

Supporting Information

What is the True Cost of Producing Propylene from Methanol? The Role of Externalities

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Supporting Information Available

A. Methodology

Economic Assessment

Herein we describe the methods employed to economically assess the MTP processes. In this study we employ the TAC , composed by the capital expenditures ($CAPEX$) and the operating expenditures ($OPEX$). In the case of chemical processes, the $CAPEX$ involves all the costs associated to build and have ready to operate a chemical facility. We employ the module costing approach where all and each of the direct and indirect plant costs are proportional to the equipment purchased costs. Hence, it is possible to calculate the total $CAPEX$ of a chemical facility from the equipment purchased costs and a series of correction factors.¹

The bare module cost associated to an equipment k ($C_{BM,k}$) is obtained from its reference purchased cost ($C_{p,k}^0$) and its bare module cost factor ($F_{BM,k}$). Eq. (S2) allows the calculation of $C_{p,k}^0$ as a function of the equipment capacity (A_k) and the ratio of the chemical plant cost index ($CEPCI$) between the year of calculation (2016) and the reference year (1996). This ratio is used in order to take into account the effect of inflation over the equipment costs. $F_{BM,k}$ in Eq. (S3) is calculated from the pressure and material factors $F_{P,k}$ (Eq. S4) and $F_{M,k}$ respectively. The total capital cost is then computed from Eq. (S7), which includes the total bare module cost $C_{BM,k}$ corrected with a factor of 18% in order to take into account the contingency and fee costs along with the total grass roots cost, considered as 35% of the total bare module cost for the base conditions $C_{BM,k}^0$, which includes the costs associated to

site development, auxiliary buildings, off-sites and utilities.¹

$$C_{BM,k} = F_{BM,k} C_{p,k}^0 \quad (S1)$$

$$\log_{10}(C_{p,k}^0) = \frac{CEPCI}{CEPCI_0} [K_{1,k} + K_{2,k} \log_{10}(A_k) + K_{3,k} \log_{10}(A_k)^2] \quad (S2)$$

$$F_{BM,k} = B_{1,k} + B_{2,k} F_{P,k} F_{M,k} \quad (S3)$$

$$\log_{10}(F_{P,k}) = C_{1,k} + C_{2,k} \log_{10}(P_k) + C_{3,k} \log_{10}(A_k)^2 \quad (S4)$$

$$C_{BM,k}^0 = F_{BM,k}^0 C_{p,k}^0 \quad (S5)$$

$$F_{BM,k}^0 = B_{1,k} + B_{2,k} \quad (S6)$$

$$CAPEX = 1.18 \cdot \sum_{k=1}^K C_{BM,k} + 0.35 \sum_{k=1}^K C_{BM,k}^0 \quad (S7)$$

On the other hand, the *OPEX* costs are those involved in maintaining a chemical facility in operation, directly related with the production rate and include the costs of raw materials (C_{rm}), utilities (C_u), waste treatment (C_{wt}), operating and labour (C_{ol}), etc. As in the case of capital costs, the total operating costs associated to a chemical plant can be quantified from a set of relations between the costs. Thus, each of the operating costs are directly proportional to one or the sum of: $CAPEX$, C_{rm} , C_u , C_{wt} and C_{ol} .¹ The total operating cost including and without including depreciation costs are computed according to expressions (S8) and (S9), respectively, while Eqs. (S10)–(S12) are used to calculate C_{rm} , C_u and C_{wt} , which are computed from its respective flows and prices. C_{ol} is estimated from Eq. (S13) based on the the number of operators required to run the process per shift, N_{op} (specified as 28), and the year-average salary for one operator S_{op} .

