Reviewed by Michael Overcash 11-7-16
Rereviewed by Michael Overcash 11-10-16
Rereviewed by Michael Overcash 11-10-16 Final

Triethylaluminum from ethylene, aluminum and hydrogen [97-93-8]

CONTENTS OF FACTORY GATE TO FACTORY GATE

LIFE CYCLE INVENTORY SUMMARY

Authors	E. Vozzola
Peer reviews, name (date)	Reviewed by MR Overcash on 11-10-2016: route, stoichiometry, and calculations reviewed and found to be representative.
Gtg report last modified on	11-10-2016
Additional notes	

Checked for database consistency on	11-10-2016
First gtg version finalized on	11-10-2016
Modification history, Author (date)	EMV (11-10-2016)

Products	triethylaluminum
Standard inputs	Ethylene, Hydrogen, Aluminum

Methodology: Environmental Clarity gtg lci reports are based on industrial practice information, standard methods of engineering process design, and technical reviews. These reports are intended to be representative of industrial production based on the stated route.

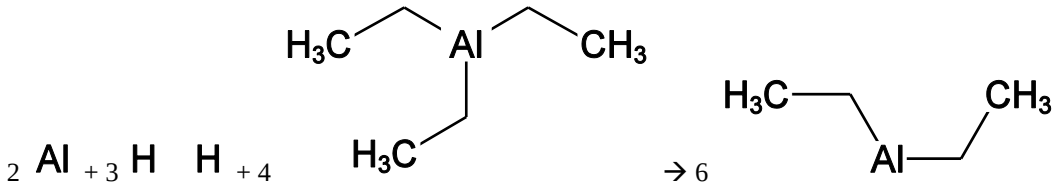
Terms of use: Environmental Clarity does not assume any liability due to use of these lci data. Integration of these data with lci data based on other methodologies is the responsibility of the user. Each report may be updated to improve model accuracy or representativeness.

Users of this report should cite: E. Griffing and M. Overcash, Chemical Life Cycle Database, www.environmentalclarity.com, 1999 - present.

Chemistry

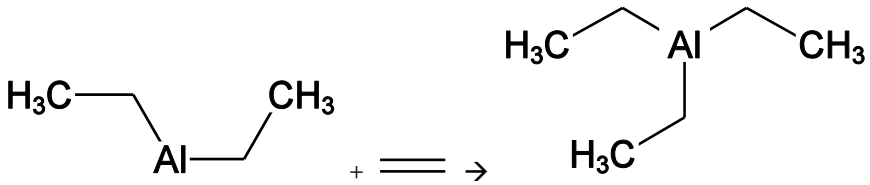
Primary reaction:

$$2\ Al + 3\ H_2 + 4\ (C_2H_5)_3Al \rightarrow 6\ (C_2H_5)_2AlH \qquad (1)$$



aluminum + hydrogen + triethylaluminum → diethylaluminum hydride

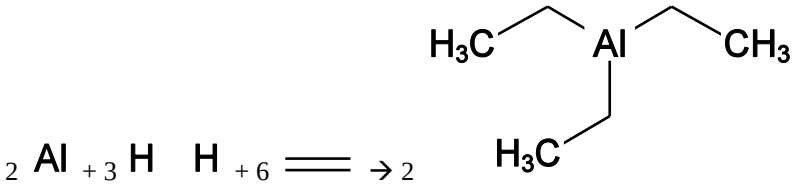
$$6\ (C_2H_5)_2AlH + 6\ C_2H_4 \rightarrow 6\ (C_2H_5)_3Al \qquad (2)$$



diethylaluminum hydride + ethylene → triethylaluminum

Net reaction:

$$2\ Al + 3\ H_2 + 6\ C_2H_4 \rightarrow 2\ (C_2H_5)_3Al \qquad (3)$$



aluminum + hydrogen + ethylene → triethylaluminum

Process Summary

Literature

Triethylaluminum [97-93-8] is an organoaluminum compound. It is a colorless liquid that requires careful handling because it is highly pyrophoric, igniting immediately upon exposure to air or water. Triethylaluminum is often prepared and immediately used in the same chemical plant to prevent exposure to air and water. Alternatively, it can be stored in a stainless steel container under an inert atmosphere as a pure liquid or in solution with a hydrocarbon solvent. Triethylaluminum is used as a catalyst or intermediate in the production of polyethylene, polypropylene, and medium chain alcohols.

