Supporting Information for

Process Intensified Lauric Acid Self-ketonization and its Economic and Environmental Impact on Biolubricant Base Oil Production

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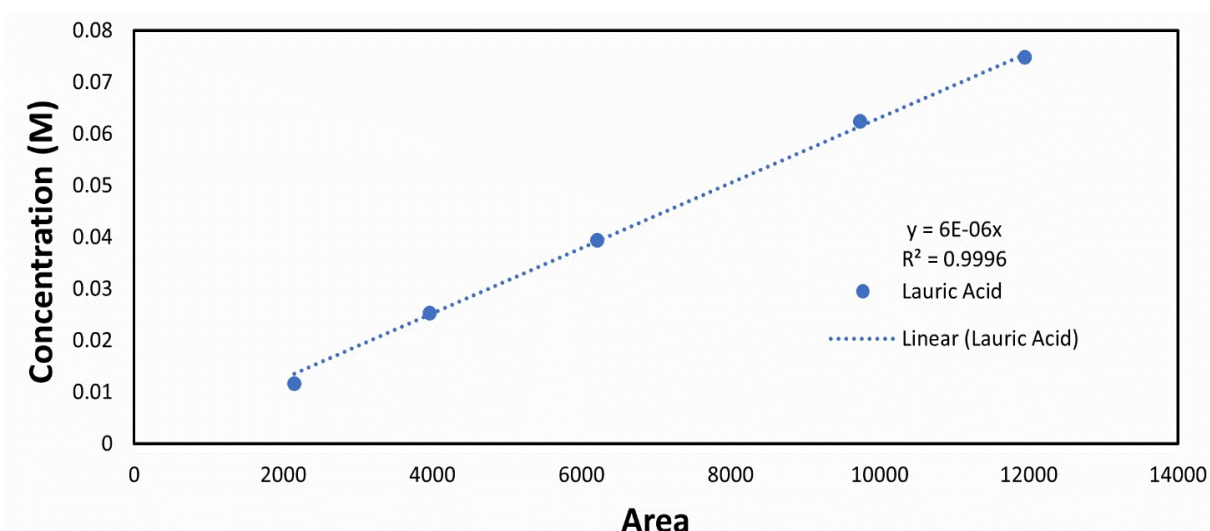**Corresponding author. Email: vlachos@udel.edu*

Figure S1. GC calibration curve used for quantification of the reactant lauric acid.
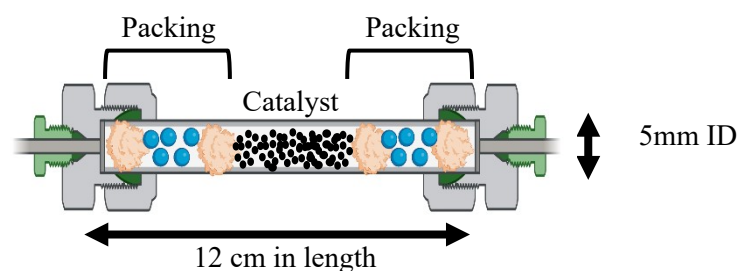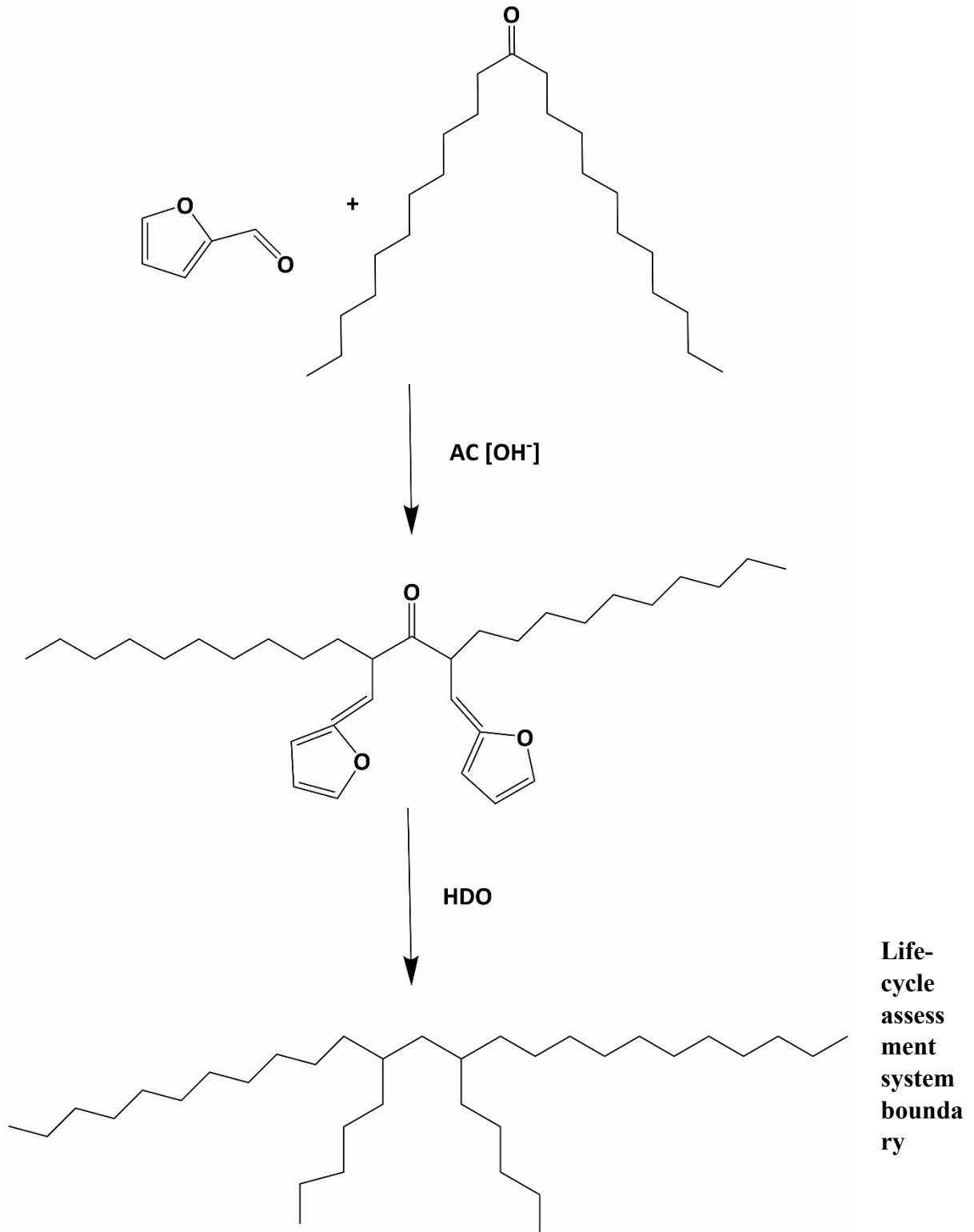

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Figure S3. Illustration of packed bed reactor contents.

