Rereviewed by Michael Overcash
4/29/08 Final

2-Methyltetrahydrofuran (MTHF)

CONTENTS OF FACTORY GATE TO FACTORY GATE

LIFE CYCLE INVENTORY SUMMARY

Authors	E. Griffing
Peer reviews, name (date)	MR Overcash (4-29-2008)
Gtg report last modified on	7-12-2011
Additional notes	

Checked for database consistency on	7-12-2011
First gtg version finalized on	4-29-2008
Modification history, Author (date)	EMG (4-29-2008) and EMG (7-12-2011)

Products	MTHF
Standard inputs	2-methyl furan, Hydrogen

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.

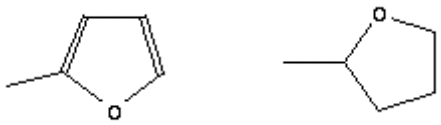
Users of this report should cite: E. Griffing and M. Overcash, Chemical Life Cycle Database, www.environmentalclarity.com, 1999 - present.

Chemistry

Primary reaction:

$C_5H_6O + 2H_2 \rightarrow C_5H_{10}O$ (1)

methylfuran + hydrogen → methyltetrahydrofuran



nickel catalyzed

Side reactions: (type of side rxns)

$C_5H_{10}O \rightarrow C_5H_{10}O$ (2)

Methyltetrahydrofuran → 2-pentanone

Process Summary

Literature

2-Methyl tetrahydrofuran (MTHF) is produced by hydrogenation of 2-methylfuran (MF). The reaction proceeds in the liquid phase (under 2 MPa H_2) or in the vapor phase over a nickel catalyst at 60 – 140 ^oC (Ullmann's, 2007). Alternatively, MTHF can be isolated as a byproduct of oxidizing furfural (Kirk-Othmer, 2000). In addition, a route based on cyclization and hydrogenation of levulinic acid has been patented, but not used industrially. The levulinic acid route uses the Biofine process (Kamm et al. 2006), which is being studied at the pilot scale. A commercial plant is near completion in Italy (IAGS, 2008). Here, we model production from 2-methylfuran.

2-Methyl furan is vaporized and sent to a reactor with hydrogen vapor. According to US 6,852,868, hydrogen is added in 2:1 molar ratio (to MF). The reaction inputs are heated to 180 ^oC in a vaporizer, and the reaction proceeds at 115 - 130 ^oC over a nickel-based catalyst (U.S. 6,852,868). The reaction is exothermic, and requires heat removal to control the temperature. The reaction product is a mixture that includes 2-MTHF. In general, reaction products are separated by condensation, molecular sieves, or distillation (U.S. 6,852,868). Preferably, 2-MTHF is condensed at –10 oC, and recovered by a single distillation (U.S. 6,852,868).

If the feed is furfuryl alcohol (FA) free, the hydrogenator produces high yields of 2-MTHF. Impurities are low concentrations of 2-pentanone, 2-pentanol (impurities in the MF input). The composition of the organic phase is > 75% 2-MTHF, 15% MF, and < 1 % impurities (U.S. 6,852,868).

LCI design

Hydrogen gas is combined with recycle hydrogen 20% of input flow, heated to 180 ^oC and fed to the reactor. Liquid 2-methyl furan is combined with recycled 2-methyl furan, vaporized, heated to 180 ^oC and fed to the reactor. The molar ratio of H_2 to methyl furan into the reactor is 2.05.

The reactor runs at 123 ^oC. Excess heat is removed by cooling water. Reaction products are cooled to 25 ^oC (with heat recovery), and then refrigerated to –10 ^oC. Hydrogen is recovered via a flash. The remaining product stream is distilled. The distillation overhead, mostly 2-methylfuran, is recycled. The bottoms are distilled again to recover MTHF in the overhead. The bottoms of the second columns are 2-pentanone waste (with MTHF).

IAGS (2008). Institute for the Analysis of Global Security. http://www.iags.org/biofine.htm
Kamm, B.; Gruber, P.R.; Kamm, M (2006). Biorefineries-Industrial processes and products.
Ullmann's (2006). Furfural and Derivatives, (Hoydonckx, H.E.; Van Rhijn, W.M.; Rhijn, W.; De Vol, D.E.; Jacobs, P.A., section authors), accessed online, February, 2008.
Kirk Othmer (2000). Kirk-Oothmer Encyclopedia of Chemical Technology. Furan Derivatives (Kottke, R.H. article author). Accessed online, 2008.
U.S. 6,852,868 (2005). Processes for the preparation of 2-methylfuran and 2-methyltetrahydrofuran. Assined to Pure Energy Corporation.

