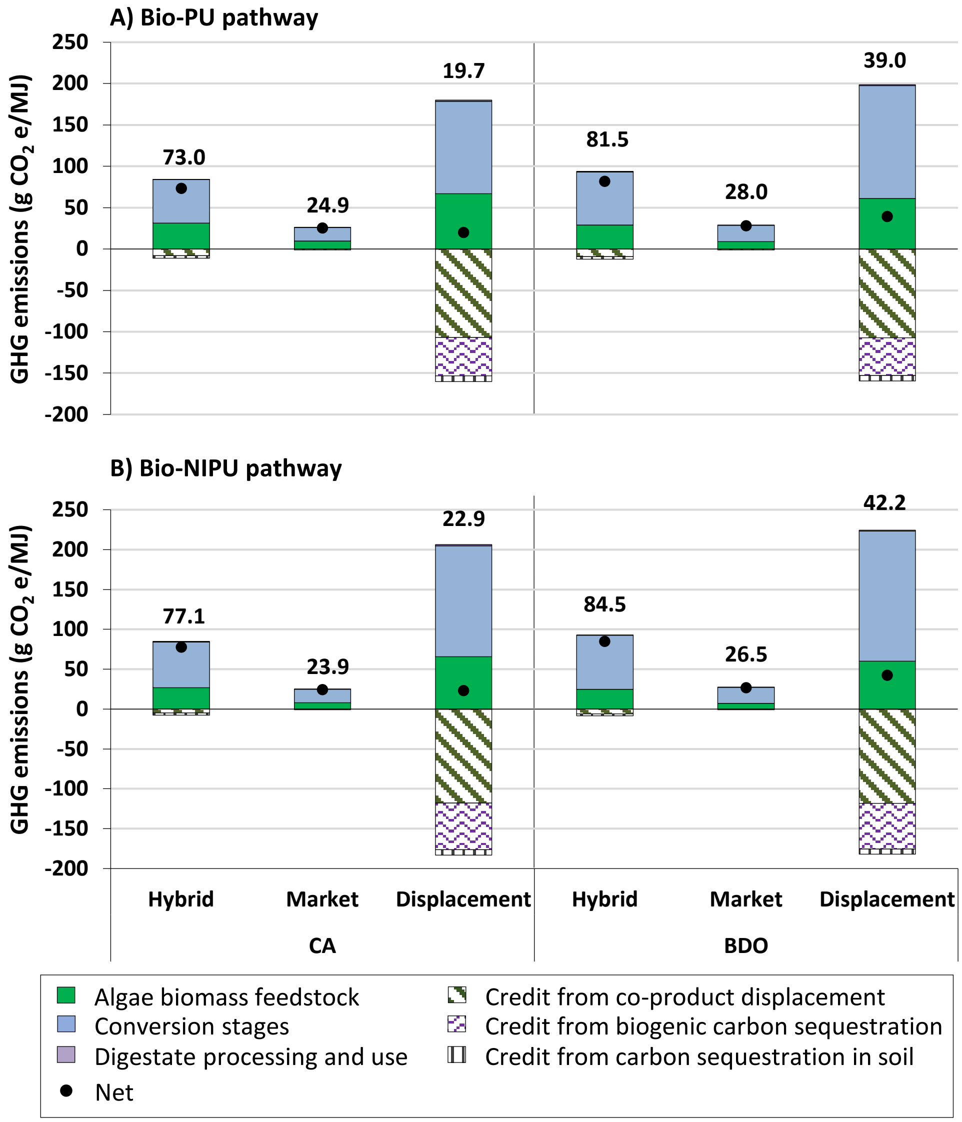

Figure S6. GHG emissions of the production of fuels from A) the Bio-PU pathway and B) the Bio-NIPU pathway. The credit from coproduct displacement comprises the avoided GHG emissions to produce conventional PU and grid electricity.

