SUPPORTING INFORMATION: Techno-Economic Analysis of a Chemical Process to Manufacture Methyl-ɛ-Caprolactone from Cresols

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1) Stream Information for Process Flow Diagram

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Molar Flow (kmol/hr)								
p-Cresol	11.600	0.000	0.357	0.000	0.001	0.357	0.000	0.315
n-Dodecane	0.021	0.000	62.176	0.000	0.012	62.163	0.012	62.143
МСОН	0.000	0.000	0.233	0.000	0.001	0.232	0.000	0.000
MCH	0.000	0.000	11.438	0.000	0.107	11.396	0.042	0.006
MCL	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
4-M-6-HHA	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H_2	0.000	24.950	0.056	224.548	224.600	0.052	0.004	0.000
H_2O	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
H_2O_2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Temperature (°C)	25	25	75	75	75	45	45	214
Pressure (bar)	1	1	1	1	1	1	1	1
	9	10	11	12	13	14	15	16
Molar Flow (kmol/hr)								
p-Cresol	0.042	0.000	0.042	0.000	0.000	0.000	0.000	0.000
n-Dodecane	0.021	0.000	0.021	0.000	0.000	0.000	0.000	0.000
МСОН	0.231	0.001	0.230	0.549	0.000	0.000	0.549	0.001
MCH	11.322	0.067	0.222	55.394	0.001	0.000	44.284	0.008
MCL	0.000	0.000	0.044	0.000	0.000	0.000	9.999	9.954
4-M-6-HHA	0.000	0.000	0.000	0.000	0.000	0.000	1.111	1.080
H_2	0.002	0.050	0.000	0.002	0.000	0.000	0.002	0.000
H_2O	0.000	0.000	0.000	0.007	0.000	20.916	32.026	0.000
H_2O_2	0.000	0.000	0.000	0.001	0.000	11.078	0.000	0.000
Temperature (°C)	140	140	170	157	157	25	50	181
Pressure (bar)	1	1	1	1	1	1	1	0.2
	17	18	19	20	21	22	23	-
Molar Flow (kmol/hr)								_
p-Cresol	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
n-Dodecane	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
МСОН	0.548	0.000	0.001	0.000	0.608	0.548	0.060	
MCH	44.294	0.000	0.008	0.000	52.397	44.294	8.103	
MCL	0.044	0.010	9.945	0.000	0.045	0.044	0.000	
4-M-6-HHA	0.000	1.079	0.001	0.000	0.000	0.000	0.000	
H_2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
H ₂ O	29.649	0.000	0.000	29.642	3.035	0.007	3.028	
H_2O_2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
Temperature (°C)	30	202	145	40	40	160	81	
Pressure (bar)	0.2	0.056	0.056	1	1	1	1	

Table S1. Stream data for labeled streams (from process flow diagram in Figure 2).

2) Economic Parameters for Net Present Value Method Analysis

Plant Lifetime	30 years
Discount Rate	15%
Depreciation Method	150% Declining balance (MACRS)
Recovery Period	5 years
Federal Tax Rate	35%
Construction Period	12 months
Yearly Operation Time	8000 hours
Working capital	5% of total capital investment
Start-up time	3 months
Revenues during startup	0%
Variable costs incurred during startup	100%
Fixed costs incurred during startup	100%

Table S2. Discounted Cash Flow Analysis Parameters.

Plant Lifetime: Taken to be 30 years. The impact of plant lifetime on MSP is shown in Figure S1.

Discount Rate: A report released by McKinsey & Company, which analyzed data from 118 chemicalcompany business units each with sales in above \$2,000,000,000 found that on average for successful new specialty chemical products (such as the monomer produced here) the internal rate of return ranged from 13% to 17%^[1]. Here 15% is used as an estimate.

Depreciation Method / Recovery Period: IRS Publication 946 states that a chemical manufacturing plant belongs to asset class 28.0 which has a 5 year recovery period. The IRS Modified Accelerated Cost Recovery System (MACRS) allows use of a 200% or 150% declining balance depreciation method that is switched to the straight-line method once it allows a larger deduction.^[2] The 150% declining balance method is used, because it gives a larger cumulative tax break in this case.