Critical parameters

Conversion / Yield information from both reactors			
		Conversion of or Yield from hydrogen	Conversion of or Yield from methyl furan
Total conversion in reactor 1: (% of reactant entering the process that reacts)	From mass balance	99.9	99.9
Total per pass conversion in reactor 1: (% of reactant entering the reactor that reacts)	From mass balance	83	83
Total yield of reactor 1: (% yield ProductChem produced in the reactor based on reactant input to process)	From mass balance	98.4	98.4
Total yield of Process: (% yield produced by the overall process based on reactant input to process)	From mass balance	97.2	96.6
Notes: Industrial source claim better than 97% yield from methyl furan.			

Product purity			
	MTHF		Comments
Used here	99.9		
LiteratureSource			

Summary of LCI Information

Inputs					
Input UID	Input Name	Input Flow	Input purity	Units	Comments
534-22-5	2-methyl furan	986		[kg/hr]	includes replacement of fugitive emissions
1333-74-0	Hydrogen	47.8		[kg/hr]	
	Total	1033		[kg/hr]	
Non-reacting inputs					
UID	Name	Flow	Purity	Units	Comments
No non-reacting inputs					
Ancillary inputs					
UID	Name	Flow	Purity	Units	Comments
No ancillary inputs					
Products					
Product UID	Product Name	Product Flow	Purity	Units	Comments
96-47-9	MTHF	1000	99.9	[kg/hr]	
	Total	1000		[kg/hr]	
Benign Outflows					
UID	Name	Flow	Purity	Units	Comments
No benign outflows					

Chemical Emissions							
Emission UID	Emission Name	Gas Flow	Liquid Flow	Solid Flow	Solvent Flow	Units	Comments
534-22-5	2-methyl furan	11.7	4.89e-3	0	0	[kg/hr]	
96-47-9	MTHF	10.1	5.02	0	0	[kg/hr]	
1333-74-0	Hydrogen	0.285	0	0	0	[kg/hr]	
107-87-9	2-pentanone	0.165	16.4	0	0	[kg/hr]	
Totals		22.2	21.4	0	0	[kg/hr]	

Mass Balance		
Total inputs	1033	
Total outflows	1044	
Net input	-10.2	

Energy use			
Energy type	Amount	Comments	
electricity	47.9	[MJ/hr]	
heating steam	2735	[MJ/hr]	
Net input requirement	2783	[MJ/hr]	Net of energies input to system
cooling water	-4273	[MJ/hr]	
potential recovery	-1043	[MJ/hr]	
Net energy	1740	[MJ/hr]	Net input requirement - potential recovery