S6.3 Scenario, sensitivity, and uncertainty analyses

Figure S7 presents the biorefinery-level analysis for substituting natural gas with renewable natural gas. For Bio-PU and Bio-NIPU under the CA and BDO routes. Figure S8 and Figure S9, show the results of the sensitivity and uncertainty analysis for Bio-PU and Bio-NIPU, respectively. The results shown in these Figures are discussed in the main manuscript.

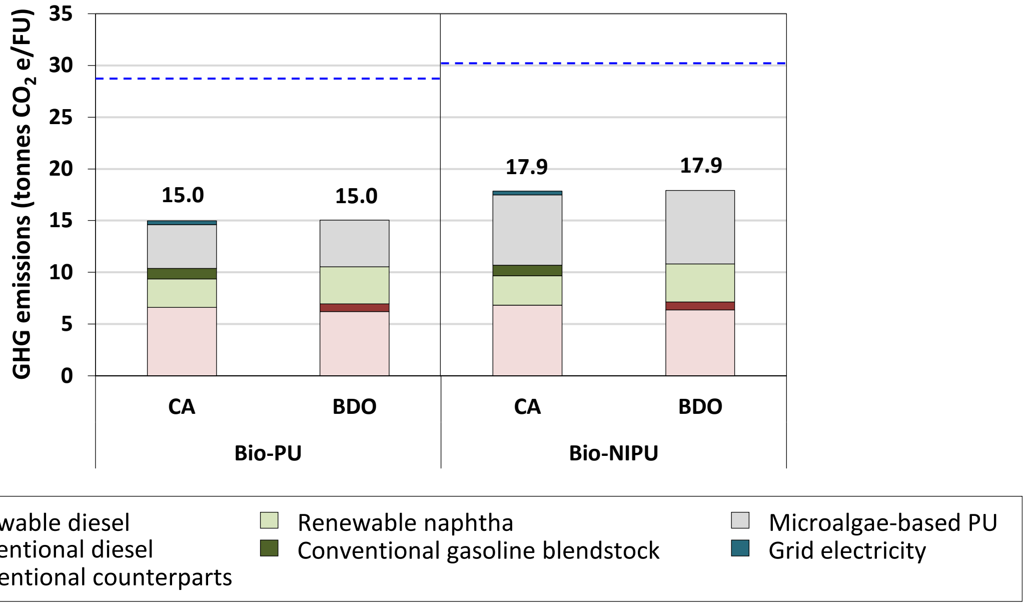

Figure S7. GHG emissions for the scenario analysis substituting natural gas with renewable natural gas at the biorefinery-level. The dashed lines indicate the GHG emissions of conventional counterparts.