Triethylaluminum exists almost entirely as a dimer in solution, with the molecular formula expressed as 2 $Al(C_2H_5)_3$, $[Al(C_2H_5)_3]_2$, or $C_{12}H_{30}Al_2$. Physical properties in the literature are typically given for the monomer $Al(C_2H_5)_3$, thus in this gate-to-gate life cycle inventory (gtg lci) the physical properties are given on a monomer basis.

Triethylaluminum is prepared from aluminum, hydrogen, and ethylene in a one or two-step process (Kirk Othmer, 2000). Many embodiments of the reaction are given in the encyclopedia, patent, and journal literature. The two-step process favors higher yields and is thus the preferred method (US 3,373,179; US 3,960,912).

The process shown in this gtg lci is based on a two-step process described in detail by Ullmann's (2000). In the first step, a slurry is prepared containing 7 wt % aluminum powder, 45 wt % recycled triethylaluminum, and 52 wt % paraffin hydrocarbon solvent (b. p. 177-260 °C). The slurry is pumped into a reactor operating at 132 °C. A zirconium catalyst is used at 0.1 wt %. Hydrogen is introduced at the bottom of the reactor to maintain a partial pressure of about 100 atm (10 MPa). The exit stream from this reactor contains 83 wt % diethylaluminum hydride and is fed to a second reactor operating at 85 °C and 30 atm (3 MPa). Sufficient ethylene is added to this reactor to completely react with the diethylaluminum hydride. Excess ethylene and hydrogen are removed in flash drums, and pure diethylaluminum is recovered from the solvent by distillation.

LCI design

Aluminum at 25 °C and 1 atm is mixed with recycled triethylaluminum and dodecane solvent to form a slurry (5 wt % Al, 45% triethylaluminum, 50% solvent). The slurry temperature is 98 °C and 1 atm. The slurry is pumped to 100 atm and fed to a continuous rector. Hydrogen gas at 25 °C and 17 atm is compressed to 100 atm and also fed to the reactor. The reaction conditions are 132 °C and 100 atm. Triethylaluminum reacts with aluminum to form diethyl aluminum hydride. The reactor effluent is depressurized to 30 atm in a gas/liquid separator. Hydrogen gas from the separator is cooled to 25 °C and sent as a waste. The liquid stream from the separator is fed to a second reactor operating at 85 °C and 5 atm. Ethylene at 25 °C is compressed to 5 atm and also fed to the reactor. Diethylaluminum hydride and ethylene react to form triethylaluminum. The reactor effluent is depressurized to 1 atm in a gas/liquid separator. Ethylene gas from the separator is sent as a waste. The liquid stream from the separator contains triethylaluminum in dodecane solvent. About 70% of this stream is recycled to the slurry mixer. The remaining 30% is distilled to remove triethylaluminum at 193 °C and 1 atm. The distillation bottoms contain dodecane solvent and are recycled to the slurry mixer. The distillation overhead contains pure triethylaluminum, This stream is cooled to 25 °C and sent as the main product.

References

Kirk Othmer (2000) *Kirk Othmer Encyclopedia of Chemical Technology*, Alcohols, Higher Aliphatic, Synthetic Processes (J. D. Wagner, G. R. Lappin, J. R. Zietz, article authors)

Ullmann's (2000) *Ullmann's Encyclopedia of Industrial Chemistry*, Aluminum Compounds, Organic (M. J. Krause, F. Orlandi, A. T. Saurage, J. R. Zietz, article authors)

US 3,373,179 (1968) Method for the manufacture of dialkyl aluminum hydride compounds (A. L. Lewis, inventor ; Continental Oil Company, assignee)

US 3,960,912 (1976) Process for the preparation of trialkyl aluminum compounds (K. H. Mueller, H.-J. Hubert, inventors; Schering Aktiengesellschaft, assignee)

Conversion / yield data, molar percentage basis, data used in gtg design

	Basis	Conversion of or Yield from aluminum	Conversion of or Yield from hydrogen	Conversion of Or Yield from ethylene
Process conversion in reactor 1: % of reactant entering the process that reacts	reactant into process	100	95.2	N/A
Per pass conversion in reactor 1: % of reactant entering the reactor that reacts	reactant into reactor per pass	100	95.2	N/A
Yield of reactor 1: % yield produced in the reactor based on reactant input to process	reactant into process or produced in other reactor	100	100	N/A
Total conversion in reactor 2: % of reactant entering the process that reacts		N/A	N/A	95.2
Total per pass conversion in reactor 2: % of reactant entering the reactor that reacts		N/A	N/A	95.2
Total yield of reactor 2: % yield produced in the reactor based on reactant input to process		N/A	N/A	100
Total yield of Process: % yield produced by the overall process based on reactant input to process		100	95	95
	Notes:			