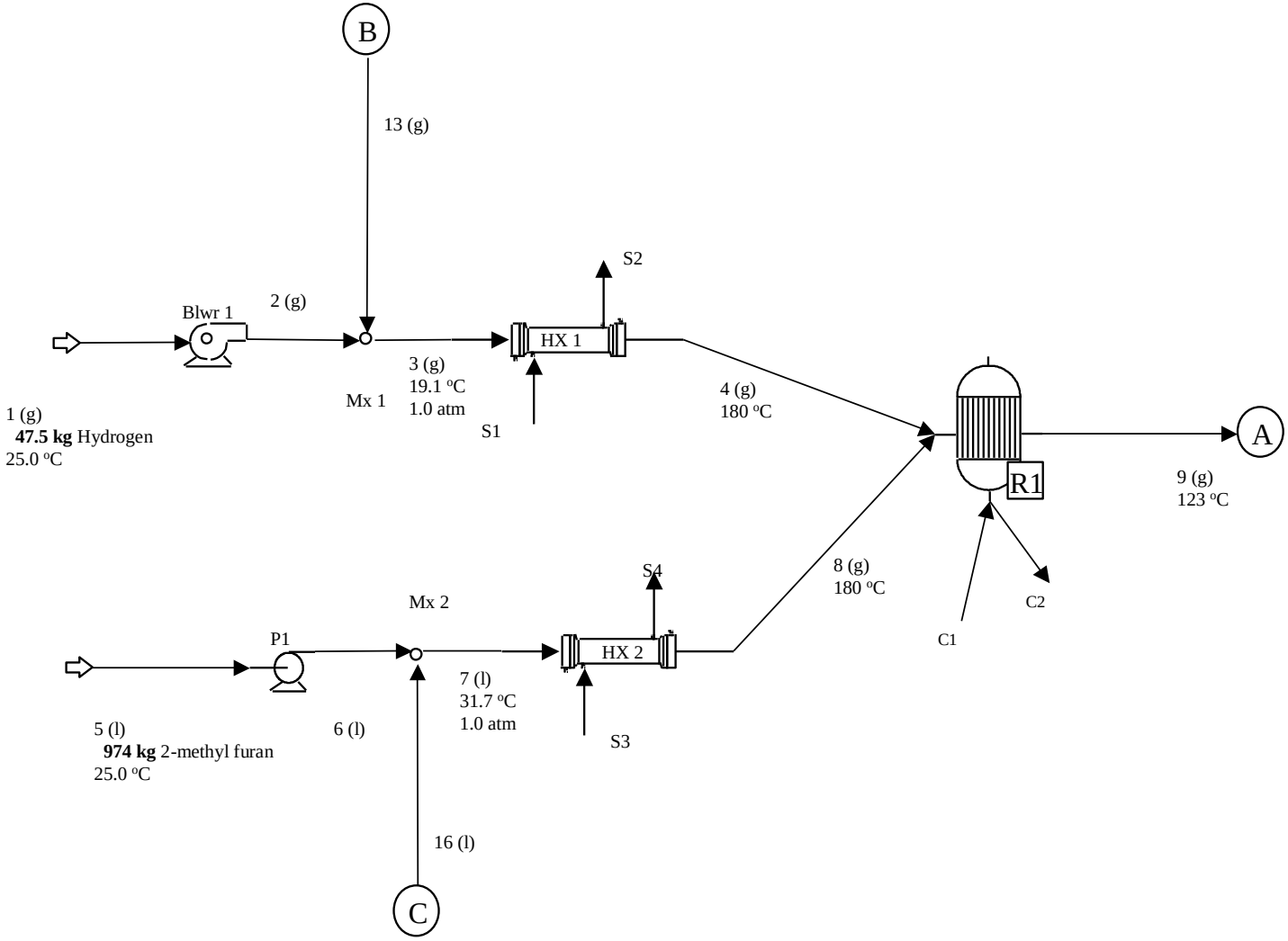
Process Diagram Interpretation Sheet

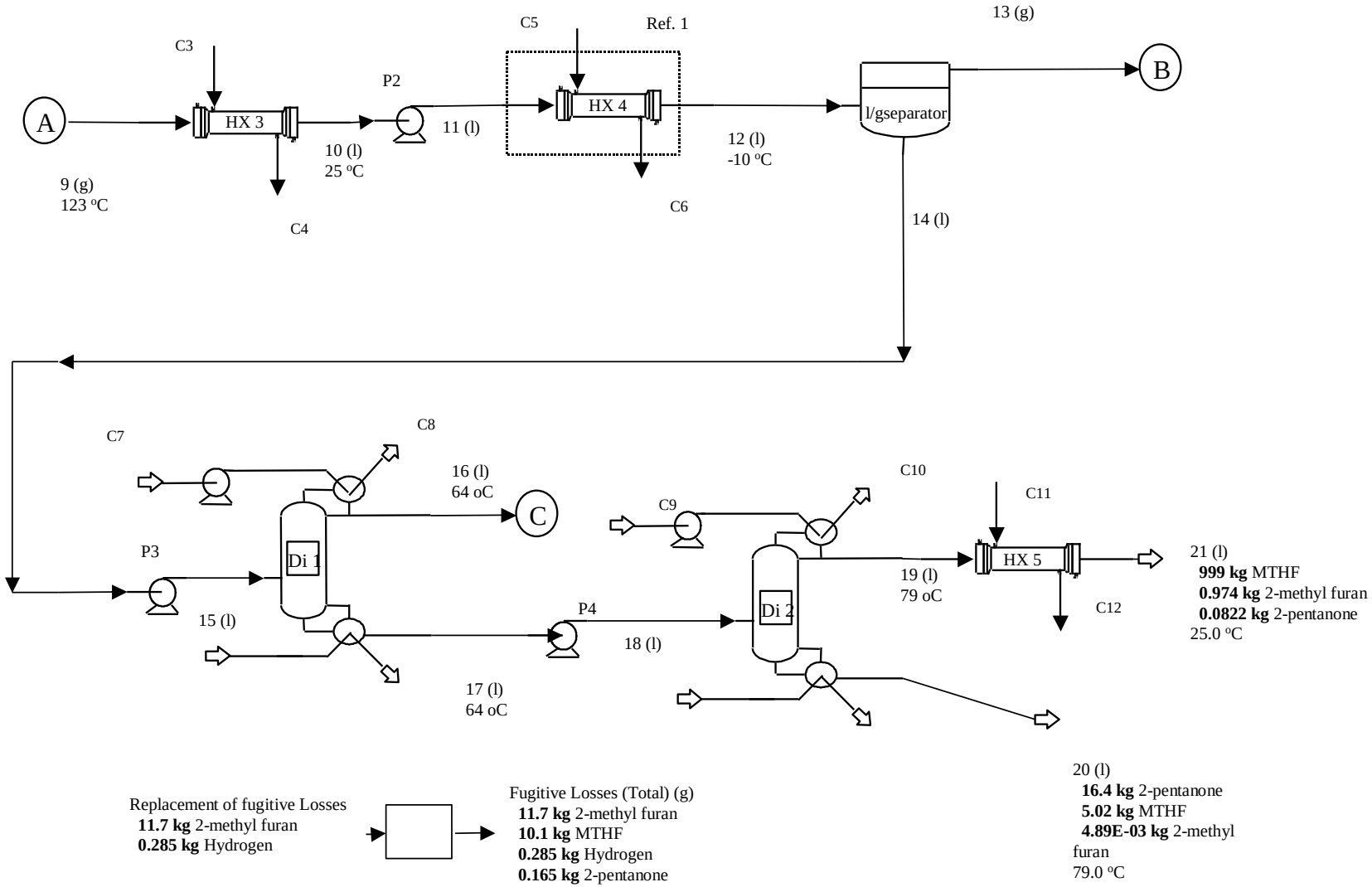
1) As much as possible, standard symbols are used for all unit processes.
2) Only overall input and output chemicals are labeled on these diagrams. All intermediate information is given on the attached Process Mass Balance sheet
3) The physical state of most streams is shown (gas, g; liquid, l; solid, 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.