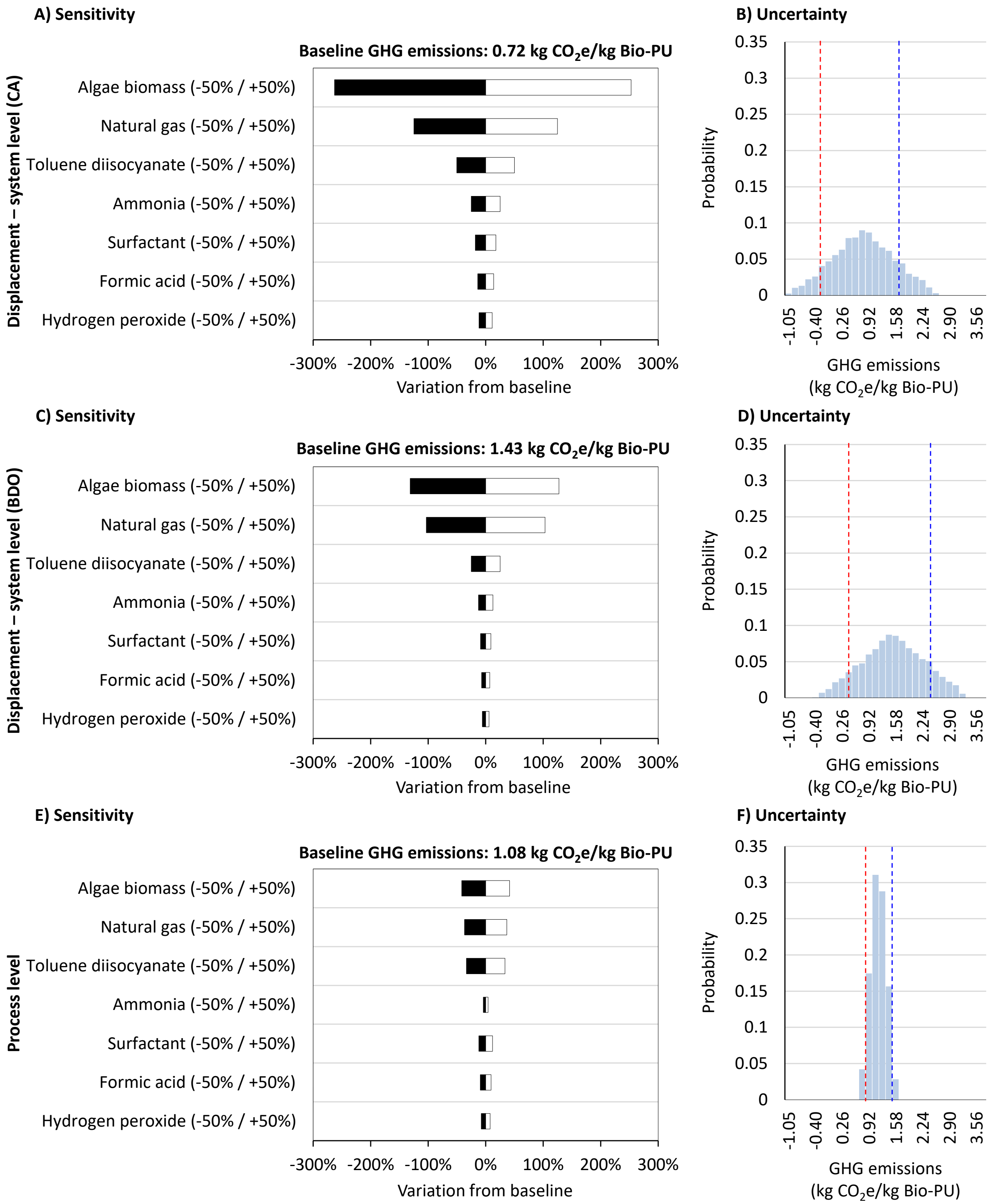

Figure S8. Sensitivity (A, C, and E) and uncertainty (B, D, and F) analyses of the GHG emissions for Bio-PU under displacement – system level (CA and BDO routes) and process level approaches. Red and blue dashed lines indicate the 10th and 90th percentiles, respectively.