Product purity

	triethylaluminum	Comments
Used here	100%	

Summary of LCI Information

Standard inputs					
UID	Name	Flow	Purity	Units	Comments
74-85-1	Ethylene	778	-	[kg/hr]	
1333-74-0	Hydrogen	27.8	-	[kg/hr]	
7429-90-5	Aluminum	237	-	[kg/hr]	
	Total	1042		[kg/hr]	
Non-reacting inputs					
UID	Name	Flow	Purity	Units	Comments
	Total	0		[kg/hr]	
Ancillary inputs					
UID	Name	Flow	Purity	Units	Comments
	Total	0		[kg/hr]	
Products					
UID	Name	Flow	Purity	Units	Comments
97-93-8	triethylaluminum	1000	100	[kg/hr]	
	Total	1000		[kg/hr]	
Benign outflows					
UID	Name	Flow	Purity	Units	Comments
	Total	0		[kg/hr]	

Process emissions							
UID	Name	Gas	Liquid	Solid	Solvent	Units	Comments
1333-74-0	Hydrogen	1.45	0	0	0	[kg/hr]	
74-85-1	Ethylene	40.7	0	0	0	[kg/hr]	
	Total	42.2	0	0	0		

Mass balance	
Total inputs	1042
Total outflows	1042
Net input	2.24E-04

Energy use			
Energy type	Amount	Units	Comments
electricity	382	[MJ/hr]	Net electricity use at plant
heating steam	2293	[MJ/hr]	heating by steam (0.85 efficiency included)
Net input requirement	2675	[MJ/hr]	Net of energies input to system
cooling water	-5072	[MJ/hr]	net cooling by cooling water
potential recovery	-1663	[MJ/hr]	potential energy recovery (negative)
Net energy	1011	[MJ/hr]	Net input requirement - potential recovery

Process Diagram Interpretation Sheet

1) As much as possible, standard symbols are used for all unit processes.

2) Only overall input and output chemicals are labeled on these diagrams. All intermediate information is given on the attached Process Mass Balance sheet

3) The physical state of most streams is shown (gas, g; liquid, l; solid, s)

4) The process numbering is as follows,

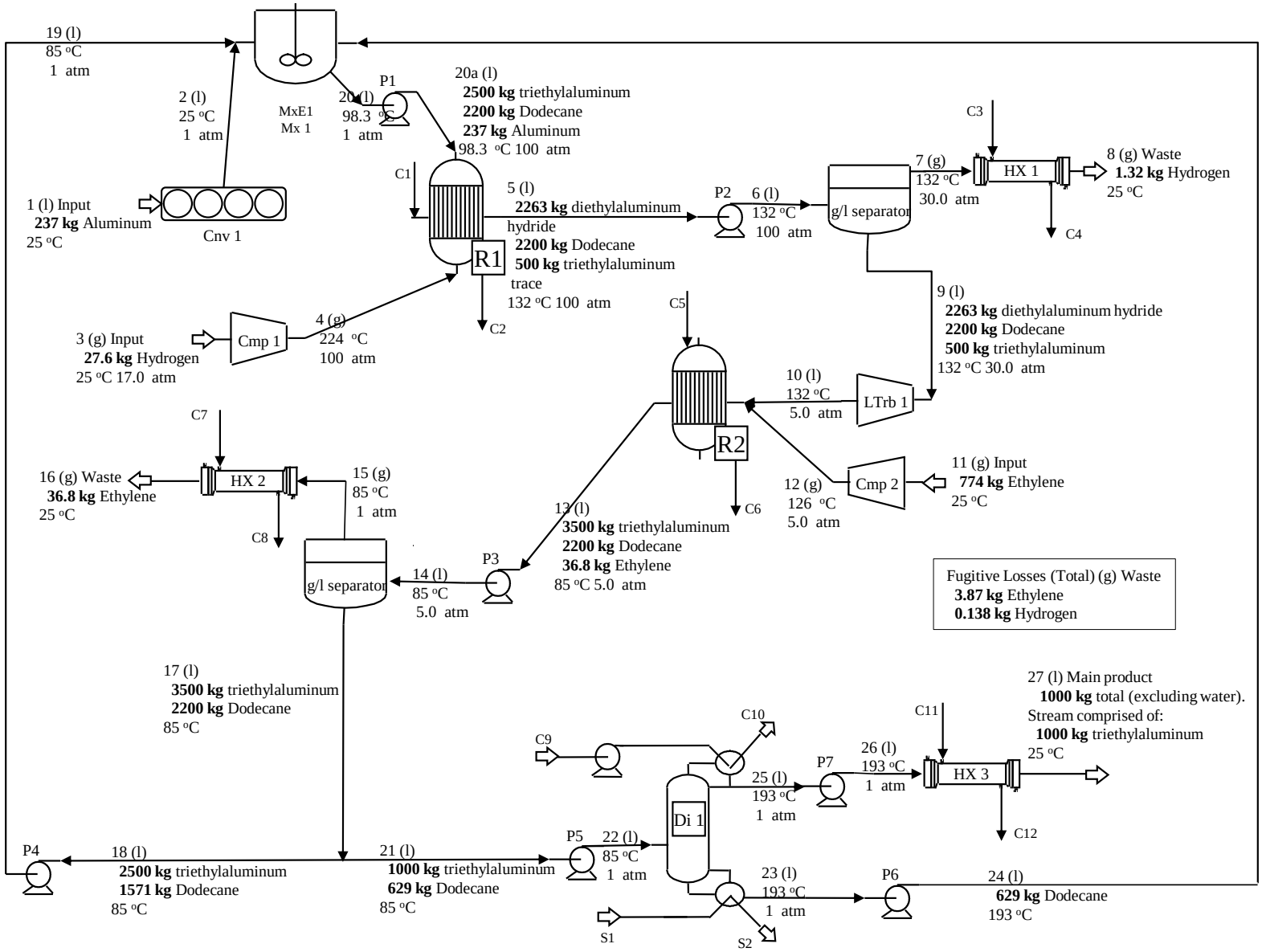
- generally numbers progress from the start to the end of the process
- numbers are used for process streams
- C i , i = 1,..n are used for all cooling non-contact streams
- S j, j = 1,...n are used for all steam heating non-contact streams