A
C3
HX 3
9 (g)
123 ºC
10 (l)
25 ºC
C4
P2
11 (l)
C5
Ref. 1
HX 4
C6
12 (l)
-10 ºC
13 (g)
l/gseparator
B
14 (l)
C7
C8
16 (l)
64 oC
C
P3
Di 1
15 (l)
17 (l)
64 oC
P4
C9
C10
C11
HX 5
19 (l)
79 oC
Di 2
18 (l)
C12
21 (l)
999 kg MTHF
0.974 kg 2-methyl furan
0.0822 kg 2-pentanone
25.0 ºC
20 (l)
16.4 kg 2-pentanone
5.02 kg MTHF
4.89E-03 kg 2-methyl furan
79.0 ºC
Replacement of fugitive Losses
11.7 kg 2-methyl furan
0.285 kg Hydrogen
Fugitive Losses (Total) (g)
11.7 kg 2-methyl furan
10.1 kg MTHF
0.285 kg Hydrogen
0.165 kg 2-pentanone

Mass Balance of Chemicals in Each Process Stream

All flow rates are given in kg / hr
Physical state of chemical losses:

Gas
Liquid
Solid

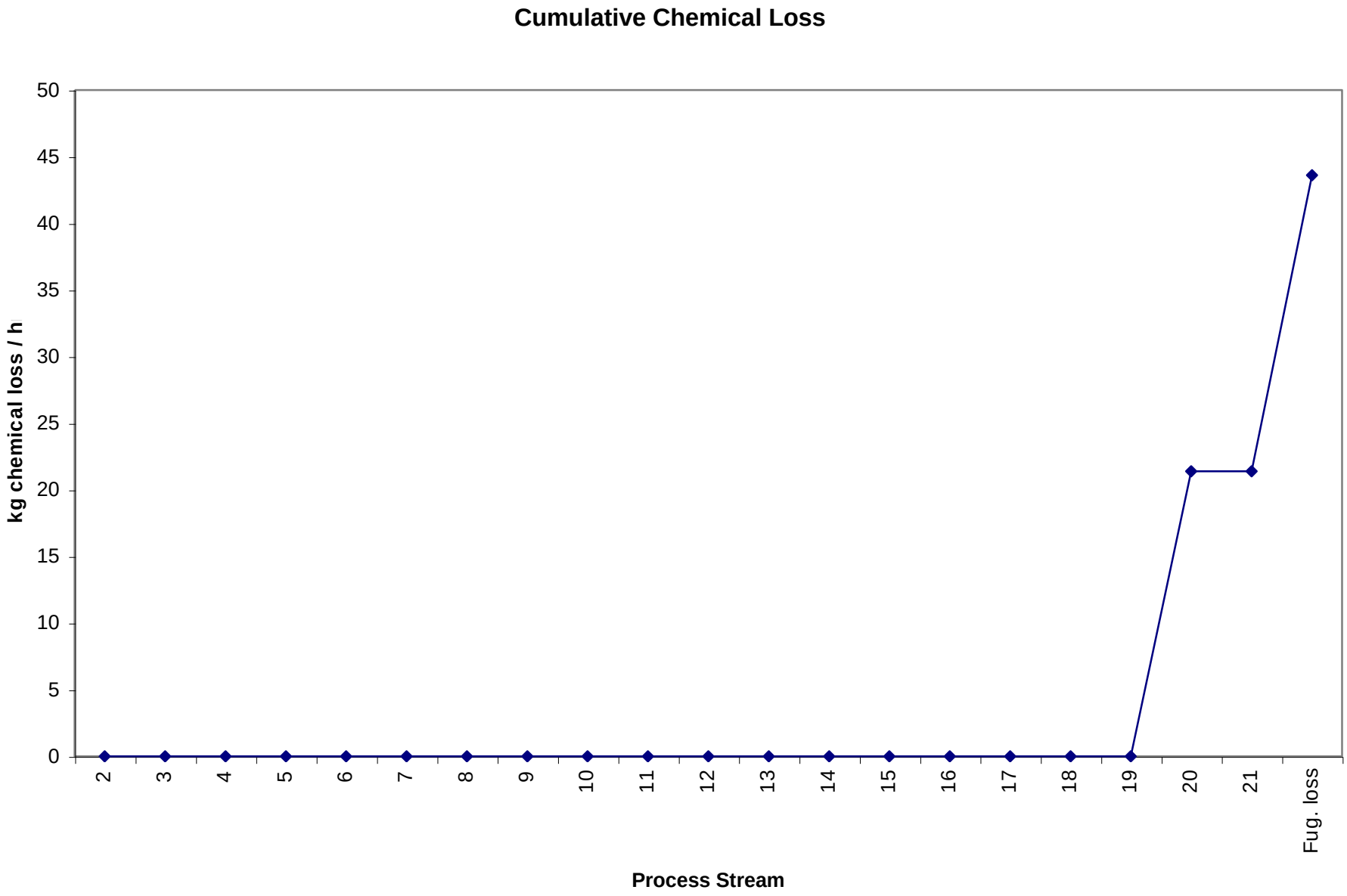
	Comments	Streams	Temp [C]	P	Phase	Total Flow	Water	2-methyl furan	MTHF	Hydrogen	2-pentanone	Steam	Water
Input		1	25.0	1.00	g	47.5				47.5			
		2	25.0	1.00	g	47.5				47.5			
		Stream 13:Recycle input				9.50				9.50			
		Stream 13:Recycle calculated				9.55	0	0	0	9.55	0		
		Stream 13:Recycle residue				-0.0508	0	0	0	-0.0508	0		
		3	19.1	1.00	g	57.0	0	0	0	57.0	0		
		4	180	1.00	g	57.0	0	0	0	57.0	0		
Input		5	25.0	1.00	l	974		974					
		6	25.0	1.00	l	974		974					
		Stream 16:Recycle input				200		195	5.00		0.0500		
		Stream 16:Recycle calculated				200	0	195	5.05	0	0.0165		
		Stream 16:Recycle residue				-0.0325	0	-0.0211	-0.0450	0	0.0335		
		7	31.7	1.00	l	1174	0	1169	5.00	0	0.0500		
		8	180	1.00	l	1174	0	1169	5.00	0	0.0500		
R1	973	kg	2-methyl furan			is converted in rxn 1 (83.2 % of reactor input)							