Scheme S1. Aldol condensation of furfural with 12-tricosanone followed by the hydrodeoxygenation of the intermediate to yield bio-lubricants.
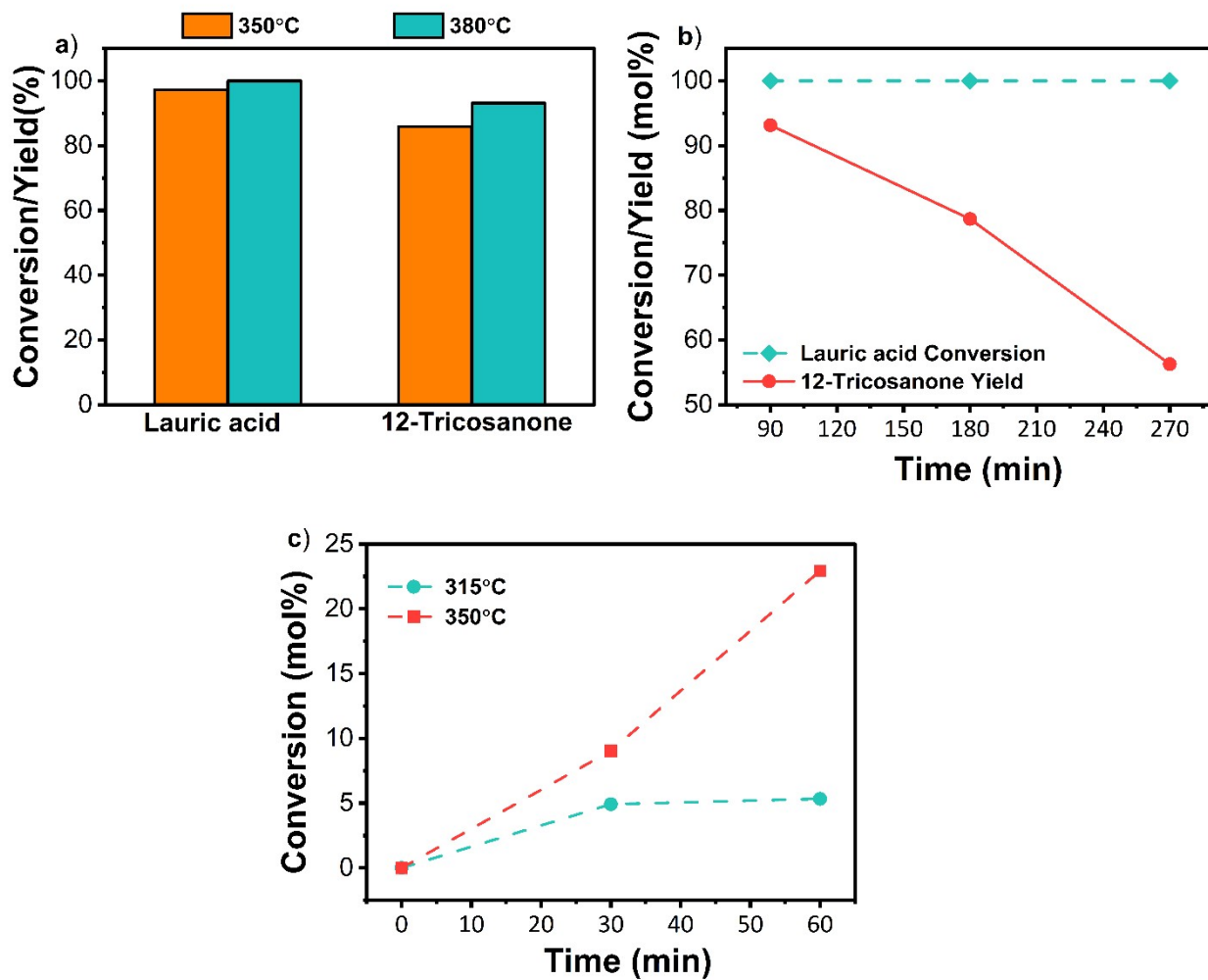
a)

Figure Process system boundaries for cycle assessment.

0.5g of Quartz
wool +2.5 g
silica beads

Figure S8. Reaction conditions 0.15 M lauric acid, 30 ml dodecane, 20 bar N_2, 800 rpm, 0.2 g catalyst. a) Temperature optimization on MgO. b) Time optimization on MgO at 380 °C. c) Decomposition of 12-tricosanone in the absence of lauric acid and MgO. This result explains the drop in yield with an increase in reaction time seen in b).