$$OPEX_d = 2.73 C_{ol} + 0.304 CAPEX + 1.23 (C_{rm} + C_{wt} + C_u) \quad (S8)$$

$$OPEX = 2.73 C_{ol} + 0.180 CAPEX + 1.23 (C_{rm} + C_{wt} + C_u) \quad (S9)$$

$$C_{rm} = \sum_{k=1}^K F_{rm,k} P_{rm,k} \quad (S10)$$

$$C_u = \sum_{k=1}^K F_{u,k} P_{u,k} \quad (S11)$$

$$C_{wt} = \sum_{k=1}^K F_{wt,k} P_{wt,k} \quad (S12)$$

$$C_{ol} = N_{op} S_{op} \quad (S13)$$

Finally, the profitability of the proposed design is quantified by the TAC computed by Eq. (S14) assuming a 10-year lifespan (N) for the plant and a minimum return on investment rate (Γ) of 29%.

$$TAC = OPEX + \frac{\Gamma(1 + \Gamma)^N}{(1 + \Gamma)^N - 1} CAPEX \quad (S14)$$

Life-Cycle Assessment

LCA is a quantitative environmental methodology for assessing the environmental burdens associated with a product, process or activity through its entire life cycle. It is based on energy and material flows that enter, exist in or leave the system under study.^{2,3} Today, LCA is considered as the principal tool for the environmental design of chemical processes, because it can be used to effectively improve or restructure any design in order to improve its environmental performance in its entire life cycle. The methodological framework of LCA that allows the computation of the environmental impacts associated to our process is done according to four phases or steps.⁴

Goal and Scope Definition This step involves defining the system boundaries, the impact categories and the functional unit, which allows a clear specification of the detail

and time frame set for the process under study. Regarding the boundaries of the system, its important to clarify that this should include the entire life cycle of the product. However, in this study we focus on assessing the environmental burdens up to the manufacturing stage and accordingly, the analysis is done in a "cradle-to-gate" approach, which implies that downstream processes such as product use, secondary processing and disposal are not included.

For the impact categories, we employ the ReCiPe 2016 methodology,⁵ which derives characterization factors that indicate the environmental impact per unit of stressor at either midpoint or endpoint level. The former gathers the impact categories into 22 environmental mechanisms while the endpoint approach defines three areas of protection (human health, ecosystem quality and resources) by clustering those midpoints through damage pathways. Finally, we define the desired production rate of the main product (propylene), as the functional unit to perform the analysis.

Inventory Analysis The second step involves the life cycle inventory (LCI) where the inputs and outputs of the system under study are defined to then calculate the environmental burdens. In our work, this information is retrieved from the simulation results. In chemical processes, the main sources of emissions and wastes are linked with co-products, reaction agents, separation agents and purges or leaks that may be present in the system. Besides these sources, the emission of the utilities employed to satisfy the process energy requirements need to be also considered. In this study the environmental burdens of the upstream processes associated to the production of raw materials and utilities are considered as input parameters, which are taken from SimaPro⁶ which contains an extensive inventory emission information for a great variety of chemical processes.

Impact Assessment In this phase, the process information defined in the inventory step, is transformed into environmental information. We employ midpoint and endpoint impact categories to quantify the environmental burdens of the process. Human health, expressed in terms of disability adjusted life years (DALYS), represents the years that a person is disabled

due to a disease or accident. On the other hand, the ecosystem quality represents the local species loss integrated over time (species · year). Finally, the resources scarcity stands for the money (US\$ 2013) associated to the extra costs involved in future mineral and fossil resource extraction.⁵ In SimaPro, the impact assessment can be performed according to three perspectives that are based on "Cultural Theory". The individualistic perspective (a short-time prospective) only includes proven effects. The hierarchist perspective, which is the one employed in our study, is based on scientific accord regarding the time frame and validity of the impact mechanism. The egalitarian perspective considers the longest time frame and includes effects with minimum scientific proof.⁶

Interpretation Interpretation is the phase of LCA where the findings from the inventory analysis and the impact assessment are combined aiming to generate a set of conclusions and recommendations for the studied system,⁴ which offer improvements for the environmental performance of the system. In addition to improvements and innovations, this phase also allows the identification of the stages in the life cycle of the MTP process that mostly contribute to the environmental impacts.

