

Electronic Supporting Information

Conversion of Plastic Waste into High-Value Lubricants: Techno-Economic Analysis and Life Cycle Assessment

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Methodology

Simulation parameters and results

The block diagram for HDPE conversion process to HQL is shown in Figure S1. A100 is the HDPE pretreatment and recycled H₂ compression section. Feedstock is then moved to A200, where the hydrogenolysis of plastics takes place. Liquid products are separated from the slurry phase via candle filters, while the gas stream goes through PSA to recover unreacted H₂. Then, hydrocarbons in the range C₃-C₈ are recovered via the Joule-Thomson unit (Figure S2). The catalyst is washed with hexane in A300. The remaining fuel gas is combusted to produce power and steam. In Table S1 and S2, the stream properties are listed for the cases with 60% (LY) and 90% (HY) lubricant yield, respectively.

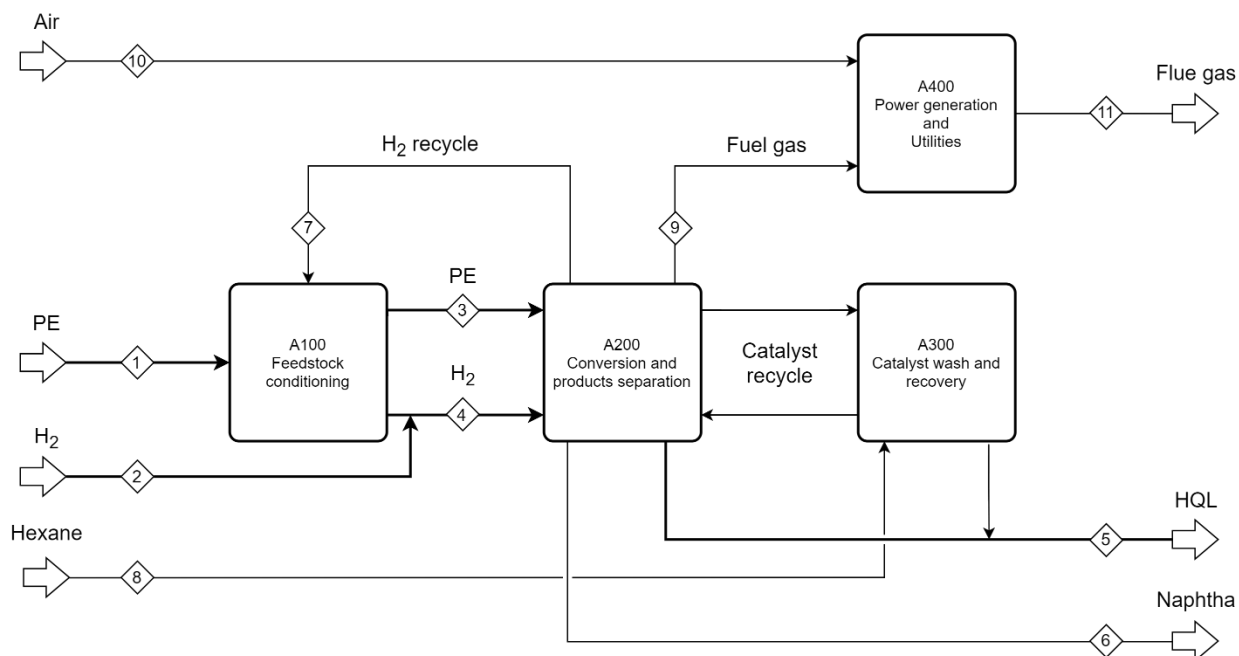


Figure S1. Simplified block diagram with the main streams highlighted.

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Table S1. Summary stream table of the process with lubricant yield of 60%. The components flow rates are listed in mole basis.