Construction Time: Gary and Handwerk^[3] estimate the construction time for petroleum refineries with capital investments on the order of \$1.5 billion to be two years. The scope and capital investment of our plant is significantly less than that of a petroleum refinery, so the construction time is estimated to be one year in this case.

Start-up Time: Perry and Green^[4] estimate that for a moderately complex plant, startup should be approximately 25% of the total construction time, or three months in our case. A conservative estimate that all costs and no revenues are incurred during this time is taken.

3) Equipment and Installed Cost Table

	equipment units for th	ne ouse euse design (1		p ereser rea).
Process Block	Equipment Type	Equipment Number	Purchase Cost	Installed Cost
Cresol	Reactor	R-1	\$161,600	\$434,800
Hydrogenation	Flash Tank	F-1	\$18,500	\$126,600
	Blower	B-1	\$22,300	\$32,600
	Heat Exchanger	HX-1 /HX-2	\$19,500	\$98,400
	Pump	P-1	\$4,700	\$37,200
Ketone	Distillation Column	C-1 / C-2	\$6,375,700	\$12,976,300
Purification	Pump	P-2 / P-3	\$8,500	\$63,300
Ketone Oxidation	Reactor	R-2	\$148,800	\$428,600
& Recycle	Distillation Column	C-4	\$396,100	\$1,608,300
	Decant Tank	D-1	\$17,300	\$107,800
	Heat Exchanger	HX-3 / HX-4	\$19,400	\$96,800
	Pump	P-4 / P-5 / P-6	\$12,800	\$91,500
Caprolactone	Distillation Column	C-3 / C-5	\$2,429,400	\$7,527,700
Purification	Pump	P-7 / P-8	\$8,600	\$50,600
	Vacuum Pump	V-1 / V-2	\$117,489	\$236,044

Table S3. Cost of equipment units for the base case design (10,000 tons yr⁻¹ of p-cresol fed).

4) Hydrogenation Reactor Sizing

Operating the hydrogenation reactor at atmospheric pressure allows significant cost savings associated with recycle and compression costs of effluent hydrogen gas from the reactor but amplifies mass transfer limitations. Xu, et al. report the sensitivity of hydrogenation reaction kinetics to mass transfer of hydrogen into solvent at atmospheric pressure; the time to reach 100% conversion of phenol to cyclohexanone decreased from 36 to 3 hours when the magnetic stir bar speed was increased from 500 to 1200 revolutions per minute. To mitigate mass transfer limitations, a countercurrent trickle-bed reactor was modeled for the hydrogenation of MCH. Countercurrent operation of a two-phase fixed bed trickle bed reactor provides increased mass transfer driving force for the dissolution of hydrogen leading to higher levels of conversion⁵⁶. The volume fraction of the reactor occupied by catalyst particles in trickle bed reactors varies based on configuration and packing. Neglecting the volume of vapor in the reactor, we approximate that the catalyst and reaction solvent should occupy equal volumes, which would be appropriate for a single-phase fixed bed reactor or packed bubble column⁷. Using the reported Pd-HAP catalyst performance of 0.0142 *mol. Cresol hydrogenated per hr.gcat*, and the assumption that residence time is equal to space time, a residence time of 660 seconds was chosen for the reactor. The amount of catalyst required for this reactor was calculated as follows,

$$\begin{aligned} \text{Catalyst Required } (g) &= \frac{\text{Molar Flow Rate of } p - \text{Cresol}\left(\frac{\text{mol}}{s}\right)}{\text{Residence Time } (hr) * 0.0142 \text{ mol. Cresol hydrogenated. } hr^{-1}. \text{ gcat}^{-1}} \\ &= \frac{11.6 \frac{\text{kmol } p - \text{Cresol}}{hr} * \left(\frac{1000 \text{kmol}}{\text{mol}}\right) * \left(\frac{1}{3600} \text{ s/hr}\right)}{\left(\frac{660}{3600} \text{ hr}\right) * 0.0142 \text{ mol. Cresol hydrogenated. } hr^{-1}. \text{ gcat}^{-1}} \\ &= \left[4.460,000 \text{ g catalyst}\right] \end{aligned}$$

This amount of catalyst occupies a volume of 3030 L (based on a density for the Pd-HAP catalyst of 3.1 g.cm⁻³). The fraction of reactor volume occupied by catalyst is then calculated, knowing the volumetric flow rate of feed,

Reactor Volume Occupied by Catalyst (%)

$$= \frac{Volume \ of \ Catalyst}{Volume \ of \ Catalyst + Residnce \ Time * Feed \ Volumetric \ Flow \ Rate} * 100$$

$$= \frac{3030 \ L}{3030 \ L + (660 \ s) * \left(4.6 \frac{L}{s}\right)} * 100 = \boxed{50\%}$$

This value validates our original reactant/catalyst occupied volume assumption.