a) **Solventless Ketonization: 50% product yield**

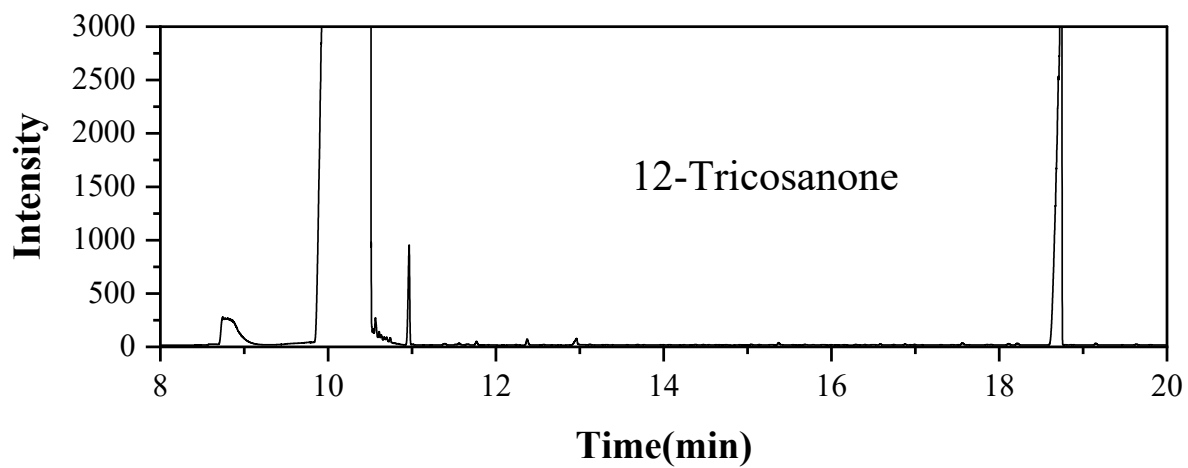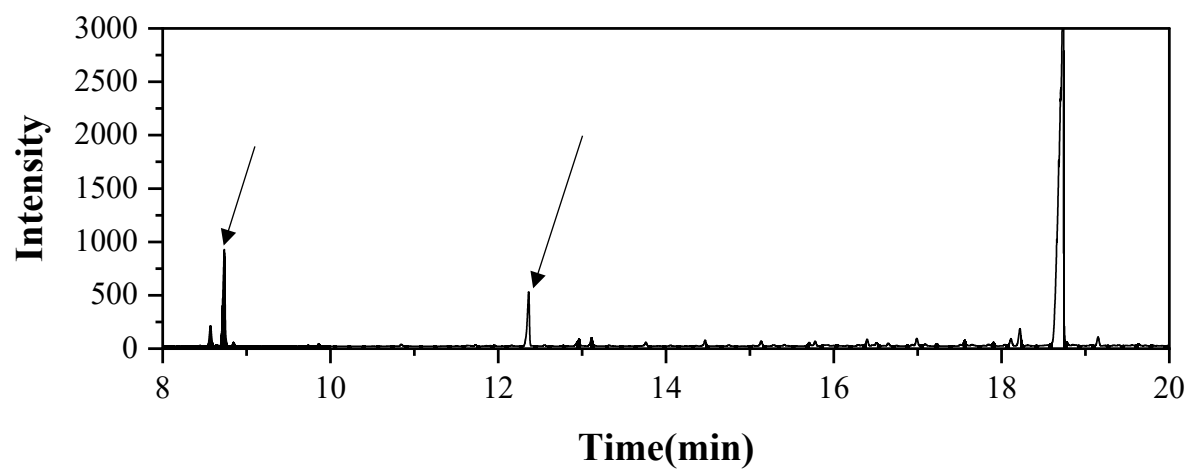Undecane   Lauraldehyde

Figure S9. GC chromatograms of the products of the a) Solventless and with b) Solvent reactions. Thermal cracking was observed only in the solventless reaction.
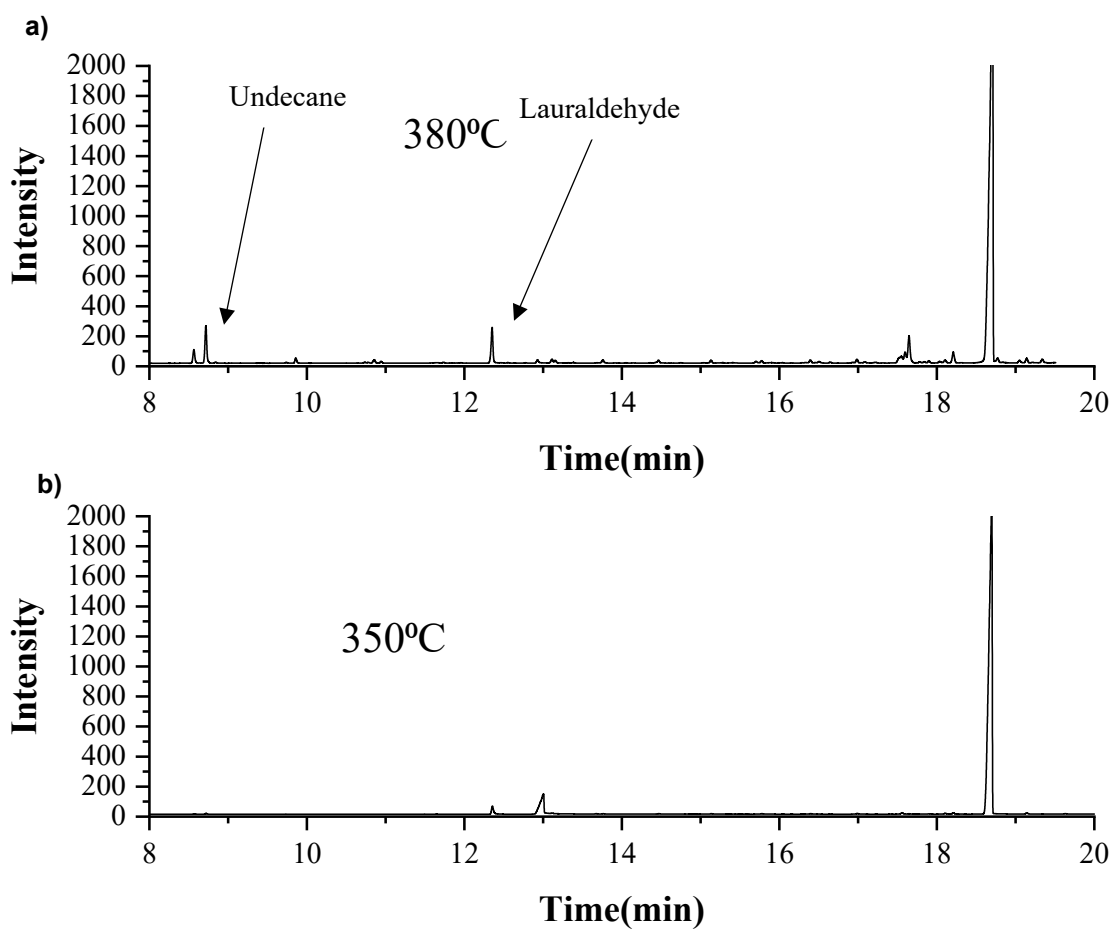
Figure S10. Comparison of the GC chromatograms of the product solution at a) 380 and b) 350 ⁰C reactions. Negligible cracking was observed at 350 ⁰C.

Table S1. XRF results of the collected effluent solution.