	1	2	3	4	5	6
Temperature / °C	25.00	25.00	25.00	41.87	43.28	29.13
Pressure / bar	1.01	20.00	1.01	11.72	1.01	10.95
Phase	Solid	Gas	Solid	Gas	G+L	G+L
Mass flowrate / t day ⁻¹	250.00	8.59	250.00	14.21	152.88	47.12
Mole flowrate / kmol h ⁻¹	0.30	177.54	0.30	293.10	14.21	31.20
HDPE	0.30	0	0.30	0	0	0
H ₂	0	177.54	0	293.02	0.16	0.01
CH ₄	0	0	0	0.08	0.19	0.94
C ₂ H ₆	0	0	0	0	0.10	3.10
C ₃ H ₈	0	0	0	0	0.07	5.43
C ₄ H ₁₀	0	0	0	0	0.11	9.85
C ₅ H ₁₂	0	0	0	0	0.07	3.96
C ₆ H ₁₄	0	0	0	0	0.43	3.80
C ₇ H ₁₆	0	0	0	0	0.20	2.76
C ₈ H ₁₈	0	0	0	0	0.14	1.34
C ₃₅ H ₇₂	0	0	0	0	12.73	0
O ₂	0	0	0	0	0	0
N ₂	0	0	0	0	0	0
CO ₂	0	0	0	0	0	0
H ₂ O	0	0	0	0	0	0
	7	8	9	10	11	
Temperature / °C	43.03	25.00	3.76	25.00	130.06	
Pressure / bar	8.00	1.01	5.00	1.01	1.30	
Phase	Gas	Liquid	Gas	Gas	Gas	
Mass flowrate / t day ⁻¹	5.62	0.59	59.18	1192.25	1251.43	
Mole flowrate / kmol h ⁻¹	115.56	0.29	132.41	1721.89	1866.47	
HDPE	0	0	0	0	0	
H ₂	115.48	0	20.36	0	0	
CH ₄	0.08	0	79.07	0	0	
C ₂ H ₆	0	0	23.53	0	0	
C ₃ H ₈	0	0	7.36	0	0	
C ₄ H ₁₀	0	0	1.92	0	0	
C ₅ H ₁₂	0	0	0.13	0	0	
C ₆ H ₁₄	0	0.29	0	0	0	
C ₇ H ₁₆	0	0	0	0	0	
C ₈ H ₁₈	0	0	0	0	0	
C ₃₅ H ₇₂	0	0	0	0	0	
O ₂	0	0	0	361.60	60.27	
N ₂	0	0	0	1360.29	1360.29	
CO ₂	0	0	0	0	156.75	
H ₂ O	0	0	0	0	289.16	

Table S2. Summary stream table of the process with lubricant yield of 90%. The components flow rates are listed in mole basis.

	1	2	3	4	5	6
Temperature / °C	25.00	25.00	25.00	54.28	44.16	33.98
Pressure / bar	1.01	20.00	1.01	11.72	1.01	10.95
Phase	Solid	Gas	Solid	Gas	G+L	G+L
Mass flowrate / t day ⁻¹	250.00	4.41	250.00	14.18	226.80	7.67
Mole flowrate / kmol h ⁻¹	0.30	91.21	0.30	293.04	20.03	4.43
HDPE	0.30	0	0.30	0	0	0
H ₂	0	91.21	0	293.02	0.43	0.01
CH ₄	0	0	0	0.02	0.07	0.10
C ₂ H ₆	0	0	0	0	0.04	0.30
C ₃ H ₈	0	0	0	0	0.03	0.45
C ₄ H ₁₀	0	0	0	0	0.04	1.03
C ₅ H ₁₂	0	0	0	0	0.02	0.65
C ₆ H ₁₄	0	0	0	0	0.25	0.86
C ₇ H ₁₆	0	0	0	0	0.04	0.69
C ₈ H ₁₈	0	0	0	0	0.03	0.34
C ₃₅ H ₇₂	0	0	0	0	19.10	0
O ₂	0	0	0	0	0	0
N ₂	0	0	0	0	0	0
CO ₂	0	0	0	0	0	0
H ₂ O	0	0	0	0	0	0
	7	8	9	10	11	
Temperature / °C	43.03	25.00	19.36	25.00	130.00	
Pressure / bar	8.00	1.01	10.95	1.01	1.30	
Phase	Gas	Liquid	Gas	Gas	Gas	
Mass flowrate / t day ⁻¹	9.77	0.46	20.41	435.10	455.51	
Mole flowrate / kmol h ⁻¹	201.83	0.22	66.97	628.39	687.37	
HDPE	0	0	0	0	0	
H ₂	201.81	0	35.61	0	0	
CH ₄	0.02	0	19.88	0	0	
C ₂ H ₆	0	0	6.35	0	0	
C ₃ H ₈	0	0	2.74	0	0	
C ₄ H ₁₀	0	0	1.90	0	0	
C ₅ H ₁₂	0	0	0.37	0	0	
C ₆ H ₁₄	0	0.22	0	0	0	
C ₇ H ₁₆	0	0	0	0	0	
C ₈ H ₁₈	0	0	0	0	0	
C ₃₅ H ₇₂	0	0	0	0	0	
O ₂	0	0	0	131.96	21.99	
N ₂	0	0	0	496.43	496.43	
CO ₂	0	0	0	0	50.99	
H ₂ O	0	0	0	0	117.96	