5) Recycle streams are shown with dotted lines

For most streams, the temperature and pressure are shown, if the pressures are greater than 1 atm

Process Diagram or Boundary of LCI

Steam enters the process as a gas at 207 °C and leaves as a liquid at 207 °C. Cooling water enters at 20 °C and leaves at 50 °C.
Unless otherwise indicated, all processes are at 1 atm and 25 °C.



Mass Balance of Chemicals in Each Process Stream

All flow rates are given in kg / hr.

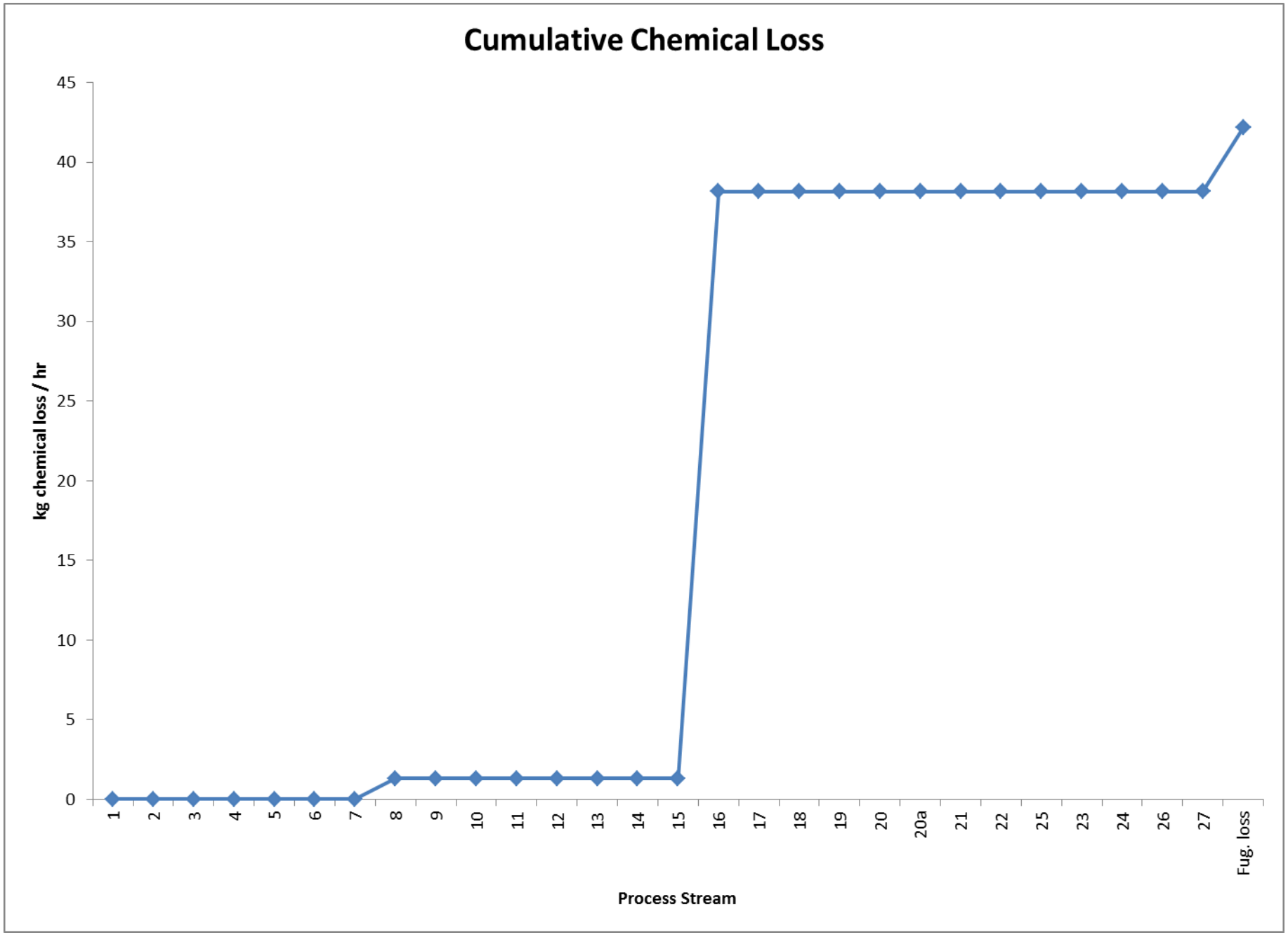
Physical state of chemical losses: Gas, Liquid, Solid.