	16.4	kg	MTHF			is lost in rxn 2							
		kg				is lost in rxn 3							
		Input to reactor			:	1231	0	1169	5.00	57.0	0.0500		
		R1 Reaction Coefficient 1			:			-1.00	1.00	-2.00			
		R1 Conversion 1			:	0		-973	1020	-47.5			

	Comments	Streams	Temp [C]	P	Phase	Total Flow	Water	2-methyl furan	MTHF	Hydrogen	2-pentanone	Steam	Water
		[kg/hr]											
		R1 Conversion 1 [kgmol/hr]			:	11.9		-11.9	11.9	-23.7			
		R1 Reaction Coefficient 2			:				-1.00		1.00		
		R1 Conversion 2 [kg/hr]			:				-16.4		16.4		
		R1 Conversion 2 [kgmol/hr]			:	0.191			-0.191		0.191		
		R1 Reaction Coefficient 3			:								
		R1 Conversion 3 [kg/hr]			:								
		R1 Conversion 3 [kgmol/hr]			:								
		Flow out of reactor			:	1231	0	196	1009	9.55	16.5		
		Primary product			:	MTHF							
		Total conversion			:		NA	99.9	NA	99.9	NA		
		Per pass conversion			:			83.2	NA	83.2	NA		
		Total yield from reactor			:			98.4	NA	98.4			
		9	123	1.00	g	1231	0	196	1009	9.55	16.5		
		10	25.0	1.00	l	1231	0	196	1009	9.55	16.5		
		11	25.0	1.00	l	1231	0	196	1009	9.55	16.5		
		12	-10.0	1.00	l	1231	0	196	1009	9.55	16.5		
		13	-10.0	1.00	g	9.55				9.55			
		14	-10.0	1.00	l	1221	0	196	1009	0	16.5		
	Feed	15	-10.0	1.00	l	1221	0	196	1009	0	16.5		
Di 1		percentage of input in distillate			:			99.5	0.500		0.100		
		percentage of input in bottoms			:			0.500	99.5		99.9		
		Boiling Temperature (Tb) [oC]			:			63.9	78.9		102		
	Distillate	16	64.0	1.00	l	200	0	195	5.05	0	0.0165		
	Bottoms	17	64.0	1.00	l	1021	0	0.979	1004	0	16.4		