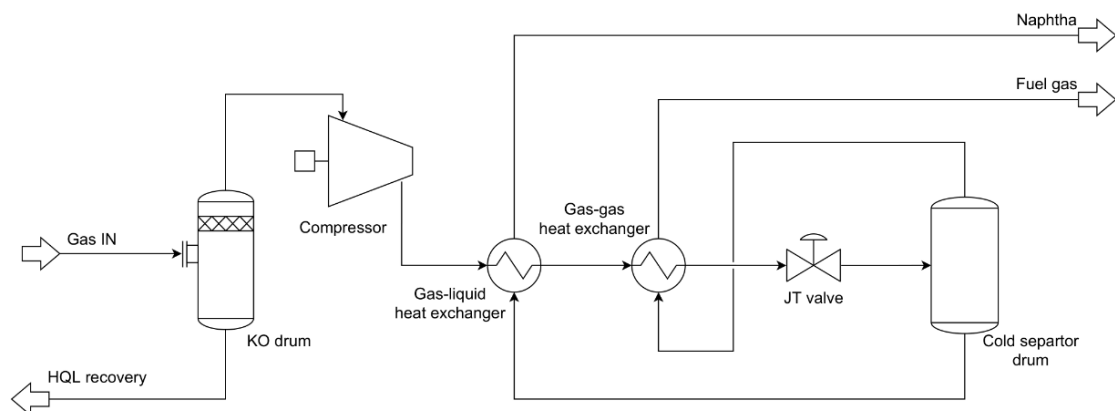


Figure S2 - Flow scheme of Joule-Thomson plant used to recover the light naphtha fraction.

Reactor design and stoichiometry

Mechanically agitated reactors are commonly used in slurry systems where a high degree of suspension is required. In fermentation processes, large vessels up to 500 m³ can be encountered.² At larger scale, axial impellers are used together with a bottom radial impeller to avoid formation of concentration gradients and maintain a high mass transfer. For the calculation of the reaction volume, 122 batches/year and 219 batches/year were considered for a reaction time of 72 h (LY case) and 40 h (HY case), respectively. By considering an average slurry density of 900 kg/m³, the slurry volume was 946 m³/batch for a 72 h runtime, while it was 527 m³/batch for a 40 h runtime. For the latter case, two reactors with half capacity were considered. The value of 0.01 HP/gal (i.e. 1.97 kW/m³) was preliminarily used to estimate the energy required for the agitation of the three-phase system.³ Moreover, the number of reactors for both scenarios was doubled to maintain continuous operation. The reactors were modeled with the *Rstoic* model.

Table S3. Reactor volume and energy requirements.

Cases	Reaction time / h	Volume / m ³ batch ⁻¹	Energy / MW
LY	72	946	1.86
HY	40	527	1.04

Table S4. Fractional conversions and stoichiometry defined for the reactor model. The conversion values to C1-C8 were based on the data published in Celik et al.¹ A total conversion of HDPE was assumed for both cases.