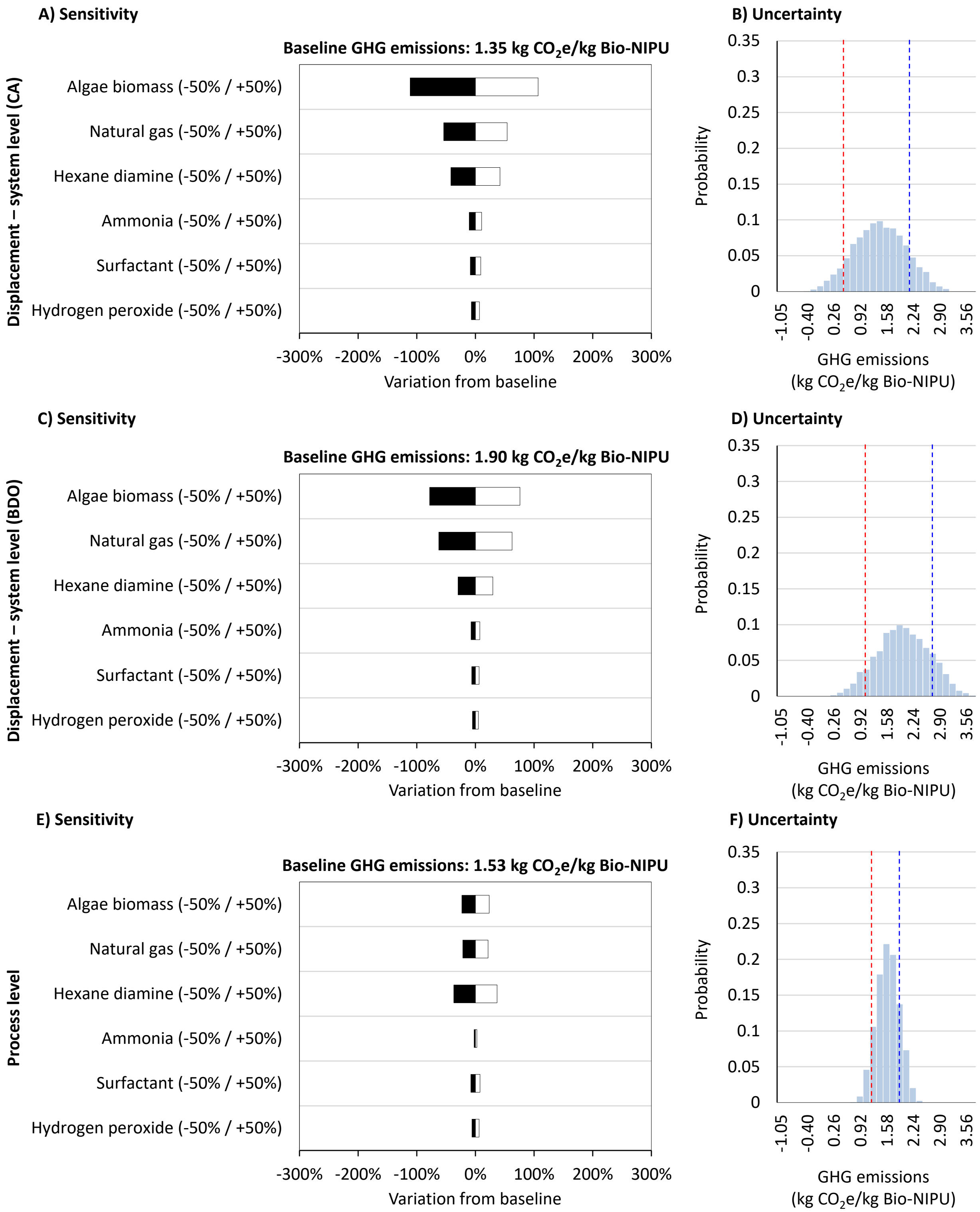

Figure S9. Sensitivity (A, C, and E) and uncertainty (B, D, and F) analyses of the GHG emissions for Bio-NIPU under displacement – system level (CA and BDO routes) and process level approaches. Red and blue dashed lines indicate the 10^{th} and 90^{th} percentiles, respectively.

S6.4 Tabulated data from Figures

Tabulated data for Figure 2 of the main manuscript is presented in Table S20 and Table S21 and tabulated data for Figure S2, Figure S3, Figure S4, and Figure S5 in this SI is presented below in Table S22, Table S23, Table S24, and Table S25, respectively.

Table S20. Tabulated data of the GHG emissions results (kg CO_2 e/kg) presented in Figures 2A and 2B of the main manuscript.

Product	Bio-PU			Bio-NIPU		
Case	Displacement - System level		Process level	Displacement - System level		Process level
	CA	BDO	Mass	CA	BDO	Mass
Algae biomass feedstock	2.56	2.38	0.63	1.99	1.85	0.49
Combined stages	1.29	1.59	0.82	1.02	1.26	0.65
Fuel-only stages	0.80	1.26	0.00	0.63	1.00	0.00
PU-only stages	2.19	2.46	1.45	2.57	2.78	1.98
Credits due to nutrient recovery	−0.01	−0.01	0.00	−0.01	−0.01	0.00
Credit from co-product displacement	−4.12	−4.28	−0.03	−3.13	−3.27	−0.02
Carbon uptake credits	−1.78	−1.78	−1.78	−1.55	−1.55	−1.55
Credit from carbon sequestration in soil	−0.26	−0.25	−0.01	−0.21	−0.20	−0.01
Digestate processing and use	0.05	0.05	0.00	0.04	0.04	0.00
Net	0.72	1.43	1.08	1.35	1.90	1.53

Table S21. Tabulated data of the GHG emissions results (tonnes CO_2 e/FU) presented in Figures 2C and 2D of the main manuscript.

