

# Glyphosate from PMIDA [1071-83-6]

## CONTENTS OF FACTORY GATE TO FACTORY GATE

### LIFE CYCLE INVENTORY SUMMARY

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|                             |                         |
|-----------------------------|-------------------------|
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| Peer reviews, name (date)   | MR Overcash (5-30-2011) |
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| Additional notes            |                         |

|                                     |             |
|-------------------------------------|-------------|
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|                 |               |
|-----------------|---------------|
| Products        | glyphosate    |
| Standard inputs | Oxygen, PMIDA |

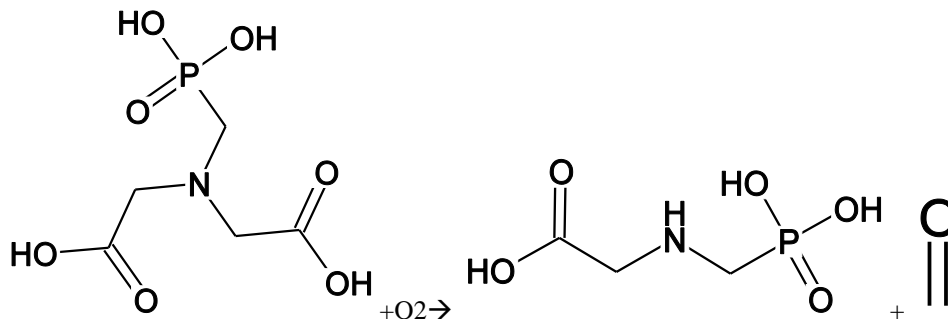
Methodology: Environmental Clarity gtg lci reports are based on industrial practice information, standard methods of engineering process design, and technical reviews. These reports are intended to be representative of industrial production based on the stated route.

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

## Chemistry

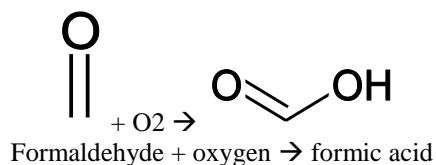
Primary reaction:



N-phosphonomethyliminodiacetic acid (PMIDA) + oxygen  $\rightarrow$  glyphosate + formaldehyde +  $\text{CO}_2$

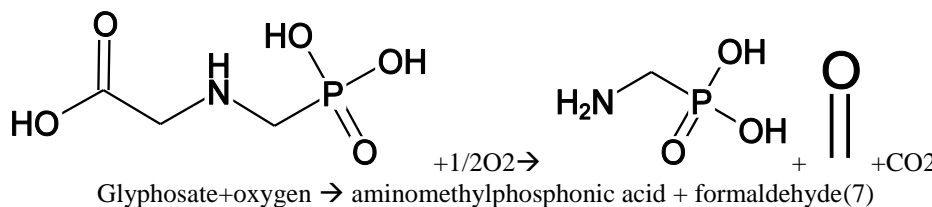
Notes: glyphosate is the common name for (N-(phosphonomethyl)glycine)

Oxidation of formaldehyde:



Notes: Depending on the catalyst and reaction conditions, this can proceed to different extents. We assume that 20% of formaldehyde is oxidized further. US 5,606,107 describes strategies for increasing oxidation of byproducts to  $\text{CO}_2$ . Any unreacted formaldehyde must be sent to aerated waste treatment for further oxidation.

Side reactions: (oxidation of glyphosate)



Notes:

# Process Summary

## Literature

Glyphosate is the active ingredient in a broad-spectrum herbicide often marketed as round-up. Popular formulations in commercial herbicides are as glyphosate salts. The most popular salt is isopropylammonium (Green, S. and Pohanish, R.P., 2007). Other salts are monoammonium, diammonium, and potassium (BCPC, 2010). These salts provide the primary function of increasing the solubility in water. The solubility of glyphosate is increased from 2 wt% in water to about 44 wt% in water when in the salt form. Typical commercial formulations are 2 to 30 wt% (US 7,049,270, 2006).

As of 2000, Monsanto was the largest producer of glyphosate. Production by competition was about 40,000 tonnes/yr (Woodburn, 2000). As of 2009, China had a capacity of 655,000 tonnes glyphosate /yr, and China produced about 70% of the world supply of technical grade glyphosate. Most of China's production is shipped to other countries to be formulated and marketed as an herbicide (R & M, 2011). Although some efficiency improvements may be achieved by producing the salt directly, we show production of the glyphosate acid and crystallizing as a product. The salts can then be formed from the solid glyphosate in a separate life cycle inventory gate-to-gate.