HDPE conversion (60% yield)	HDPE conversion (90% yield)	Stoichiometry
0.108	0.027	HDPE + 2500 H ₂ = 2500 CH ₄
0.072	0.018	2 HDPE + 2500 H ₂ = 2500 C ₂ H ₆
0.052	0.013	3 HDPE + 2500 H ₂ = 2500 C ₃ H ₈
0.064	0.016	4 HDPE + 2500 H ₂ = 2500 C ₄ H ₁₀
0.028	0.007	5 HDPE + 2500 H ₂ = 2500 C ₅ H ₁₂
0.032	0.008	6 HDPE + 2500 H ₂ = 2500 C ₆ H ₁₄
0.028	0.007	7 HDPE + 2500 H ₂ = 2500 C ₇ H ₁₆
0.016	0.004	8 HDPE + 2500 H ₂ = 2500 C ₈ H ₁₈
0.600	0.900	35 HDPE + 2500 H ₂ = 2500 C ₃₅ H ₇₂

TEA assumptions and results

Table S5. Cost parameters of the main equipment per process area. The costs reported are in USD₂₀₁₆.

Process area	Equipment	Uninstalled cost	Installation factor	Scaling factor	Reference
A100	H ₂ compressor	\$ 642,600	2.47	0.80	4
	Feedstock storage tank	\$ 2,062,830	1.70	0.60	5
	Plastic pretreatment line	\$ 446,520	1	-	Retail [†]
	Transfer conveyor	\$ 3,180,890	1.70	0.60	5
	Dome reclaiming system	\$ 1,795,250	1.70	0.60	5
A200	Reactors	\$ 2,529,980	1.73	-	APEA [*]
	Reactor discharge pump	\$ 35,360	2.30	0.80	5
	PSA	\$ 1,624,210	1	0.60	6
	Heat exchanger	\$ 98,580	2.2	0.70	5
	Gas-to-JT compressor	\$ 1,592,820	2.5	0.60	7
	JT unit	\$ 72,660	-	-	Quote from vendor ^{††}
A300	Candle filter	\$ 1,024,750	-	-	Quote from vendor ^{†††}
	Distillation column	\$ 54,060	3.68	-	APEA [*]
	Kettle reboiler	\$ 14,130	5.63	1.00	5
	Hexane cooler	\$ 98,580	2.20	0.70	5
A400	Steam boiler	\$ 33,110,160	1.80	0.60	5
	Cooling tower system	\$ 1,594,620	1.50	0.60	5
	Steam turbine	\$ 6,988,500	1.80	0.60	5

* Aspen Economic Analyzer v12.

† Estimated from prices reported in <https://xtingmachine.en.made-in-china.com> for a 3000 kg/h plastic recycling machine.

†† Budgetary quote provided by Croft Production Systems, Inc. It included installation costs.

††† Budgetary quote provided by DrM. It includes installation costs.

The required operating labor was estimated with the following correlation:⁸

$$N_{OL} = (6.29 + 31.7P^2 + 0.23N_{np})^{0.5} \quad (eq. S1)$$

where N_{OL} is the number of operators per shift, P is the number of processing steps with handling of particulate solids, and N_{np} is the number of the remaining processing steps (e.g. reaction, compression, etc.) The processing steps for the HQL process are listed in Table S6.

Table S6. Number of processing steps and operators per shift.

Equipment type	Number of equipment
Compressor	3
Heat exchanger	7
Heater/Furnace	2
Reactor	1
Separation tower	2
P	0
N_{OL}	3.23

A single operator covers 245 shifts per year (49 week/year x 5 shift/week), while the total number of shifts is 1095 shift/year (365 day/year x 3 shift/day). Therefore, the required operating labor is equal to (3.23 operator/shift) x (1095 shift/year) / (245 shift/year) ≈ 15. The estimation does not include supervisory staff nor supporting roles.

Emissions calculations using LCA

The detailed breakdown of upstream materials consumption basis, energy use and emissions are provided in Table S7 and Table S8, respectively. The data presented in Table S7 serves as the basis for emission results delineated in Table S8 and are obtained from the Aspen Plus process model developed in this study. Table S8 provides the unit emissions associated with each parameter and the total GHG emissions for the process normalized to HQL production; where the unit process emissions are obtained from the GREET database.⁹ In Table S8 the emissions associated with hydrogen and electricity production consider the steam methane reforming (SMR) process and average U.S. grid electricity mix, respectively.