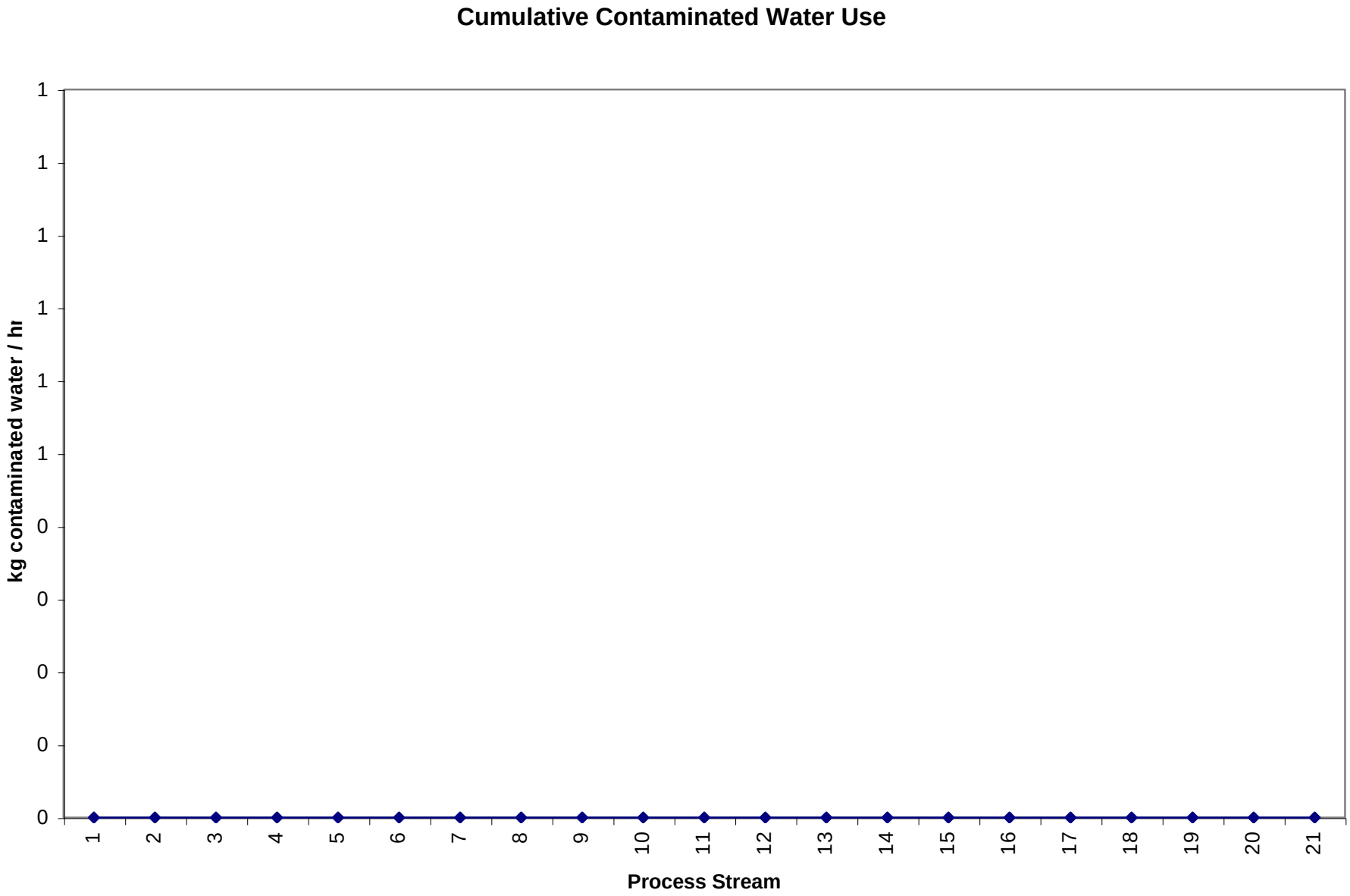
	Comments	Streams	Temp [C]	P	Phase	Total Flow	Water	2-methyl furan	MTHF	Hydrogen	2-pentanone	Steam	Water
	Feed	18	64.0	1.00	l	1021	0	0.979	1004	0	16.4		
Di 2		percentage of input in distillate			:			99.5	99.5		0.500		
		percentage of input in bottoms			:			0.500	0.500		99.5		
		Boiling Temperature (Tb) [oC]			:			63.9	78.9		102		
	Distillate	19	79.0	1.00	l	1000	0	0.974	999	0	0.0822		
Waste	Bottoms	20	79.0	1.00	l	-21.4	0	-4.89E-03	-5.02	0	-16.4	0	0
Main product		21	25.0	1.00	l	-1000	0	-0.974	-999	0	-0.0822	0	0
		Product purity (%)				99.9							
		Main product				MTHF							
		Overall Rxn coefficients						-1.00	1.00	-2.00			
		Total yield of process (from reactant)						96.6	NA	97.2			
Waste		Fugitive Losses (Total)			g	-22.2	0	-11.7	-10.1	-0.285	-0.165	0	0
		Input Sum				1021	0	974	0	47.5	0		
		Fugitive Replacement of Reactants				12.0		11.7		0.285			
		Total Input (Input + Fugitive Replacement)				1033	0	986	0	47.8	0		
		Product Sum				1000	0	0.974	999	0	0.0822		
		Main product flow				1000	0	0.974	999	0	0.0822		
		Net Input (in - out, omitting fugitives)				0.0833							
Input		C1	20.0	1.00	l	1.38E+04							1.38E+04
Cooling out		C2	50.0	1.00	l	-1.38E+04	0	0	0	0	0	0	-1.38E+04
Input		C3	20.0	1.00	l	4542							4542
Cooling out		C4	50.0	1.00	l	-4542	0	0	0	0	0	0	-4542
Input		C5	20.0	1.00	l	656							656
Cooling out		C6	50.0	1.00	l	-656	0	0	0	0	0	0	-656
Input		C7	20.0	1.00	l	7448							7448