The rate of hydrogen feed to the reactor must be significantly greater than the consumption rate to ensure adequate mass transfer into the solvent. Practically, the aspect ratio of the reactor can be varied to prevent

flooding and modify conversion at a specific vapor flow rate⁸. To conservatively estimate the effects that excess hydrogen feed to the column will have on the process, the liquid effluent from the reactor was modeled to contain the solubility limit of hydrogen (as estimated in Aspen) at the reaction temperature, and a feed rate ten times the total rate of consumption of hydrogen was used to calculate the capital and operating cost of the vapor recycle blower.

5) BVO Reactor Sizing

A packed bed plug flow reactor was modeled for the BVO of methyl-cyclohexanone to methyl- ε caprolactone. Yakabi et al. reported an equivalent space-time-yield of 24.5 grams ketone converted per cm^3 reactor volume per hour per kg catalyst from batch experiments⁹, which is where the utilized catalyst performance (90% selectivity, 20% conversion) was taken from. Additionally, flow experiments were performed with contact times of 9.75 minutes, although these experiments were not conducted at as high a selectivity as their batch experiments, their reported contact time is assumed to be suitable to achieve the reported batch performance in flow. It is noted that improvements in space-time-yield in flow compared to batch experiments were observed.

During reactor operation, 6,213,665 g/hr of methyl-cyclohexanone flows into the reactor, and overall 1,242,731 grams are converted per hour. The volumetric flow rate into the reactor is 127.7 L/min. Approximating that space-time is equal to residence time, the liquid volume is the reactor is calculated to be 1245.075 L for a 9.75 minutes residence time. Assuming that catalyst and packing occupy an equal amount of volume as reactant in the reactor total reactor volume is 2490.15 L or $2.49015 \cdot 10^6$ cm³.

The mass of catalyst required for the reactor was then calculated as follows,

$$\begin{pmatrix} \frac{1,242,731 \ g \ Ketone \ Converted}{1 \ hour} \end{pmatrix} * \left(\frac{1}{2.49015 * 10^6 cm^3 Reactor \ Volume} \right) \\ * \left(\frac{cm^3 Reactor \ Volume. \ 1 \ Hour. \ kg \ Catalyst}{24.5 \ g \ Ketone \ Converted} \right) = 0.0204 \ Kg \ Catalyst$$

The cost of this catalyst was assumed to be negligible for economic analysis.

6) Vacuum Equipment Sizing

The capital cost of vacuum pumps were sized using a capacity factor and corresponding f.o.b. purchase cost equation given by Seider^[10]. The volumetric flow at suction conditions (taken to be the condenser temperature and pressure) was calculated as the sum of vapor distillate and an estimate of air leakage. Seider provides an equation to estimate air leakage rate (*W*, lb/hr) based on system pressure (*P*, *torr*) and volume (*V*, ft^3),

$$W = 5 + \{0.0298 + 0.03088 * \ln(P) - 0.0005733 * [\ln(P)^2] \} * V^{0.66}$$

Column and vacuum specifications used for sizing the vacuum systems for columns 3 and 5 are listed in the table below.

Table S4. Vacuum Column Specifications Used for Sizing Vacuum System.