Glyphosate is produced by four routes (1) original Monsanto (2) new Monsanto, (3) Chinese chloroacetic acid route, (4) Syngenta route (Bryant, 2003). The Monsanto routes and the Chinese chloroacetic acid route all go through the intermediate iminodiacetic acid (IDA) and phosphonomethyl iminodiacetic acid (PMIDA). The differences are in production of the intermediate IDA. In world production, the primary starting point for IDA is diethyl amine (DEA). However, in China, 80% of the IDA capacity is currently from glycine (Yin, 2011). In this gtg, glyphosate acid is produced from PMIDA. In our gtg library, the disodium salt of IDA is produced from DEA.

In Monsanto's process, IDA is converted to PMIDA. PMIDA is converted to the isopropylamine salt (DSIDA). The overall yield of these steps is 85% (Woodburn, 2000). The conversion of IDA to PMIDA is 93% (see separate gtg report for PMIDA), and the conversion of PMIDA to glyphosate is 93%. The formation of the salt is assumed to be 100% efficient. US 7,049,270 gives a procedure for making the potassium salt, and there are no separation losses. Thus the overall yield in the set of gtgs is 85%. The overall yield from ethylene oxide (used to produce diethanolamine for IDA production) is 50% or lower (US 7,750,180). The reason for the low yield from ethylene oxide (<50%) is that the oxidative cleaving of the intermediate PMIDA, during which, one of the two acetic acid groups is cleaved, and is not recoverable (US 7,750,180).

PMIDA is fed to a reactor in an aqueous phase, and an oxygen source such as air or gaseous oxygen is sparged through the reactor. US 7,799,571 describes a series of three reactors. Oxygen is sparged through the reactors at different rates to achieve higher conversion of PMIDA. Total conversion is about 97 to 99.5%. In this gtg, we show a single reactor, and assume a conversion of 99%. After the reaction, catalyst (typically noble metal on carbon) is filtered then recycled, and the solution is sent to an evaporative crystallizer. In this gtg, we follow a crystallization scheme presented in US 7,799,571. After filtration, a portion of the reactor effluent is sent to an adiabatic vacuum crystallizer, and the remainder is sent to a thermal evaporative crystallizer. In this gtg, we assume that half is sent to each evaporator. The effluent is separated from the crystals by a centrifuge. Ten percent of the effluent is purged to prevent buildup of PMIDA, and the remainder is sent back to the crystallizer to recover glyphosate. Thus, substantially all of the water is evaporated in the crystallizer. The crystals from the centrifuge are dried and are considered technical grade. The size of the purge represents a trade-off between PMIDA content in product and recovery of glyphosate.

If the reaction time is long and / or the conditions are highly oxidizing, the PMIDA will be converted at a higher percentage of input. However, the product over-oxidizes glyphosate to aminomethylphosphonic acid (AMPA). Additionally, the glyphosate and AMPA can be methylated with the formaldehyde byproduct. Thus, there is a yield tradeoff between low conversion and high side product formation. Under commercial conditions, the rate constant for reaction of glyphosate with oxygen to that of PMIDA with oxygen is less than 0.017 (US 6,921,834). In the final reactor, about 7% of the PMIDA is converted. However, the ratio of glyphosate to PMIDA during this reactor is about 95 to 5. Thus, the conversion of glyphosate to AMPA is about  $95/5 * 0.017 = 0.32 * 7\% = 2.2\%$ . The overall conversion of glyphosate to

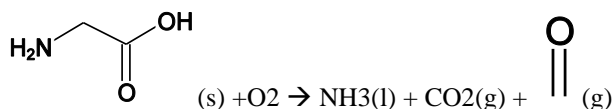
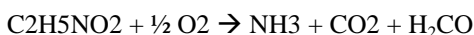
AMPA is assumed to be 2.5%. The overall yield is assumed to be 93%, and the losses to unreacted PMIDA and over-oxidized glyphosate are 1% and 2.5%, respectively. Thus, additional losses in the separation system are 3.5%.