	Comments	Streams	Temp [C]	P	Phase	Total Flow	Aluminum	Hydrogen	Ethylene	diethylaluminum hydride	triethylaluminum	Dodecane
Input		1	25.0	1.00	l	237	237					
		2	25.0	1.00	l	237	237					
Input		3	25.0	17.0	g	27.6		27.6				
		4	224	100	g	27.6		27.6				
		Stream 20a:Recycle input				4937	237				2500	2200
		Stream 20a:Recycle calculated				4937	237	0	0	0	2500	2200
		Stream 20a:Recycle residue				0	0	0	0	0	0	0
R1	237	kg	Aluminum		:	is converted in rxn (100 % of reactor input)						
		Input to reactor			:	4964	237	27.6	0	0	2500	2200
		R1 Reaction Coefficient 1			:		-2.00	-3.00		6.00	-4.00	
		R1 Conversion 1 [kg/hr]			:	0	-237	-26.3		2263	-2000	
		R1 Conversion 1 [kgmol/hr]			:	4.39	-8.77	-13.2		26.3	-17.5	
		Flow out of reactor			:	4964	0	1.32	0	2263	500	2200
		Primary product			:	diethylaluminum hydride						
		Total conversion			:		100	95.2	-0	NA	NA	NA
		Per pass conversion			:		100	95.2		NA	80.0	-0
		Total yield from reactor			:		100	100		NA	100.0	
Display in PFD		5	132	100	l	4964	0	1.32	0	2263	500	2200
		6	132	100	l	4964	0	1.32	0	2263	500	2200
		7	132	30.0	g	1.32		1.32				
Waste		8	25.0	1.00	g	-1.32	0	-1.32	0	0	0	0
Display in PFD		9	132	30.0	l	4963	0	0	0	2263	500	2200
		10	132	5.00	l	4963	0	0	0	2263	500	2200
Input		11	25.0	1.00	g	774			774			
		12	126	5.00	g	774			774			
R2	2263	kg	diethylaluminum hydride		:	is converted in rxn (100 % of reactor input)						
		Input to reactor			:	5737	0	0	774	2263	500	2200
		R2 Reaction Coefficient 1			:				-1.00	-1.00	1.00	
		R2 Conversion 1 [kg/hr]			:	0			-737	-2263	3000	
		R2 Conversion 1 [kgmol/hr]			:	26.3			-26.3	-26.3	26.3	