Uncertainty

In this study we focus on the uncertainty due to variation in the data, which was computed using SimaPro for the three cases (MTP-NG, MTP-C and BAU) under study. SimaPro assumes the data follows a lognormal distribution which is characterized by a standard deviation. This lognormal distribution has the property that its square geometric standard deviation (σ^2) encompasses the 95 % confidence interval. Since the data is not taken from large sample measurements, σ^2 is computed with Eq. (S15) based on the so called Pedigree matrix, proposed and developed by Weidema.⁷ In this approach, each data point of the system under study is assessed based on six criteria plus a basic uncertainty factor. The factors $U_1 - U_6$ refer to reliability, completeness, temporal correlation and geographical correlation respectively, while U_b is the uncertainty factor based on expert judgment. Tables

S1 and S2 includes the characterisation of the Pedigree matrix for the alternatives considered. Note that the only difference between the matrix for MTP-NG and MTP-C is the origin of methanol (i.e., natural gas or coal). Thus, when computing σ^2 the values were used accordingly.

$$\sigma^2 = \exp \left(\sqrt{\sum_{i=1}^6 \ln(U_i)^2 + \ln(U_b)^2} \right) \quad (\text{S15})$$

Table S1: Uncertainty factors for the pedigree matrix associated to the MTP-NG and MTP-C processes.

Score	Inputs							
	MeOH-NG	MeOH-C	Electricity (China mix)	Steam	R134a	Cooling water	Steel	Ww
Reliability	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Completeness	1.02	1.00	1.00	1.02	1.00	1.00	1.02	1.00
Temporal correlation	1.50	1.50	1.50	1.50	1.50	1.00	1.5	1.00
Geographical correlation	1.01	1.02	1.00	1.02	1.01	1.00	1.02	1.01
Technological correlation	1.00	1.00	1.00	1.20	1.00	1.00	1.20	1.00
Sample size	1.02	1.02	1.20	1.20	1.20	1.00	1.20	1.02
Basic factor	1.05	1.05	1.05	1.05	1.00	1.00	1.05	1.05

Table S2: Uncertainty factors for pedigree matrix of the cracking of naphtha (BAU) and propane dehydrogenation (PDH).

Score	BAU	PDH
Reliability	1.00	1.00
Completeness	1.02	1.02
Temporal correlation	1.00	1.00
Geographical correlation	1.02	1.00
Technological correlation	1.00	1.02
Sample size	1.02	1.00
Basic factor	1.05	1.05

Monetary valuation

Monetary valuation is employed to express the environmental endpoint impacts into monetary values, which allow us to compare those impacts against each other and with the annualized production cost. Thus, making possible to express the sustainability indicators into a single score. Table S3 includes the conversion factors employed in our study, which are based on the values reported in the work performed by Wiedema,⁸ who compared the Eco-Indicator 99, Stepwise2006 and ReCiPe2008 life cycle impact assessments methods in endpoint perspective.

Table S3: Monetary valuation factors for the three environmental endpoint impacts.

Endpoint impact	Units	Equivalent monetary value (US\$ 2016)
Human health	DALY	108,812
Ecosystem quality	species-yr	13,969,085
Resources	US\$	1.47

B. Kinetic Information

The reaction set considered in this study follows a power law model for the reaction rate r_j (Eq. S16) in conjunction with Arrhenius-type expressions for the pre-exponential factor. Table S4 includes the parameters employed for modelling the kinetic associated to the MTP process, while Table S5 includes the catalyst properties. As showed in Table S4, the dependence of the rate expression with $c_p^{\beta_j}$ is only valid for the methylation reactions (i.e., $j = 9 \dots 22$).

$$r_j = k_j \exp\left(\frac{E_j}{RT}\right) c_m^{\alpha_j} c_p^{\beta_j}, \quad m = \text{MeOH, DME}, \quad p = \text{olefins} \quad (\text{S16})$$

Table S4: Kinetic parameters for the MTP reaction set.