Column #	Column Volume	Column Operating	Condenser	Vapor Distillate Mass
	(ft ³)	Pressure (Torr)	Temperature (°C)	Flow Rate (lb/hr)
3	78,000	150	30	27
5	26,400	50	145.4	0

The air leakage rate for column 3 was calculated as follows,

$$W = 5 + \{0.0298 + 0.03088 * \ln(150) - 0.0005733 * [\ln(150)^2] \} * 78,000^{0.66} = 293 \, lb/hr.$$

Approximating that the density of air and the vapor distillate is identical, the volumetric flow can be calculated using a density of 0.014334 lb/ft³ for air at 30°C, 150 torr, and an estimated 10% humidity,

Volumetric Flow Rate
$$\left(\frac{ft^3}{min}\right) = \frac{\left(320\frac{lb}{hr}\right)}{0.014334\frac{lb}{ft^3}} = 22,300ft^3/hr$$

We use an overdesign factor of 1.5 which gives a volumetric flow rate of 33,450 ft³/hr and a corresponding mass flow rate of 480 lb/hr. Based on the calculated volumetric flow rate and given operating pressure, a single stage Steam-jet ejector is appropriate for column three's vacuum system^[11].

The size factor (S) for a steam-jet ejector is in units of $lb/hr\cdot torr$,

$$S = \frac{480 \frac{lb}{hr}}{150 torr} = 3.2 \frac{lb}{hr. torr}$$

The free on board purchase cost equation for a steam-jet ejector (CEP Index 567) is as follows,

$$C_p(\$) = 1,915 * S^{0.41} = 1,915 * \left(3.2 \frac{lb}{hr.torr}\right)^{0.41} = \$3085$$

Indexed to 2017 using the Chemical Engineer's Plant Cost Index (CE Index 562.1) the cost is \$3,058. Garrett states a module factor of 2.2 for a steam jet ejector¹², which gives an installed cost for the steamjet ejector accounting for supporting equipment such as a condenser. Therefore the total installed cost of a single-stage steam-jet ejector for column 3 is \$6,728. The total capital investment required for this piece of equipment was calculated to be \$13,456 using the ratio between TCI and installed capital costs for the rest of the process, as estimated by Aspen Plus Economic Analyzer V8.4 (ratio of TCI to Installed Cost of 2).

Seider estimates that 5-10 lb of 100 PSI steam is required per pound of gas being pumped. At a cost of 0.0814 \$/lb 100 PSI steam (Table 1), the utility cost of operating this steam-jet ejector would be,

$$\left(\frac{0.0814\$}{lb100 PSI Steam}\right)*\left(10\frac{lb 100 PSI Steam}{lb gas pumped}\right)*\left(480 lb gas\frac{pumped}{hr}\right) = \boxed{39.072\frac{\$}{hr}}.$$

For column 5, air leakage was calculated to be 183.75 lb/hr (75,000 ft³/hr; density 0.002448 lb/ft³) using an overdesign factor of 1.5. A single-stage liquid ring pump is appropriate for column five's vacuum system^[1010]. The free on board purchase cost equation (CEP Index 567) is as follows,

$$C_p(\$) = 8,250 * S^{0.37} = 8,250 * \left(1250 \frac{ft^3}{min}\right)^{0.37} = \$115,428$$

Applying the previously cited CE Index for 2017 and the TCI to installed capital costs ratio, the total capital investment for column 3's vacuum system is \$229,316. The power required to operate this vacuum pump was estimated to be 18.9 kW using the compressor block in Aspen operating at 40% efficiency. At a cost of \$0.0775 kW/hr (Table 1) this gives a yearly utility cost of \$11,718 / year.



Figure S1. Minimum selling price (MSP) of methyl- ε -caprolactone (MCL) versus plant lifetime. Base case denoted by red hollow marker. Decreasing plant lifetime to 15 years increases MSP by \$0.148 kg⁻¹.

7) MSP versus Plant Lifetime Figure

8) MSP versus MARR Figure



Figure S2. Minimum selling price (MSP) of methyl- ϵ -caprolactone (MCL) versus minimum annual rate of return (MARR). Base case denoted by red hollow marker.

9) MSP versus Tax Rate Figure



Figure S3. Minimum selling price (MSP) of methyl- ϵ -caprolactone (MCL) versus tax rate. Base case denoted by red hollow marker.



Figure S4. Total capital investment versus plant size. Base case shown in red.



11) MSP versus p-Cresol Purchase Price





12) Heteroazeotrope Phase Diagram of Water and MCH

Figure S6. Water/MCH Heteroazeotrope Phase Diagram At vapor-liquid mixtures that exceed 0.87 mole fraction water, the liquid phase is estimated to be pure water.