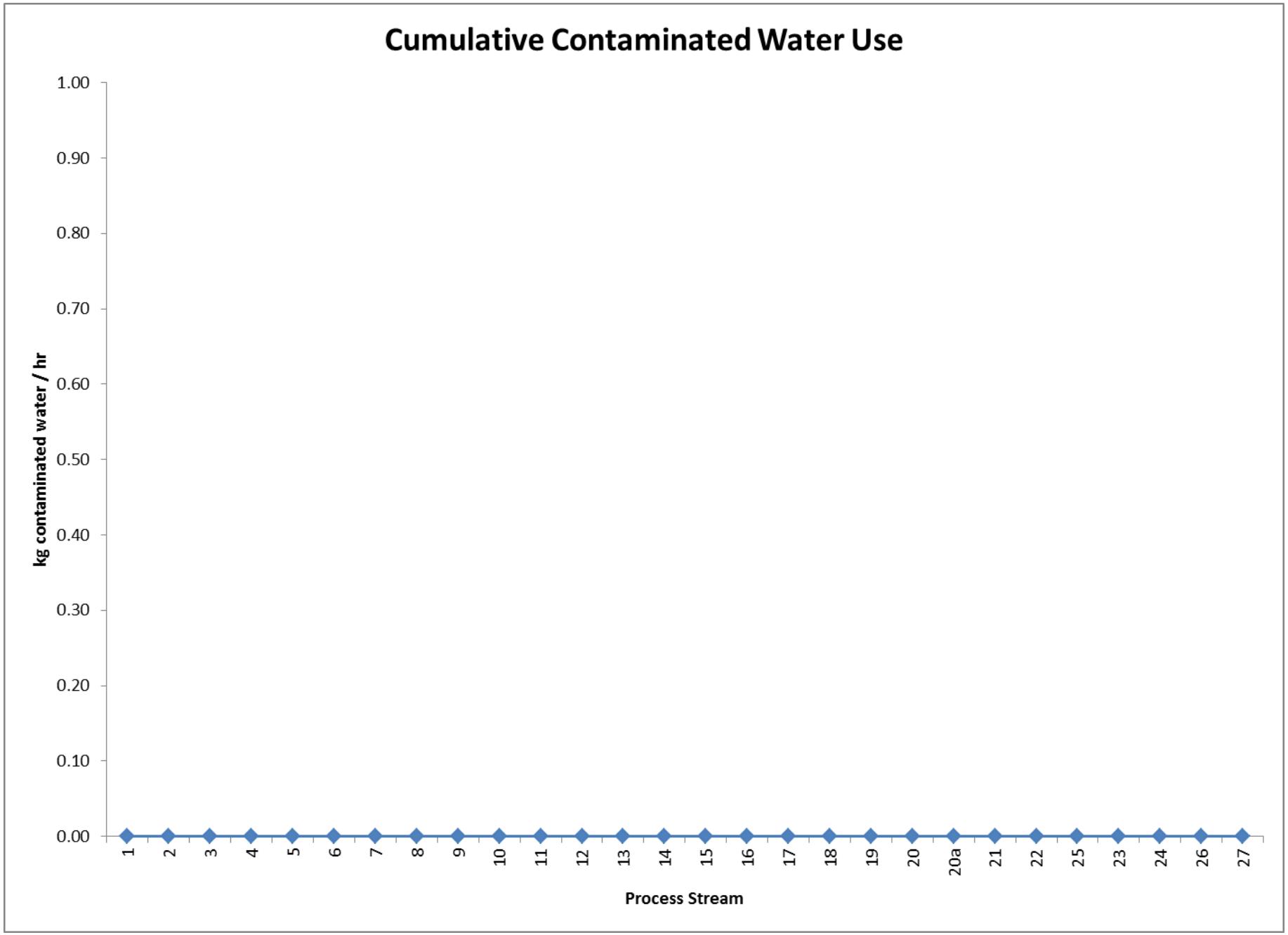
	Comments	Streams	Temp [C]	P	Phase	Total Flow	Aluminum	Hydrogen	Ethylene	diethylaluminum hydride	triethylaluminum	Dodecane
		Flow out of reactor			:	5737	0	0	36.8	0	3500	2200
		Primary product			:	triethylaluminum						
		Total conversion			:		-0	-0	95.2	NA	NA	NA
		Per pass conversion			:				95.2	100	NA	-0
		Total yield from reactor			:				100	100	NA	
Display in PFD		13	85.0	5.00	l	5737	0	0	36.8	0	3500	2200
		14	85.0	5.00	l	5737	0	0	36.8	0	3500	2200
		15	85.0	1.00	g	36.8			36.8			
Waste		16	25.0	1.00	g	-36.8	0	0	-36.8	0	0	0
Display in PFD		17	85.0	1.00	l	5700	0	0	0	0	3500	2200
Display in PFD		18	85.0	1.00	l	4071	0	0	0	0	2500	1571
		19	85.0	1.00	l	4071	0	0	0	0	2500	1571
		20	98.3	1.00	l	4937	237	0	0	0	2500	2200
Display in PFD		20a	98.3	100	l	4937	237	0	0	0	2500	2200
Display in PFD		21	85.0	1.00	l	1629	0	0	0	0	1000	629
Feed		22	85.0	1.00	l	1629	0	0	0	0	1000	629
Di <1>		percentage of input in distillate			:		0	100	100	0	100	0
		percentage of input in bottoms			:		100	0	0	100	0	100
		Boiling Temperature (Tb) [oC]			:						193	216
Distillate		25	193	1.00	l	1000	0	0	0	0	1000	0
Bottoms		23	193	1.00	l	629	0	0	0	0	0	629
Display in PFD		24	193	1.00	l	629	0	0	0	0	0	629
		26	193	1.00	l	1000	0	0	0	0	1000	0
Main product		27	25.0	1.00	l	-1000	0	0	0	0	-1000	0
		Product purity (%)			:	100						
		Main product			:	triethylaluminum						
		Overall Rxn coefficients			:		-2.00	-3.00	-6.00		2.00	
		Total yield of process (from reactant)			:		100	94.8	94.8		NA	
Waste		Fugitive Losses (Total)			g	-4.01	0	-0.138	-3.87	0	0	0
		Input Sum			:	1038	237	27.6	774	0	0	0
		Replacement of fugitive emissions of reactants			:	4.01	0	0.138	3.87			
		Total Input (Input + Fugitive Replacement)			:	1042	237	27.8	778	0	0	0
		Product Sum			:	1000	0	0	0	0	1000	0
		Main product flow			:	1000	0	0	0	0	1000	0
		Net Input (in - out, omitting fugitives)			:	0						