	Comments	Streams	Temp [C]	P	Phase	Total Flow	Water	2-methyl furan	MTHF	Hydrogen	2-pentanone	Steam	Water
Cooling out		C8	50.0	1.00	l	-7448	0	0	0	0	0	0	-7448
Input		C9	20.0	1.00	l	4884							4884
Cooling out		C10	50.0	1.00	l	-4884	0	0	0	0	0	0	-4884
Input		C11	20.0	1.00	l	816							816
Cooling out		C12	50.0	1.00	l	-816	0	0	0	0	0	0	-816
Input		S1	207	1.00	l	81.8						81.8	
Steam out		S2	207	1.00	l	-81.8	0	0	0	0	0	-81.8	0
Input		S3	207	1.00	l	366						366	
Steam out		S4	207	1.00	l	-366	0	0	0	0	0	-366	0
Input		S5	207	1.00	l	795						795	
Steam out		S6	207	1.00	l	-795	0	0	0	0	0	-795	0
Input		S7	207	1.00	l	463						463	
Steam out		S8	207	1.00	l	-463	0	0	0	0	0	-463	0

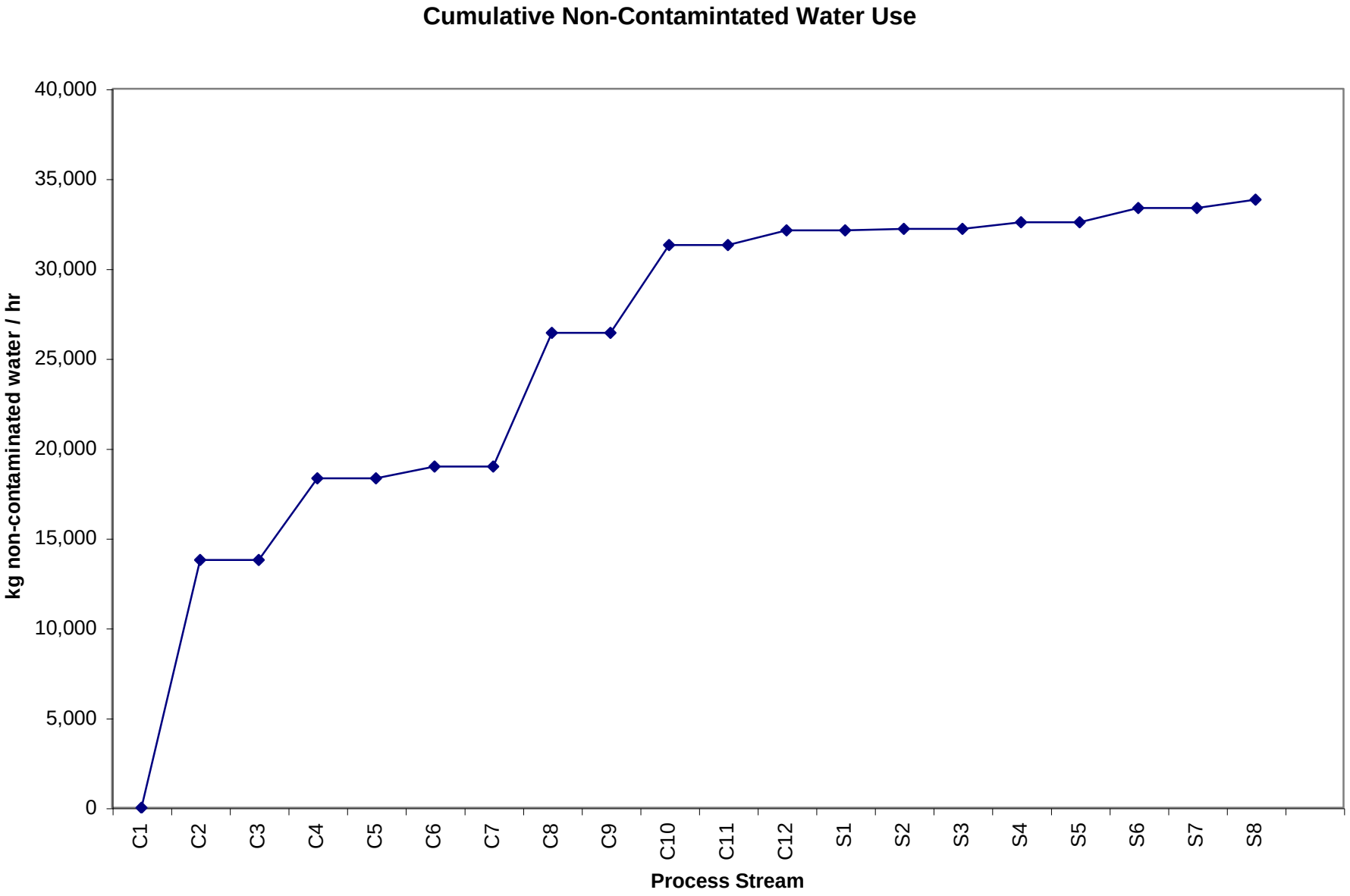
Graph of Cumulative Chemical Losses through Manufacturing Process



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	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]
Blw1	Blower 1	5.69	5.69		E	R1	Reactor 1	-2035	-2035	123	0.250	-509	-509
Hx1	Heat exchanger 1	133	139	180	S	Hx3	Heat exchanger 3	-671	-2706	123	0.250	-168	-676
P1	Pump 1	0.0568	139		E	Hx4	Heat exchanger 4	-96.9	-2803	25.0	0	0	-676
Hx2	Heat exchanger 2	595	734	180	S	Di1	Distillation condenser 1	-1100	-3902	62.9	0.250	-275	-951
P2	Pump 2	0.0719	734		E	Di2	Distillation condenser 2	-721	-4624	77.9	0.250	-180	-1132
Ref1	Refrigerator elect. 1	40.4	774	0	E	Hx5	Heat exchanger 5	-121	-4744	79.0	0.250	-30.1	-1162
P3	Pump 3	5.32E-04	774		E								
Di1	Distillation reboiler 1	1292	2066	62.9	S								
P4	Pump 4	0.0593	2066		E								
Di2	Distillation reboiler 2	753	2819	77.9	S								
	Potential recovery	-1162	1657										
	Net energy		1657				Potential recovery:						-1162
	Electricity	46.2	E	[MJ/hr]									
	DowTherm	0	D	[MJ/hr]									
	Heating steam	2772	S	[MJ/hr]									
	Direct fuel use	0	F	[MJ/hr]									
	Heating natural gas	0	G	[MJ/hr]									
	Energy input requirement	2819		[MJ/hr]									
	Cooling water	-4744		[MJ/hr]									
	Cooling refrigeration			[MJ/hr]									
	Potential heat recovery	-1162		[MJ/hr]									
	Net energy	1657		[MJ/hr]									

Graph of Cumulative Energy Requirements