Sample	Species Detected
30	Cl (99%), Ca, P
60	Cl (99%), Ca, P
120	Cl (99%), Ca, P
240	Cl (99%), Ca, P
Blank	Si, Ca, P

Table S2. BET surface area for mixed oxides.

Catalyst	Surface Area (m^2/g)
MgO	59
$Mg_3Al_1O_{4.5}$	160.1
$Mg_3Al_{0.8}Ce_{0.2}O_{4.5}$	130.5
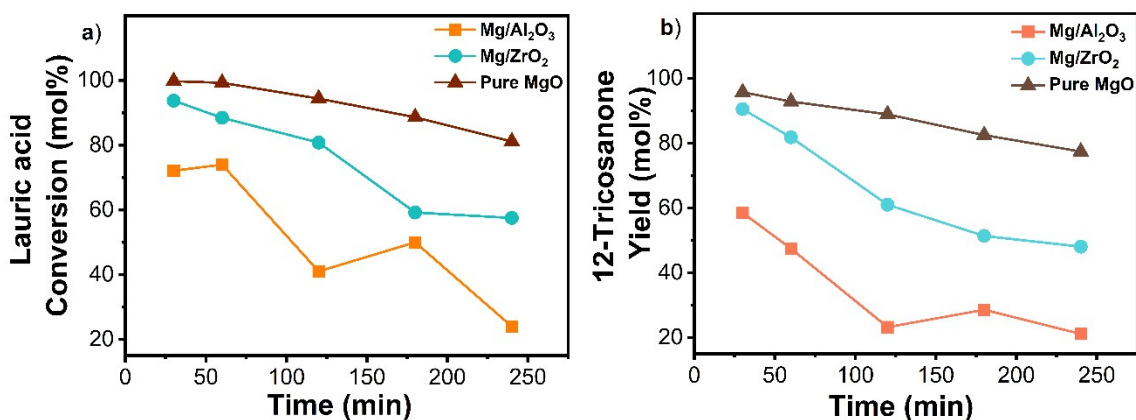
Figure S11. a) Lauric acid conversion. b) 12-tricosanone yield over pure MgO and MgO impregnated on Al_2O_3, ZrO_2, and SiO_2 with a loading of 10 wt.%. Reaction conditions: Temperature 365°C, flowrate 0.1 g min⁻¹, WHSV 0.1 min⁻¹, W/F 10 min, and residence time of 41 min.
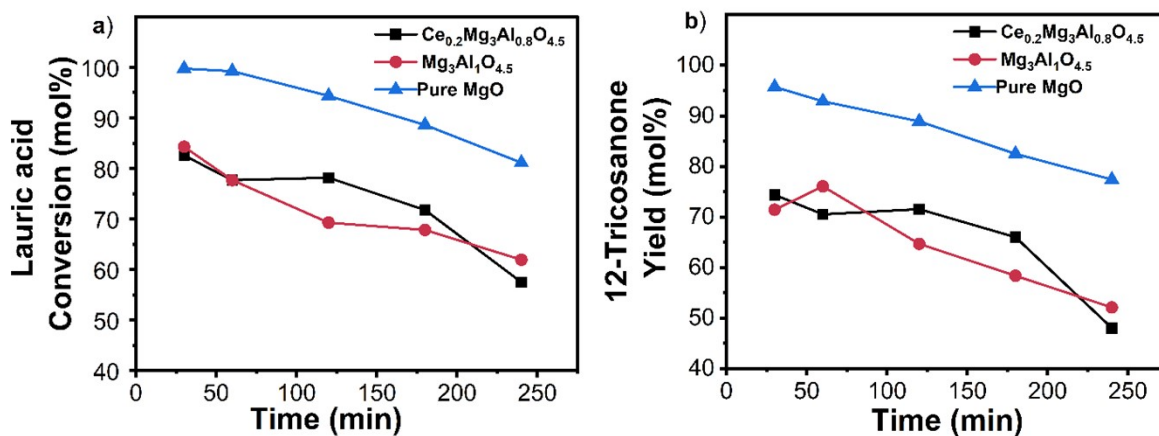
Figure S12. a) Lauric acid conversion. b) 12-tricosanone yield over pure MgO, $Mg_3Al_1O_{4.5}$, and $Mg_3Al_{0.8}Ce_{0.2}O_{4.5}$.