Type	Label	Temp, C	P, atm	Phase	Total flow	Steam	Water
Input	C1	20.0	1.00	l	1.37E+04		1.37E+04
Cooling out	C2	50.0	1.00	l	-1.37E+04		-1.37E+04
Input	C3	20.0	1.00	l	13.8		13.8
Cooling out	C4	50.0	1.00	l	-13.8		-13.8
Input	C5	20.0	1.00	l	7508		7508
Cooling out	C6	50.0	1.00	l	-7508		-7508
Input	C7	20.0	1.00	l	25.7		25.7
Cooling out	C8	50.0	1.00	l	-25.7		-25.7
Input	C9	20.0	1.00	l	1.07E+04		1.07E+04
Cooling out	C10	50.0	1.00	l	-1.07E+04		-1.07E+04
Input	C11	20.0	1.00	l	2385		2385
Cooling out	C12	50.0	1.00	l	-2385		-2385
Input	S1	207	1.00	l	1199	1199	
Steam out	S2	207	1.00	l	-1199	-1199	

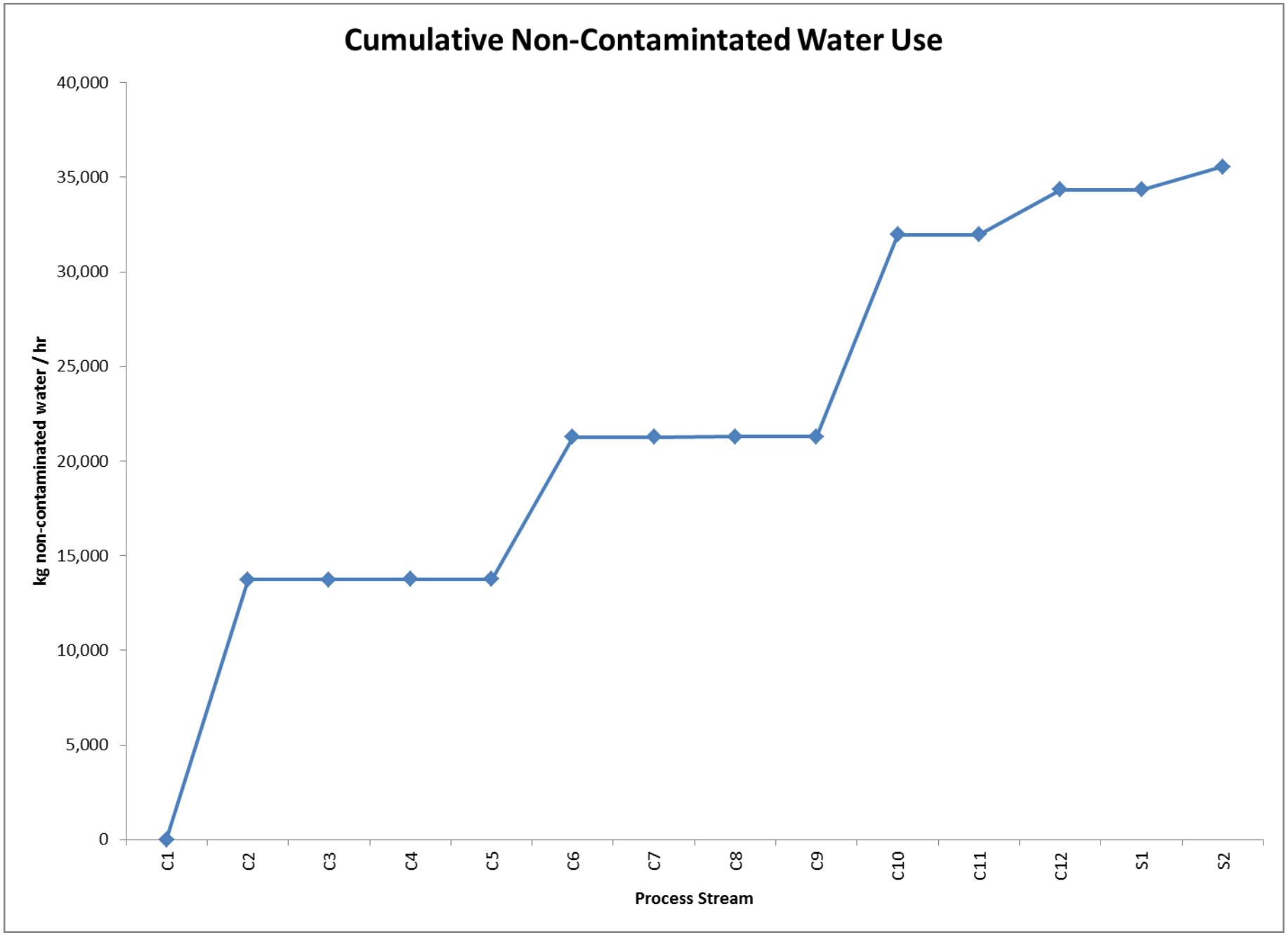
Graph of Cumulative Chemical Losses through Manufacturing Process



Graph of Cumulative Contaminated Water Use / Emission through Manufacturing Process



Graph of Cumulative Non-Contaminated Water Use / Emission through Manufacturing Process



Energy Input for each Unit Process, Cumulative Energy Requirements, Cooling Requirements (exotherms), and Assumed Heat Recovery from Hot Streams Receiving Cooling

Energy Input [MJ / hr]						Cooling Requirements [MJ / hr]							