Table S7. Process parameters basis for upstream consumption.

	PE waste	H2 from SMR WTP	U.S. electricity mix	Hexane	Naphtha	Catalyst
	kg plastic feedstock/kg lube	mmbtu/kg	mmbtu/kg	kg/kg	mmbtu/kg	kg/kg
Usage amount	1.102	0.0022	0.00019	0.002	-0.0014	0.00008

Table S8. Detailed breakdown of upstream emissions profile for energy and materials use

	PE waste	H2 from SMR WTP	U.S. electricity mix	Hexane	Naphtha	Catalyst	
Unit	per kg	per mmbtu	per mmbtu elec	per kg hexane	per mmbtu	per ton	
Total energy	btu	398	492811	2023496	56868	83784	78
Fossil fuels	btu	315	492083	1584065	56868	82496	74
Coal	btu	143	1266	638682	-	2137	25
Natural gas	btu	166	485353	924209	-	64980	45
Petroleum	btu	6	5464	21175	-	15379	5

GHG (g/kg material)	g	25	94217	131625	309	13629	6097
GHG (kg/kg HQL)		0.0272	0.208	0.0261	0.0006	-0.0196	0.0005

Exploration of lab-scale hydrogenolysis conditions

Hydrogenolysis of polyethylene was done in a Parr autoclave reactor using about 3 g of polymer and varying amounts of Pt/STO catalyst, along with variations in H₂ pressure (Figure S3), temperature (Figure S4). The largest changes with respect to run time and catalyst loading are discussed in the main text, and distribution plots for the resulting lubricant products are shown in Figure S5. Ambient atmosphere was discharged from the reactor prior to heating by flushing the lines, valves, and reactor with He. The reactor was then heated up to 300 °C at roughly 5-10 °C/min until a stable temperature was established for 30 min. To minimize mass transfer limitations, a mixing impeller was set to about 800 rpm. Characterization of the lubricant products was done by high-temperature gel permeation chromatography (HT-GPC) (Agilent-Polymer Laboratories 220) equipped with RI and viscometer detectors. Monodisperse polystyrene (ranging from 400 Da to 1.1 MDa) and monodisperse polyethylene (ranging from 300 Da to 120,000 Da) standards were tested to establish a calibration curve. The GPC column set included 3 Agilent PL-Gel Mixed B columns and 1 PL-Gel Mixed B guard column. 1,2,4-trichlorobenzene (TCB) containing 0.01 wt% 3,5-di-tert-butyl-4-hydroxytoluene (BHT) was chosen as the eluent at a flow rate of 1.0 mL/min at 150 °C. The lubricant products were prepared in TCB at a concentration of about 2.0 mg/mL and heated at 150 °C for 24 h prior to injection and analysis.

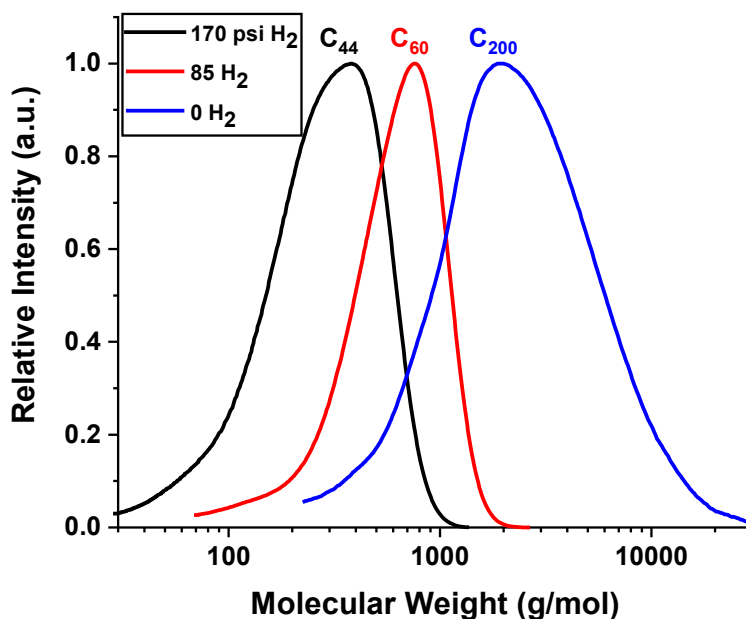


Figure S3 - Distribution plots of hydrogenolysis products at varying H_2 pressures after 72 h, as determined by GPC. The hydrogen-free run (blue) amounts to catalytic thermal degradation. Carbon number labels are roughly calculated from Mw data.