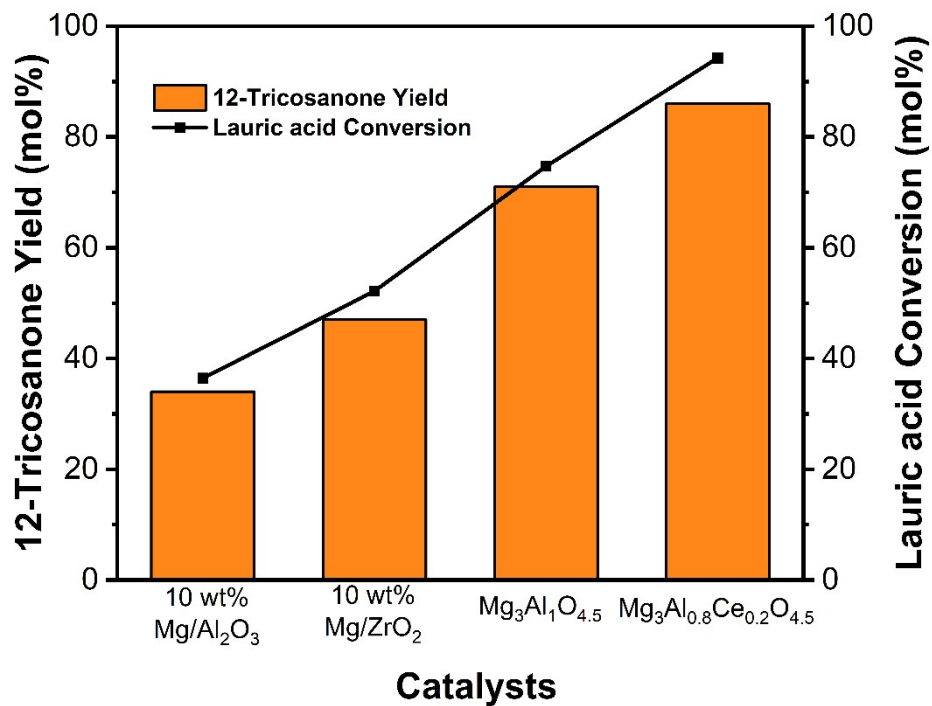
Figure S14. Reaction Conditions: 3g lauric acid, 30ml dodecane, 365 ºC, 60 min, 800 rpm, 20 bar N_2, 0.5g catalyst loading.
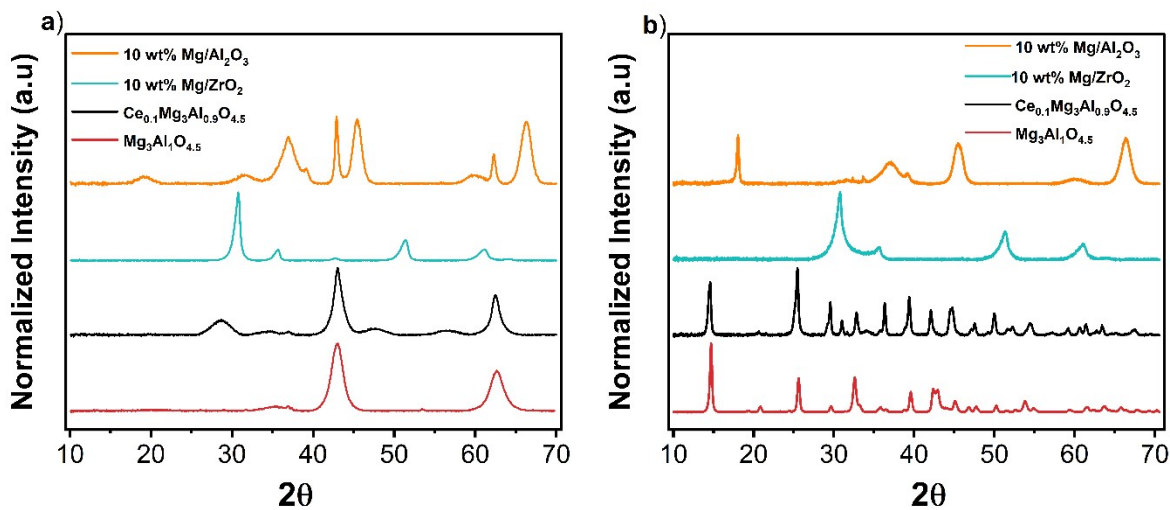
Figure S15. XRD spectra of the a) Fresh and b) Spent impregnated and mixed MgO catalysts.
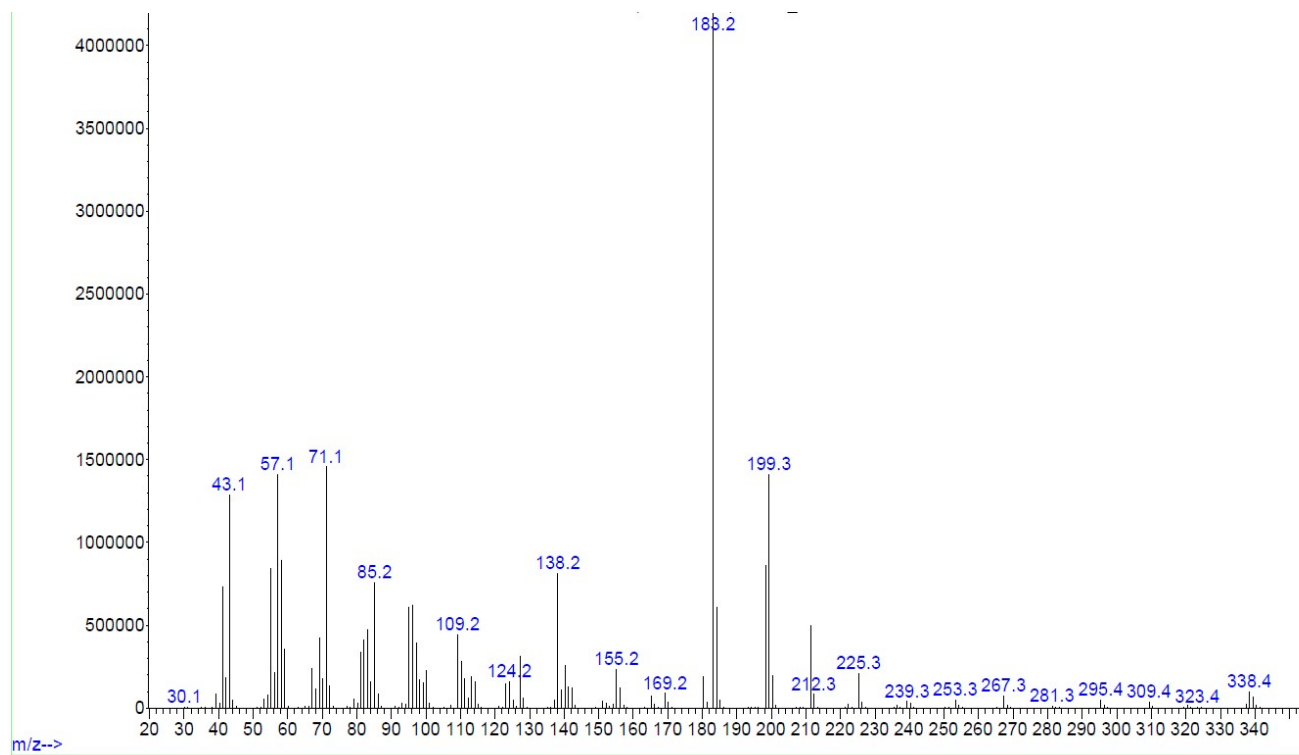
Figure S16. MS Spectra of 12-tricosanone produced in the kilogram scale flow reactor.
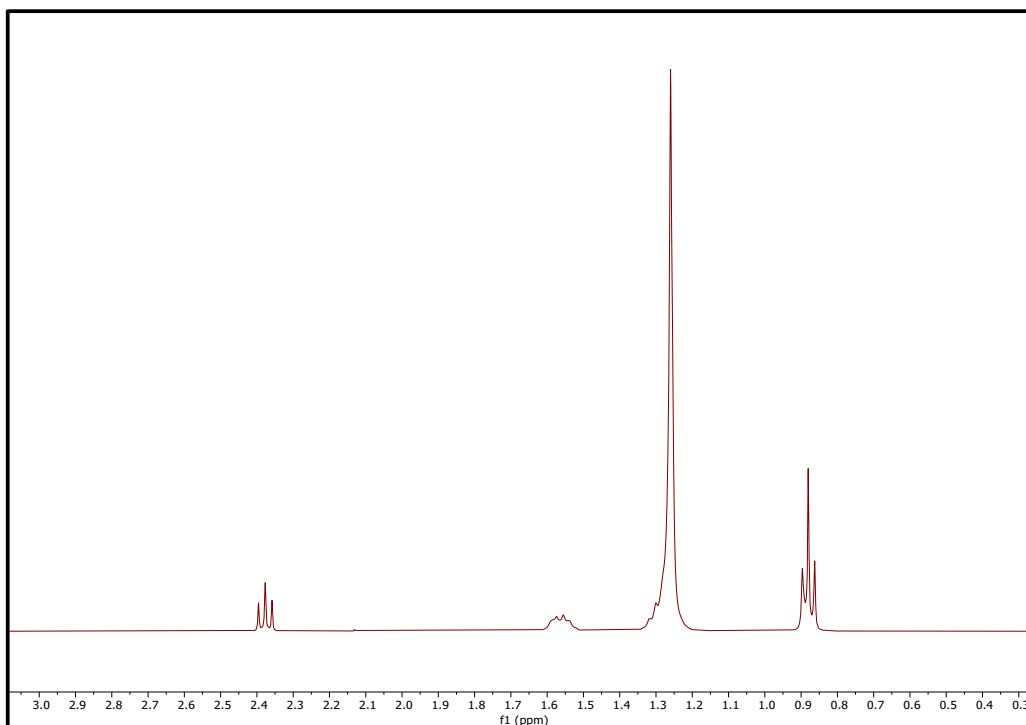
Figure S17. ¹H NMR (400 MHz, CDCl$_3$) δ 2.38 (t, J = 7.5 Hz, 4H), 1.56 (dd, J = 13.6, 6.4 Hz, 4H), 1.29 (d, J = 9.8 Hz, 4H), 1.26 (s, 28H), 0.88 (t, J = 6.7 Hz, 6H).