Process Diagram Label	Unit	Energy input [MJ / 1000 kg Product]	Cumulative energy [MJ / 1000 kg Product]	To [C] (Used to determine energy type)	Energy Type	Process diagram label	Unit	Energy Loss	Cumulative cooling water energy	Tef [C] (for recovery efficiency)	Recovery Efficiency	Energy Recovered	Cumulative recovered [MJ / 1000 kg Product]
Cnv1	Conveyer 1	0.0240	0.0240		E	R1	Reactor 1	-2029	-2029	132	0.250	-507	-507
MxE1	Mixer electricity 1	4.40	4.42		E	Hx1	Heat exchanger 1	-2.04	-2031	132	0.250	-0.509	-508
P1	Pump 1	101	105		E	LTrb1	Liquid turbine 1	-9.46	-2031		1.00	-9.46	-517
Cmp1	Compressor 1	106	211		E	R2	Reactor 2	-1109	-3139	85.0	0.250	-277	-794
P2	Pump 2	0.0401	211		E	Hx2	Heat exchanger 2	-3.79	-3143	85.0	0.250	-0.949	-795
Cmp2	Compressor 2	171	381		E	Di1	Distillation condenser 1	-1577	-4720	192	0.450	-709	-1505
P3	Pump 3	0.0673	381		E	Hx3	Heat exchanger 3	-352	-5072	193	0.450	-158	-1663
P4	Pump 4	0.0263	381		E								
P5	Pump 5	2.16E-03	381		E								
Di1	Distillation reboiler 1	1949	2331	192	S								
P6	Pump 6	1.73E-04	2331		E								
P7	Pump 7	0.0693	2331		E								
	Potential recovery	-1663	668										
	Net energy		668				Potential recovery:						-1663

Electricity	382	E	[MJ/hr]
Heating steam	1949	S	[MJ/hr]
Energy input requirement	2331		[MJ/hr]
Cooling water	-5072		[MJ/hr]
Potential heat recovery	-1663		[MJ/hr]
Net energy	668		[MJ/hr]

Graph of Cumulative Energy Requirements