Product	Bio-PU			Bio-NIPU		
Case	Microalgae system		Conventional	Microalgae system		Conventional
	CA	BDO		CA	BDO	
Renewable diesel	7.88	8.07	0	7.96	8.03	0
Conventional diesel	0	0.76	8.90	0	0.76	8.90
Renewable naphtha	3.26	4.66	0	3.30	4.64	0
Conventional gasoline blendstock	1.04	0	4.78	1.04	0	4.78
Microalgae-based PU	6.25	7.81	0	9.08	10.81	0
Conventional flexible PU	0	0	12.33	0	0	0
Conventional rigid PU	0	0	0	0	0	14.60
Grid electricity	0.37	0	2.73	0.37	0	1.95
Total	18.80	21.30	28.73	21.75	24.25	30.22

Note: The functional unit (FU) for Bio-PU is defined as the production of 3.6 tonnes of Bio-PU, 97 GJ of renewable diesel, 51 GJ of renewable naphtha and 21 GJ of electricity internally-generated and exported to the grid and the FU for Bio-NIPU comprises the production of 4.5 tonnes of Bio-NIPU, 97 GJ of renewable diesel, 51 GJ of renewable naphtha and 15 GJ of electricity internally-generated and exported to the grid.

Table S22. Tabulated data of the GHG emissions results (kg CO_2 e/kg) presented in Figure S2 of this SI.

Product	Bio-PU			Bio-NIPU		
Case	Displacement - System level		Process level	Displacement - System level		Process level
	CA	BDO	Mass	CA	BDO	Mass
Algae biomass feedstock	2.56	2.38	0.63	1.99	1.85	0.49
Natural gas	1.80	2.96	0.79	1.46	2.37	0.66
Hydrogen	0.28	0.49	0.00	0.22	0.39	0.00
Ammonia	0.36	0.36	0.09	0.29	0.29	0.07
Corn steep liquor	0.35	0.05	0.00	0.27	0.04	0.00
Toluene diisocyanate (TDI)	0.72	0.72	0.72	-	-	-
Hexane diamine (HDMA)	-	-	-	1.13	1.13	1.13
Surfactant	0.26	0.26	0.26	0.24	0.24	0.24
Other chemicals	0.50	0.47	0.41	0.61	0.58	0.53
Credits due to nutrient recovery	−0.01	−0.01	0.00	−0.01	−0.01	0.00
Credit from co-product displacement	−4.12	−4.28	−0.03	−3.13	−3.27	−0.02
Carbon uptake credits	−1.78	−1.78	−1.78	−1.55	−1.55	−1.55
Credit from carbon sequestration in soil	−0.26	−0.25	−0.01	−0.21	−0.20	−0.01
Digestate processing and use	0.05	0.05	0.00	0.04	0.04	0.00
Net	0.72	1.43	1.08	1.35	1.90	1.53

Table S23. Tabulated data of the fossil energy consumption results (MJ/kg) presented in Figure S3 of this SI.

Product	Bio-PU			Bio-NIPU		
Case	Displacement - System level		Process level	Displacement - System level		Process level
	CA	BDO	Mass	CA	BDO	Mass
Algae biomass feedstock	36.82	34.16	9.07	28.62	26.51	7.05
Combined stages	20.39	25.29	13.31	16.12	20.00	10.54
Fuel-only stages	9.66	19.69	0.00	7.64	15.57	0.00
PU-only stages	32.83	37.15	20.93	50.85	54.27	41.44
Credits due to nutrient recovery	−0.05	−0.05	0.00	−0.04	−0.04	0.00
Credit from co-product displacement	−54.02	−56.40	−0.44	−40.54	−42.43	−0.29
Digestate processing and use	0.67	0.64	0.04	0.53	0.51	0.04
Net	46.31	60.49	42.91	63.19	74.40	58.78

Table S24. Tabulated data of the water consumption results (L/kg) presented in Figure S4 of this SI.