Additional Assumptions for Techno-economic Analysis

Figure S18. ¹³C NMR (101 MHz, CDCl$_3$) δ 211.78, 42.83, 31.94, 29.62, 29.49, 29.43, 29.37, 29.34, 29.29, 23.92, 22.69, 14.11.

1. Catalysts can be recovered, and the equipment cost is not considered.
2. A separator separates hydrodeoxygenation's by-products from the major product. This assumption is made as the exact composition of the by-product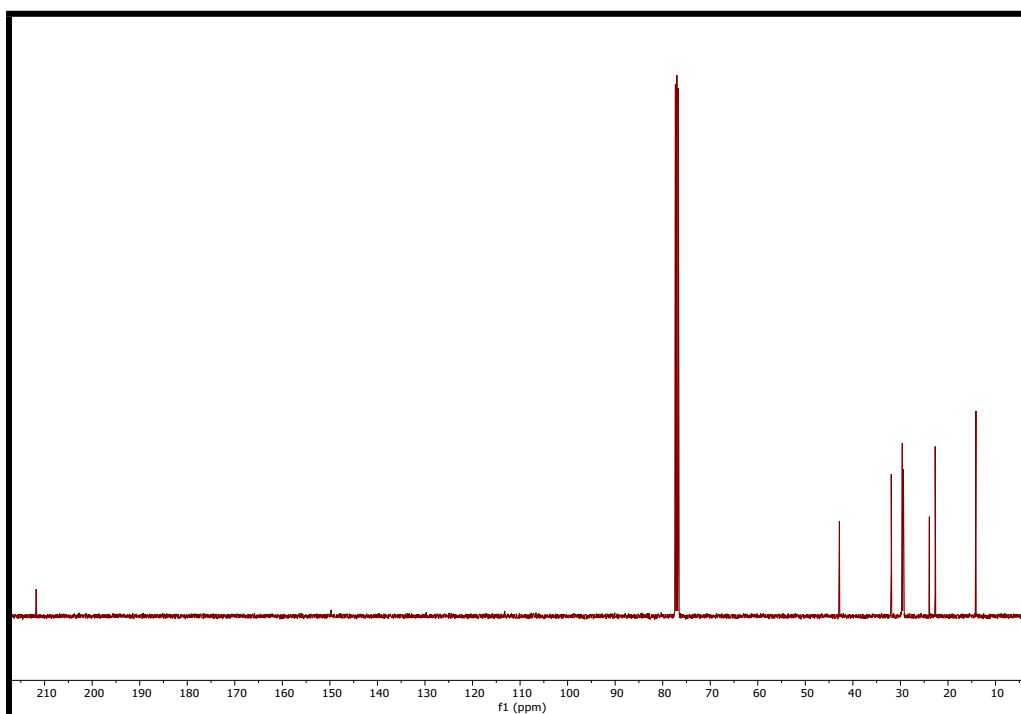s is not reported in the previous study because the formation of $C_1 - C_6$ alkanes from the solvent, cyclohexane, made characterization of the exact product composition difficult. Instead, it is reported that the by-products are mostly composed of short-chain alkanes, gases, and some oxygenated species[1]. The cost of the separator is approximated based on its size.
3. The residence time of the reactions for aldol condensation and hydrodeoxygenation is taken from the reaction time reported in the literature[1] for equipment sizing.
4. From our previous study, the hydrodeoxygenation catalyst $Ir-ReO_X/SiO_2$ costs \$2,062,856/ton[2].
5. The catalyst life for Ir-ReO/SiO and MgO is 12 months, and 99% of the metal can be recovered[2].
6. The price of the MgO catalyst is taken from Alibaba to be \$110/ton[3].
7. The mass of the catalyst needed is calculated by keeping the ratio of the mass of the catalyst and the product of inlet reactant mass flow rates and residence time used in experiments the same as reported in the literature below. For aldol condensation, the ratio between NaOH (1M, 0.2g) and the limiting reactant, 12-tricosanone (0.10g) is kept the same. For hydrodeoxygenation, the ratio between the catalyst $Ir-ReO_X/SiO_2$ and 12-tricosanone (0.10g) is maintained, as mentioned in the reaction procedures in our previous study.
8. The catalyst for aldol condensation(NaOH) is assumed to be nonrecoverable[1] and therefore calculated as a solvent.
9. No electricity generation is considered.
10. No by-product sale is considered in the process.
11. Transportation and wastewater treatment costs are not considered.
12. Prices for key material are as follows: H_2 \$1,570/ton[4], methanol \$595/ton[5], cyclohexane \$1300/ton[6], dichloromethane \$880/ton[7], NaOH \$300/ton[8], and hydrochloric acid \$153/ton[9].