Table 1. Process parameters

|                  | Reactor T                   | Reactor P, atm           | Water, kg / kg PMIDA | O2, kg / kg PMIDA        | Catalyst, kg/kg PMIDA | Reaction time       | Notes   |
|------------------|-----------------------------|--------------------------|----------------------|--------------------------|-----------------------|---------------------|---------|
| US 6,921,834     | 75                          | 7                        | 10 to 49             |                          | 0.15                  |                     | 6       |
| US 7,799,571     | 90                          | 4                        | 12 to 37             | 0.08-0.11<br>(0.55-0.83) | 0.13 to 0.375         |                     | 1,2,3,7 |
| US 5,962,729     | Preheated to 70 oC          | 4                        | 190                  | 2.8 (20 mol/mol)         |                       | Order of 20 minutes |         |
| US 3,969,398     | 75 – 90 oC<br>90 in example | 1 to 7<br>3.1 in example | 25                   | 1.4 (10 mol/mol)         | 0.05 to 0.2           | 3 hrs.              | 4       |
| Used in this gtg | 90                          | 3.5                      | 36                   | 0.14 (1 mol/mol)         | 0.15                  | 2 hrs               | 5       |

1. Exothermic with cooling
2. O2 source can be air, oxygen enriched air or pure oxygen
3. Per pass conversion in a series of reactors is 97 to 99.5%
4. Industrial separations not discussed. Water and byproducts were evaporated from product at vacuum.
5. The solubility of glyphosate is 2 wt% in water (Monig et al.). The water flow into the reactor is set so that the output is saturated with glyphosate.
6. Concentration of PMIDA specified as between 2 and 10wt% into oxidation reactor.
7. This corresponds to 60 to 90% utilization of O2 in primary reaction.

The oxidation reaction is exothermic and heat is removed by heat exchangers. The heat of reaction is estimated by a proxy reaction of glycine oxidation.



Glycine + oxygen → ammonia + carbon dioxide + formaldehyde

The effect of the  $-\text{CH}_2\text{COOH}$  and  $-\text{CH}_2\text{HPO}_3$  groups is neglected. The heat of reaction is  $-69.2-393.5-115.9-(-527+0) = -51.6$  kJ/gmol. The heat of reaction for over-oxidation of glyphosate to AMPA is also 51.6 kJ/gmol.

The solubility of PMIDA (2 % at 75C and 6 % at 105C [6921834 p. 12 line 25]; 1 % at 25C, 4 % at 95C, 10 % at 150C [3,969,398 p. 2 line 36] is close to that of glyphosate (on mass basis) (1.01% at 20C, [Wikipedia]; 1.9 wt% Monig et al.). The ratio of PMIDA to glyphosate in the recycle is at least 1.5 and typically 5 to 8 times the ratio of PMIDA to glyphosate after the reaction (US 7,799,571, 2010). The purge (up to 10%) prevents buildup of PMIDA. In this gtg, the purge is 10% and the PMIDA concentration relative to glyphosate is 5 times the ratio after the reactor.

## LCI design

PMIDA is fed as a 2.7 wt% aqueous solution. It is combined with an aqueous recycle stream, heated to 90 oC and fed to a reactor. Oxygen (100% stoichiometric excess) is bubbled through a continuous stirred tank reactor. The residence time is 2 hours, and mechanical mixing is used. The reactor effluent is filtered to recover catalyst. The liquid phase is split equally between two evaporators. The first evaporator utilizes vacuum to evaporate water adiabatically. The amount of water evaporated is calculated based on the temperature drop (90 oC to 35 oC), and is about 10%. The liquid passes through a filter to recover glyphosate, and the filtrate is recycled to the reactor. The remainder of the filtered reactor effluent is sent to a steam evaporator, where the majority of water is removed from the process. The concentrated stream exiting the evaporator is combined with glyphosate from the vacuum evaporator and solid glyphosate is recovered in a centrifuge. The liquid is returned to the thermal evaporator after a 10% purge to prevent buildup of PMIDA. The crystals from the centrifuge are dried and cooled to standard temperature.

### Notes:

There is a large water flow into the reactor. Sending water through the vacuum evaporator saves energy by reducing the fresh water input. However, it is not clear how much of the filtered reactor effluent goes through this loop. The energy required for the thermal evaporation is 50 MJ/kg. If we put more through that evaporator, it could nearly double. However, expensive multi-effect evaporators could be used to reduce this (not sure if this would be used at this production volume).