Product	Bio-PU			Bio-NIPU		
Case	Displacement - System level		Process level	Displacement - System level		Process level
	CA	BDO	Mass	CA	BDO	Mass
Algae biomass feedstock	8.14	8.20	2.01	6.39	6.44	1.58
Combined stages	14.78	16.68	6.27	11.69	13.19	4.97
Fuel-only stages	26.47	13.86	0.00	20.93	10.96	0.00
PU-only stages	8.05	8.09	4.24	9.03	9.07	6.02
Credits due to nutrient recovery	−0.02	-0.02	0.00	−0.02	−0.02	0.00
Credit from co-product displacement	-6.49	-7.10	-0.17	−4.31	−4.79	−0.11
Digestate processing and use	0.24	0.23	0.01	0.19	0.18	0.01
Net	51.16	39.94	12.36	43.91	35.03	12.46

Table S25. Tabulated data of the GHG emissions results (kg CO_2 e/kg) presented in Figure S5 of this SI.

Product	Bio-PU			Bio-NIPU		
Case	Displacement - System level		Process level	Displacement - System level		Process level
	CA	BDO	Mass	CA	BDO	Mass
Algae biomass feedstock	1.06	0.93	0.26	0.81	0.71	0.20
Combined stages	1.27	1.58	0.81	1.00	1.25	0.64
Fuel-only stages	0.76	1.25	0.00	0.60	0.99	0.00
PU-only stages	2.14	2.41	1.40	2.42	2.63	1.83
Credits due to nutrient recovery	−0.01	−0.01	0.00	−0.01	−0.01	0.00
Credit from co-product displacement	−3.40	−3.46	0.00	−2.72	−2.78	0.00
Carbon uptake credits	−1.78	−1.78	−1.78	−1.55	−1.55	−1.55
Credit from carbon sequestration in soil	−0.26	−0.25	−0.01	−0.21	−0.20	−0.01
Digestate processing and use	0.01	0.01	0.00	0.01	0.00	0.00
Net	−0.20	0.67	0.69	0.35	1.03	1.11

Table S26. Tabulated data of the GHG emissions variations of Bio-PU in the sensitivity analysis presented in Figure S8A, Figure S8C, and Figure S8E.

	System level CA route		System level BDO route		Process level	
Input variation	−50%	+50%	−50%	+50%	−50%	+50%
Algae biomass	−263%	+253%	−131%	+127%	−42%	+42%
Natural gas	−125%	+125%	−103%	+103%	−37%	+37%
Toluene diisocyanate	−50%	+50%	−25%	+25%	−34%	+34%
Ammonia	−25%	+25%	−13%	+13%	−4%	+4%
Surfactant	−18%	+18%	−9%	+9%	−12%	+12%
Formic acid	−14%	+14%	−7%	+7%	−9%	+9%
Hydrogen peroxide	−11%	+11%	−6%	+6%	−8%	+8%

Table S27. Tabulated data of the GHG emissions variations of Bio-NIPU in the sensitivity analysis presented in Figure S9A, Figure S9C, and Figure S9E.

	System level CA route		System level BDO route		Process level	
Input variation	−50%	+50%	−50%	+50%	−50%	+50%
Algae biomass	−111%	+107%	−78%	+76%	−23%	+23%
Natural gas	−54%	+54%	−62%	+62%	−22%	+22%
Hexane diamine	−42%	+42%	−30%	+30%	−37%	+37%
Ammonia	−11%	+11%	−8%	+8%	−2%	+2%
Surfactant	−9%	+9%	−6%	+6%	−8%	+8%
Hydrogen peroxide	−7%	+7%	−5%	+5%	−6%	+6%

Table S28. 90th and 10th percentiles from the uncertainty analysis of microalgae-based foams (kg CO_2e/kg).