Type of reaction	Reaction j	Order		Kinetic parameters		
		α_j	β_j	k_j	k_j units	E_j (kJ mol ⁻¹)
Primary reactions	1	1.5	0	1	m ^{4.5} mol ^{-0.5} kg ⁻¹ s ⁻¹	45.87
	2	1.5	0	1	m ^{4.5} mol ^{-0.5} kg ⁻¹ s ⁻¹	45.87
	3	0.8	0	45.14	m ^{2.4} mol ^{0.2} kg ⁻¹ s ⁻¹	49.49
	4	0.8	0	45.14	m ^{2.4} mol ^{0.2} kg ⁻¹ s ⁻¹	49.49
	5	0.85	0	35.88	m ^{2.55} mol ^{0.15} kg ⁻¹ s ⁻¹	68.75
	6	0.85	0	35.88	m ^{2.55} mol ^{0.15} kg ⁻¹ s ⁻¹	68.75
	7	0.95	0	42.72	m ^{2.85} mol ^{0.05} kg ⁻¹ s ⁻¹	74.51
	8	0.95	0	42.72	m ^{2.85} mol ^{0.05} kg ⁻¹ s ⁻¹	74.51
Methylation	9	0.75	0.25	7.29	m ³ kg ⁻¹ s ⁻¹	40.02
	10	0.75	0.25	7.29	m ³ kg ⁻¹ s ⁻¹	40.02
	11	0.70	0.30	4.12	m ³ kg ⁻¹ s ⁻¹	37.45
	12	0.70	0.30	4.12	m ³ kg ⁻¹ s ⁻¹	37.45
	13	0.65	0.35	3.07	m ³ kg ⁻¹ s ⁻¹	35.17
	14	0.65	0.35	3.07	m ³ kg ⁻¹ s ⁻¹	35.17
	15	0.65	0.35	3.07	m ³ kg ⁻¹ s ⁻¹	35.17
	16	0.65	0.35	3.07	m ³ kg ⁻¹ s ⁻¹	35.17
	17	0.65	0.35	3.07	m ³ kg ⁻¹ s ⁻¹	35.17
	18	0.65	0.35	3.07	m ³ kg ⁻¹ s ⁻¹	35.17
	19	0.65	0.35	3.07	m ³ kg ⁻¹ s ⁻¹	35.17
	20	0.65	0.35	3.07	m ³ kg ⁻¹ s ⁻¹	35.17
	21	0.65	0.35	3.07	m ³ kg ⁻¹ s ⁻¹	35.17
	22	0.65	0.35	3.07	m ³ kg ⁻¹ s ⁻¹	35.17
Cracking	23	0.70	0	4000	m ^{2.25} mol ^{0.25} kg ⁻¹ s ⁻¹	77.5
	24	0.75	0	4000	m ^{2.25} mol ^{0.25} kg ⁻¹ s ⁻¹	77.5
	25	0.75	0	4000	m ^{2.25} mol ^{0.25} kg ⁻¹ s ⁻¹	77.5
	26	0.75	0	4000	m ^{2.25} mol ^{0.25} kg ⁻¹ s ⁻¹	77.5
	27	0.75	0	4000	m ^{2.25} mol ^{0.25} kg ⁻¹ s ⁻¹	77.5

Table S5: Catalysts properties.

Property	Value
Diameter (m)	0.02
Sphericity	0.685
Bulk density (kg m ⁻³)	466.9
Void fraction	0.5

C. Complementary Information

Table S6: Capital cost summary.

Equipment	Characteristics	Cost (US\$)
MTP reactor	$V = 27.5 \text{ m}^3$	71,038 ^a
DME reactor	$V = 27.5 \text{ m}^3$	50,490
LV separator	D = 2.8 m L = 8.7 m	94,216
LLV separator	D = 0.2 m L = 0.3 m	83,332
Distillation column 1	D = 2.2 m L = 25 m Plates: 31	778,331
Distillation column 2	D = 1 m L = 33 m Plates: 27	933,880
Compressors	Units: 4 Power: 2004 kW	5,852,719
Turbine	Units: 1 Power: 1974 kW	1,096,575
HEN	Units: 45 A = 1575.72 m ²	6,432,430
Pumps	Units: 2 Power: 13.14 kW	53,221

^aIt may differ with values reported in the literature due to scale differences, calculation methods and/or reactor configurations found at industrial level.

Table S7: Prices considered for the economic assessment.