Table S3. Summary of operating, capital, and total cost of the base scenario.

Operating Cost	Cost (Million \$/yr)	Capital Cost	Cost (Million \$)
Material Cost	294.01	Purchased Equipment	33.77
Catalyst Cost	2.54	Other Capital Cost	50.04
Utility Cost	16.97	General and Administrative Overheads	4.19
Other Operating Cost	6.83	Contract Fee	2.51
General and Administrative Cost	25.63	Contingencies	8.38
Annualized Total Cost	15.8	Working Capital	9.89
Total Operating Cost Including Annualized Cost	361.78	Total Capital Cost	108.78

Table S4. Summary of operating, capital, and total cost of the alternative scenario.

Operating Cost	Cost (Million $/yr)	Capital Cost	Cost (Million $)
Material Cost	558.66	Purchased Equipment	40.92
Catalyst Cost	2.54	Other Capital Cost	46.9
Utility Cost	15.28	General and Administrative Overheads	4.39
Other Operating Cost	6.55	Contract Fee	2.63
General and Administrative Cost	46.64	Contingencies	8.78
Annualized Total Cost	16.6	Working Capital	10.36
Total Operating Cost Including Annualized Cost	646.27	Total Capital Cost	113.98

Additional Assumptions for Life-cycle Assessment

1. The inventory data for furfural and lauric acid are obtained from previous literature[10,11].
2. The contribution of the buildings is not included because they can be used for other purposes[4].
3. For biomass-based production of furfural and lauric acid, carbon is absorbed during plant growth[4,10,12]. Biomass-based furfural is mostly produced from corn cob, and its carbon sequestration effect is estimated based on previous literature[4]. The lauric acid is assumed to be from palm oil[4,10,12].
4. The GWP associated with oil palm plantation is highly influenced by the land use change (LUC)[12–14]. We considered three scenarios for estimating the global warming potential (GWP) shown in **Table S5**. The GWP for Scenarios 2 and 3 were taken from the work of Noël et al[12]. **Figure S20-22** illustrate the assumptions made for lauric acid production.
5. The GWP for lubricant production from petroleum-based process was obtained from the Energy Information Administration to be 10.70 kg CO_2 eq./gallon lubricants[15]. To convert the GWP to mass unit, we take the density of polyalphaolefins at 833 kg/m^3 for lubricants. The GWP of lubricants from petroleum-based process is then 3.39 CO_2 eq/kg[16].
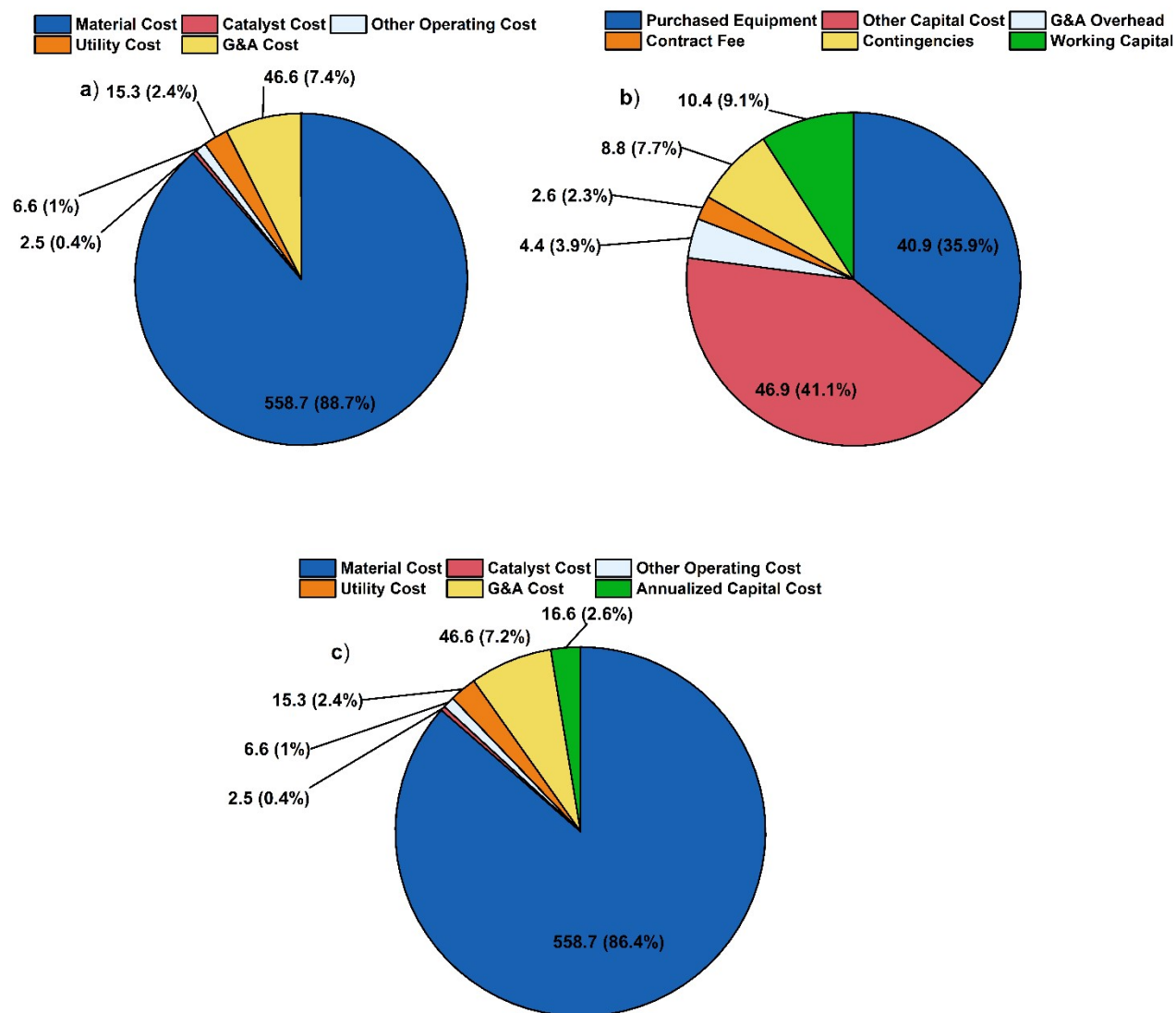
Figure S19. a) Operating cost breakdown, graph labels refer to cost in million $/yr along with the percentage of total operating cost b) Capital cost breakdown, in million $ and c) Total cost breakdown, numbers are presented in million $/year. This figure is for the alternate scenario where 12-tricosanone is purchased at market price.