	Bio-PU		Bio-NIPU	
Case	10th percentile	90th percentile	10th percentile	90th percentile
System level CA route	−0.28	1.70	0.50	2.18
System level BDO route	0.41	2.45	1.07	2.76
Process level	0.82	1.32	1.17	1.90

References

1 Argonne National Laboratory, Greenhouse gases, Regulated Emissions, and Energy use in Technologies Model (GREET)® (2022 Excel) DOI: 10.11578/GREET-Excel-2022/dc.20220908.1 2022.

2 H. Cai, L. Ou, M. Wang, R. Davis, M. Wiatrowski, A. Bartling, B. Klein, D. Hartley, P. Burli, Y. Lin, M. Roni, D. N. Thompson, L. Snowden-Swan, Y. Zhu, S. Li, Y. Xu and P. Valdez, *Supply Chain Sustainability Analysis of Renewable Hydrocarbon Fuels via Hydrothermal Liquefaction, Combined Algal Processing, and Biochemical Conversion: Update of the 2022 State-of-Technology Cases*, Argonne National Laboratory, Lemont, IL, United States, 2023.

3 B. Klein and R. Davis, *Algal Biomass Production via Open Pond Algae Farm Cultivation: 2022 State of Technology and Future Research*, National Renewable Energy Laboratory, Golden, CO, United States, 2023.

4 M. Wiatrowski and R. Davis, *Algal Biomass Conversion to Fuels via Combined Algae Processing (CAP): 2022 State of Technology and Future Research*, National Renewable Energy Laboratory, Golden, CO, United States, 2023.

5 T. Dong, E. Dheressa, M. Wiatrowski, A. P. Pereira, A. Zeller, L. M. L. Laurens and P. T. Pienkos, *ACS Sustainable Chem. Eng.*, 2021, **9**, 12858–12869.

6 Franklin Associates, *Cradle-to-gate life cycle analysis of toluene diisocyanate resin precursor*, 2023.

7 A. B. Dros, O. Larue, A. Reimond, F. D. Campo and M. Pera-Titus, *Green Chem.*, 2015, **17**, 4760–4772.

8 P. García-Gutiérrez, R. M. Cuéllar-Franca, D. Reed, G. Dowson, P. Styring and A. Azapagic, *Green Chem.*, 2019, **21**, 4100–4114.

9 A. G. Parvatker and M. J. Eckelman, *ACS Sustainable Chem. Eng.*, 2020, **8**, 8519–8536.

10 D. Yoffe, R. Frim, S. D. Ukeles, M. J. Dagani, H. J. Barda, T. J. Benya and D. C. Sanders, *Ullmann’s Encyclopedia of Industrial Chemistry*, 2013.

11 H. Cai, L. Ou, M. Wang, R. Davis, A. Dutta, K. Harris, M. Wiatrowski, E. Tan, A. Bartling, B. Klein, D. Hartley, Y. Lin, M. Roni, D. N. Thompson, L. Snowden-Swan and Y. Zhu, *Supply Chain Sustainability Analysis of Renewable Hydrocarbon Fuels via Indirect Liquefaction, Ex Situ Catalytic Fast Pyrolysis, Hydrothermal Liquefaction, Combined Algal Processing, and Biochemical Conversion: Update of the 2020 State-of-Technology Cases*, Argonne National Laboratory, Lemont, IL, United States, 2021.

12 R. Hasanzadeh, P. Mojaver, S. Khalilarya, T. Azdast, A. Chitsaz and M. Mojaver, *Polymers*, 2022, **14**, 4938.

13 U.S. Bureau of labor statistics, Average energy prices for the United States, regions, census divisions, and selected metropolitan areas, https://data.bls.gov/pdq/SurveyOutputServlet, (accessed May 16, 2023).

14 J. Zhang, Y. Zhu, T. R. Hawkins, B. C. Klein, A. M. Coleman, U. Singh, R. Davis, L. Ou, Y. Xu, S. Kar, M. Wiatrowski, S. Gao and P. Valdez, *Sustainable Energy Fuels*, DOI:10.1039/D4SE01423E.