Description	Price (US\$)
Methanol-NG ⁹	0.25 \$/kg
Methanol-C ⁹	0.21 \$/kg
Catalyst	120 \$/kg
Ethylene ¹	1.43 \$/kg
Propylene ¹	1.41 \$/kg
Naphtha	0.40 \$/kg
Propane ¹⁰	0.44 \$/kg
Wastewater treatment ¹	5.3×10^{-5} \$/kg
Cooling water ¹	0.21 \$/GJ
MP steam ¹	3.66 \$/GJ
Electricity ¹	18.63 \$/GJ

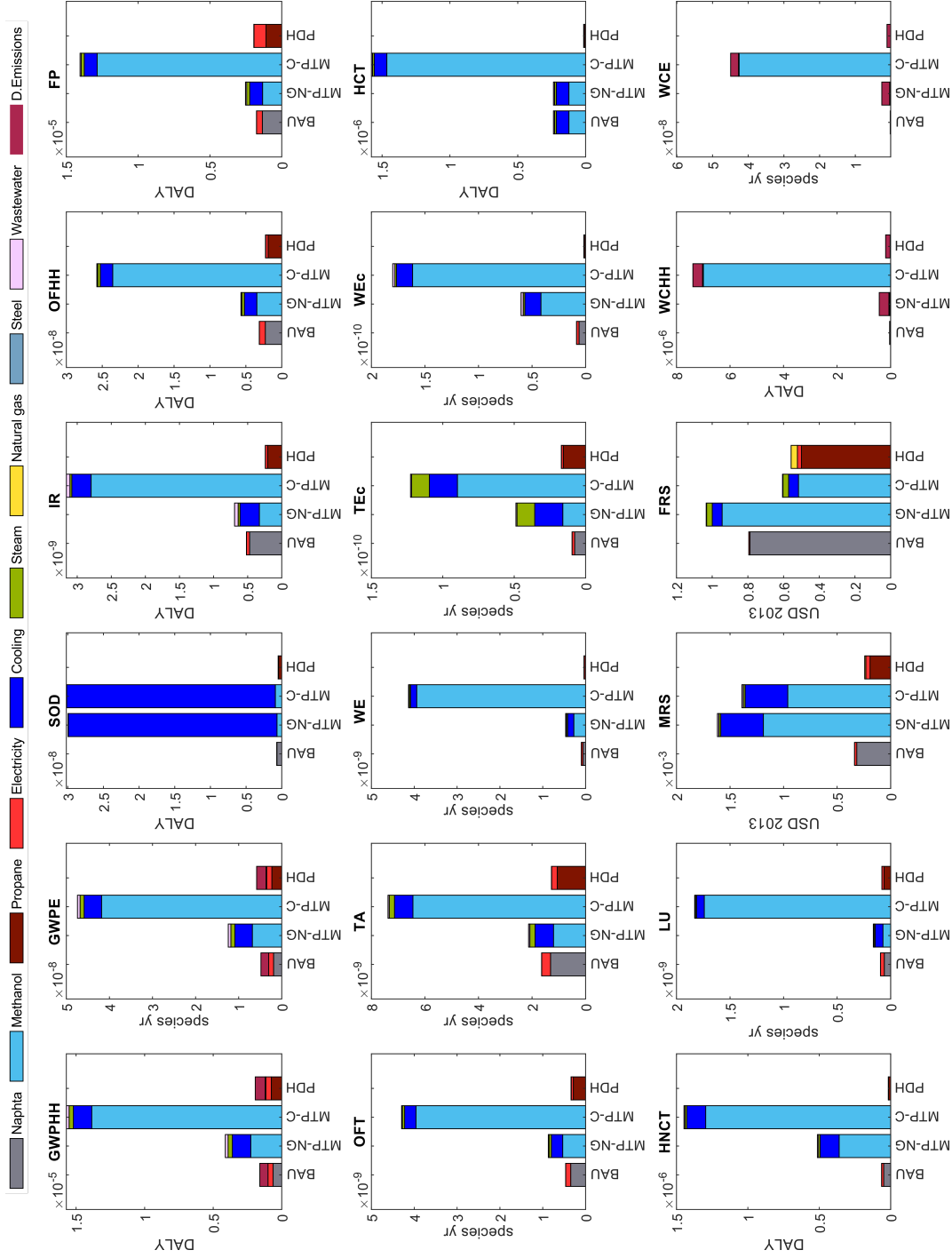


Figure S1: Midpoint environmental impacts. GWPHH:global warming human health, GWPE:global warming ecosystem, SOD:stratospheric ozone depletion, IR:ionizing radiation, OFHH:ozon formation human health, FP:fine particulate matter formation, OFT:ozon formation terrestrial ecosystem, TA:terrestrial acidification, WE:water eutrophication, TEC:terrestrial ecotoxicity, WEC:water ecotoxicity, HCT:human carcinogenic toxicity, HNCT:human non-carcinogenic toxicity, LU:land use, MRS:mineral resource scarcity, FRS:fossil resource scarcity, WCHH:water consumption human health, WCE:water consumption ecosystem.

Table S8: Stream table for the MTP process.

Property	Unit	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Temperature	°C	22.00	22.01	300.00	426.87	425.00	40.00	30.00	30.00	102.49	62.00	110.19	86.00	112.63	139.46	52.46
Pressure	kPa	100.00	165.00	165.00	165.00	145.00	145.00	145.00	145.00	700.00	700.00	1800.00	1800.00	2826.85	2826.85	2767.00
Molar Flow	kgmole/h	2371.89	2371.89	2371.89	2371.89	3054.19	3054.19	2350.92	703.27	703.27	703.27	703.27	703.27	703.27	271.69	431.59
Mass Flow	kg/h	76000.00	76000.00	76000.00	76000.32	76000.46	76000.46	42352.00	33648.46	33648.46	33648.46	33648.46	33648.46	33648.46	16595.99	17052.47
X _{MeOH}	% mol	1.00	1.00	1.00	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
X _{OME}		0.00	0.00	0.00	0.45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