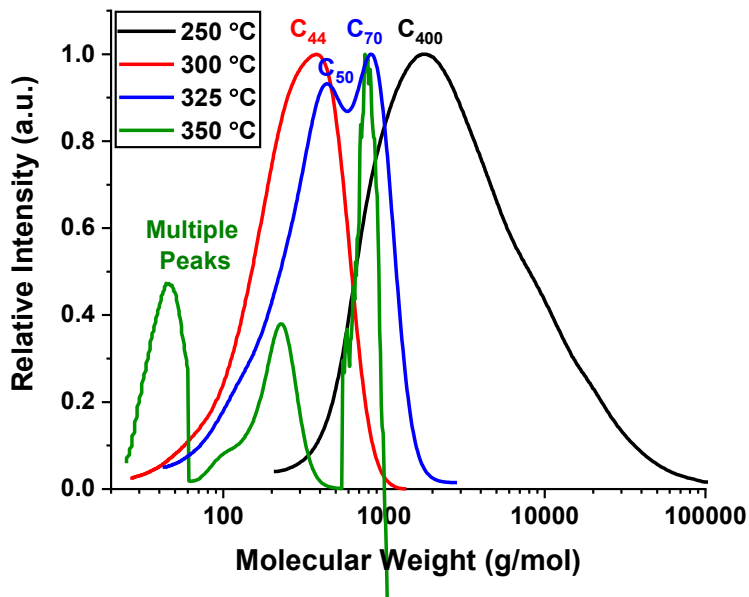


Figure S4 - Distribution plots of hydrogenolysis products at varying temperatures after 72 h, as determined by GPC. Hydrogenolysis at 325 and 350 °C (blue, green respectively) show multiple peaks and thus the presence of other degradative processes, such as catalytic pyrolysis. Carbon number labels are roughly calculated from Mw data.

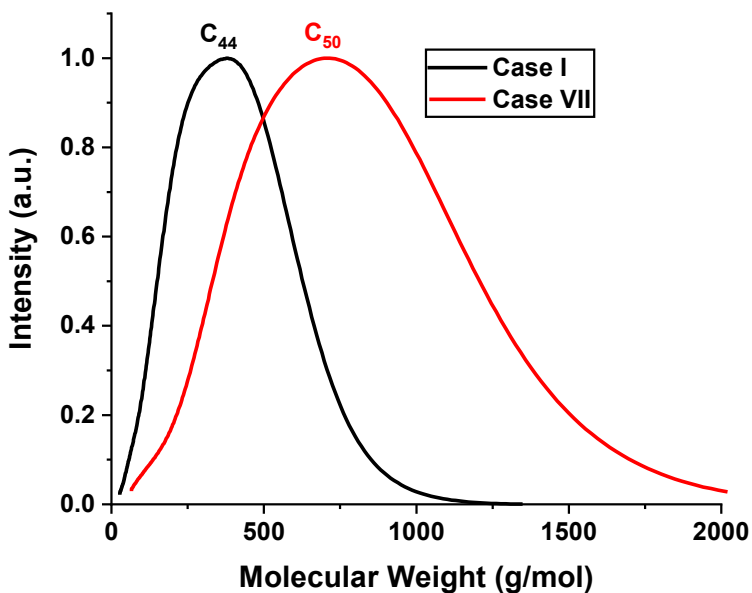


Figure S5 - Distribution plots of hydrogenolysis products from case LY and case HY described in the main text, as determined by GPC. While the molecular weight and polydispersity of case HY are larger than case LY, these differences are minor and do not greatly impact the viability of the case HY product as a lubricant. Carbon number labels are roughly calculated from Mw data.

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