Breakdown of Global Warming Potential Contribution

Table S5. Global warming potential for different scenarios.

	GWP (kg CO_2/kg lauric acid)	GWP (kg CO_2/kg lubricant base oil)
Scenario 1	0	3.09
Scenario 2	1.7^{12}	4.77
Scenario 3	-68^{12}	-64.1

Carbon Neutral

Products

Seedlings

Fresh Fruit
Bunch

Plantation

**Milling and
Preprocessing**

Lauric
Acid

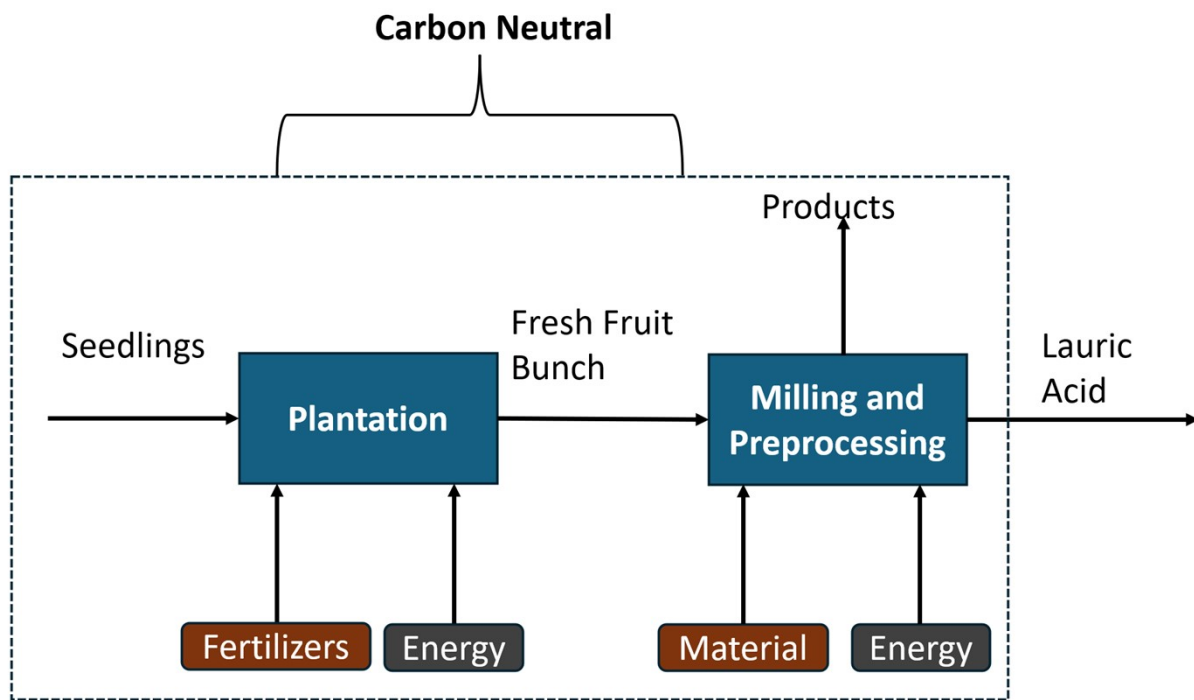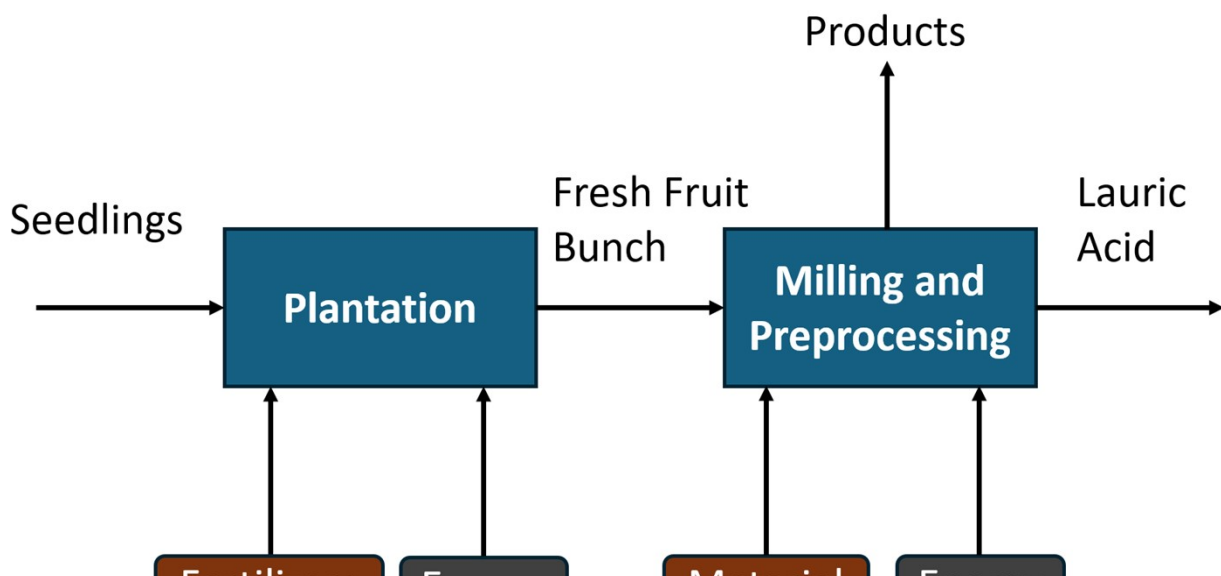Fertilizers   Energy

Material   Energy

Figure S20. Illustration for the carbon neutral assumption made in Scenario 1, in which the production is offset by the carbon sequestration effect during plant growth.

Products

Seedlings

Fresh Fruit
Bunch

Plantation

**Milling and
Preprocessing**

Lauric
Acid

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