X _{H2O}		0.00	0.00	0.00	0.45	0.78	0.78	1.00	0.03	0.03	0.03	0.03	0.03	0.03	0.00	0.05
X _{Ethylene}		0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.07	0.07	0.07	0.07	0.07	0.07	0.00	0.11
X _{Propylene}		0.00	0.00	0.00	0.00	0.12	0.12	0.00	0.52	0.52	0.52	0.52	0.52	0.52	0.01	0.84
X _{Naphtha}		0.00	0.00	0.00	0.00	0.09	0.09	0.00	0.39	0.39	0.39	0.39	0.39	0.39	0.99	0.01
X _{R134a}		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Property	Unit	16	17	18	19	20	21	22	23	24	25	26	27	28	29	
Temperature	°C	52.46	52.46	52.46	52.46	64.31	-6.56	99.57	184.12	99.41	99.41	-26.04	-26.04	-19.28	-21.98	
Pressure	kPa	2767.00	2767.00	2767.00	2767.00	2766.87	2688.96	1101.00	1101.00	100.00	100.00	101.33	101.33	121.59	121.59	
Molar Flow	kgmole/h	20.18	379.84	31.57	411.41	365.12	46.29	1463.28	1463.28	1463.28	1463.28	294.37	294.37	294.37	294.37	
Mass Flow	kg/h	363.55	15457.69	1231.23	16688.92	15397.76	1291.17	26361.18	26361.18	26361.18	26361.18	30034.94	30034.94	30034.94	30034.94	
X _{MeOH}	% mol	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
X _{OME}		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
X _{H2O}		1.00	0.00	0.00	0.00	0.00	0.02	1.00	1.00	1.00	1.00	1.00	1.00	0.00	0.00	
X _{Ethylene}		0.00	0.10	0.21	0.11	0.00	0.98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
X _{Propylene}		0.00	0.89	0.78	0.88	0.99	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
X _{Naphtha}		0.00	0.01	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
X _{R134a}		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	
Property	Unit	E1	E2	E3	E4	E5	E6	E7								
Heat Flow	kJ/h	9064.01	38198.3	8193930	3870093	2242263	957924	143317								

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