13) Solvent Optimization Discussion

Column 1, which removes hydrogenation solvent and unreacted p-cresol from MCH and MCOH, accounts for more than half of the capital and operating costs of the "Ketone Purification" block, which is the largest process block contributor to MSP. The possibility of economic improvements by changing the hydrogenation solvent to higher or lower n-alkanes was explored. The process was simulated using various n-alkane solvents in the hydrogenation reactor for identical column 1 molar recovery and purity of MCH and MCOH in the distillate. The amount of solvent used was chosen to maintain p-cresol at half its solubility limit at 75°C. Economic and process details for these simulations in shown in Table S54 below.

Solvent	Utility Costs (\$/hr)	Installed Cost (\$)	Reflux Ratio
N-Undecane	120.37	8,187,200	8.65
N-Dodecane	68.16	7,524,200	1.52
N-Tridecane	82.35	8,100,200	0.92

Table S5. Costs and reflux ratio for column 1 associated with solvent selection.

Reflux ratio was found to decrease as alkane chain length increased, due to the greater difference in relative volatility from MCH and MCOH. However, the increased heat of vaporization and subsequent reboiler heat duty and utility costs of a longer chain alkane solvent lead to worse economic performance.

Table S6.	Boiling Point	of Linear Alkar	ne Solvents and	d Selected I	Process Specie	es as Estimated b	y Aspen
Plus V8.6							

Species	Boiling Point (°C)
Pentane	36.07
Hexane	68.73
Heptane	98.43
Octane	125.68
Nonane	150.82
MCH	170.00
Decane	174.155
Undecane	195.928
p-Cresol	201.98
Dodecane	216.323
Tridecane	235.466

It is noted that a solvent with a boiling point lower than MCH but higher than the hydrogenation reaction temperature could be used, however this would necessitate an additional distillation column in the "Ketone Purification" block. Additionally, reaction temperatures above 75°C could lead to improved

hydrogenation kinetics beyond those reported by Xu et al., which would further limit the minimum boiling point of the solvent.

14) Vacuum Distillation Comments

The chosen operating pressure for C-3 and C-5 were chosen based on operating pressures listed in the patent literature for the analogous vacuum distillation purification of e-caprolactone from a mixture of assorted low boiling components, 6-HHA, and Adipic Acid. Typically a fraction of low boilers is removed in the first column (C-3) and 6-HHA/Adipic Acid are removed in the second column (C-5). The maximum preferred operating pressures and temperatures for these columns is listed in Table S.6 below.

C-3 Pressure	C-3 Top Temp. (°C)	C-3 Bottom Temp.	Patent Number
200 mmHg	40	180	US6156910A
120 mbar	120	Not listed	US4313879A
Not listed	Not listed	Not listed	US8217186B2
100 mmHg	Not listed	200	US20040087804A1
C-5 Pressure	C-5 Top Temp. (°C)	C-5 Bottom Temp. (°C)	Patent Number
50 mmHg	130	160	US6156910A
120 mbar	165	Not listed	US4313879A
150 mbar	Not listed	210	US8217186B2
50 mmHg	Not listed	200	US20040087804A1

Table S7. Distillation column conditions for MCL purification.

The operation pressures of C-3 and C-5 were chosen to be within the maximums set out in these patents. It was approximated that no loss of MCL through polymerization occurred in the base case process due to low distillation pressures and reflux ratios of these columns.

15) MSP Gradient Plot Generation and Discussion

To generate Figure 5 in the manuscript, the entire process was simulated with varying performance of the BVO catalyst (single-pass conversion of MCOH, and selectivity to MCL) for a grid of fifty-five different performances at five equally spaces points between 10% and 50% conversion and eleven equally spaces points between 80% and 100% selectivity. Economic analysis was conducted for each new simulation as previously reported and the MSP of MCL was calculated. The figure was generated in MatLab with the "fittype" function using the "linearinterp" method which creates a piecewise linear interpolation. The shape of the plot between 10% and 30% conversion is attributed to the greater than 300% decrease in molar flow rate through C-2, C-3, C-4, and R-2 as conversion is increased, in addition to the fact that the process was rigorously optimized at 20% conversion and 90% selectivity. It is noted that between 98% and 100% selectivity, TCI (and MSP) actually decreases discontinuously as C-4 is no longer needed to remove 4-M-6-HHA from MCL at 100% selectivity.

Supporting Information: References

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