From Green (via other source), the cradle-to-gate of glyphosate requires 454 MJ/kg, more than twice that of atrazine (190 MJ/kg)

### References

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**Critical parameters**

| Conversion / Yield information from both reactors   |                   |                                      |                                       |
|---|-------------------|--------------------------------------|---------------------------------------|
|   |                   | Conversion of or<br>Yield from PMIDA | Conversion of or<br>Yield from Oxygen |
| Total conversion in reactor 1:<br>(% of reactant entering the process that reacts)                            | From mass balance | 99                                   | 60                                    |
| Total per pass conversion in reactor 1:<br>(% of reactant entering the reactor that reacts)                   | From mass balance | 98                                   | 60                                    |
| Total yield of reactor 1:<br>(% yield ProductChem produced in the reactor based on reactant input to process) | From mass balance | 99                                   | 81                                    |
| Total yield of Process:<br>(% yield produced by the overall process based on reactant input to process)       | From mass balance | 93                                   | 47                                    |
| Notes:  |                   |                                      |                                       |

| Product purity |            |          |
|----------------|------------|----------|
|                | Glyphosate | Comments |
| Used here      | 98.7       |          |

# Summary of LCI Information

| Standard inputs     |            |          |        |         |          |
|---------------------|------------|----------|--------|---------|----------|
| UID                 | Name       | Flow     | Purity | Units   | Comments |
| 7782-44-7           | Oxygen     | 199      | -      | [kg/hr] |          |
| 5994-61-6           | PMIDA      | 1422     | -      | [kg/hr] |          |
|                     | Total      | 1621     |        | [kg/hr] |          |
| Non-reacting inputs |            |          |        |         |          |
| UID                 | Name       | Flow     | Purity | Units   | Comments |
| 7732-18-5           | Water      | 2.84E+04 | -      | [kg/hr] |          |
|                     | Total      | 2.84E+04 |        | [kg/hr] |          |
| Ancillary inputs    |            |          |        |         |          |
| UID                 | Name       | Flow     | Purity | Units   | Comments |
|                     | Total      | 0        |        | [kg/hr] |          |
| Products            |            |          |        |         |          |
| UID                 | Name       | Flow     | Purity | Units   | Comments |
| 1071-83-6           | glyphosate | 1001     | 98.6   | [kg/hr] |          |
|                     | Total      | 1001     |        | [kg/hr] |          |
| Benign outflows     |            |          |        |         |          |
| UID                 | Name       | Flow     | Purity | Units   | Comments |
| 7732-18-5           | Water      | 2.84E+04 | -      | [kg/hr] |          |
| 7782-44-7           | Oxygen     | 79.0     | -      | [kg/hr] |          |
|                     | Total      | 2.84E+04 |        | [kg/hr] |          |

| Process emissions |                            |      |        |       |         |         |          |
|-------------------|----------------------------|------|--------|-------|---------|---------|----------|
| UID               | Name                       | Gas  | Liquid | Solid | Solvent | Units   | Comments |
| 1071-83-6         | glyphosate                 | 0    | 50.8   | 0     | 0       | [kg/hr] |          |
| 124-38-9          | Carbon dioxide             | 277  | 0      | 0     | 0       | [kg/hr] |          |
| 64-18-6           | Formic acid                | 1.13 | 57.2   | 0     | 0       | [kg/hr] |          |
| 50-00-0           | Formaldehyde               | 1.49 | 150    | 0     | 0       | [kg/hr] |          |
| 1066-51-9         | aminomethylphosphonic acid | 0    | 2.50   | 0     | 0       | [kg/hr] |          |
| 5994-61-6         | PMIDA                      | 0    | 4.81   | 0     | 0       | [kg/hr] |          |
|                   | Total                      | 280  | 266    | 0     | 0       |         |          |

| Mass balance   |          |
|----------------|----------|
| Total inputs   | 3.00E+04 |
| Total outflows | 3.00E+04 |
| Net input      | -5.34    |

| Energy use            |            |         |   |
|-----------------------|------------|---------|---|
| Energy type           | Amount     | Units   | Comments                                    |
| electricity           | 500        | [MJ/hr] | Net electricity use at plant                |
| heating steam         | 7.72E+04   | [MJ/hr] | heating by steam (0.85 efficiency included) |
| Net input requirement | 7.77E+04   | [MJ/hr] | Net of energies input to system             |
| cooling water         | - 6.53E+04 | [MJ/hr] | net cooling by cooling water                |
| potential recovery    | - 1.48E+04 | [MJ/hr] | potential energy recovery (negative)        |
| Net energy            | 6.29E+04   | [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
  - $C_i$ ,  $i = 1, \dots, n$  are used for all cooling non-contact streams
  - $S_j$ ,  $j = 1, \dots, n$  are used for all steam heating non-contact streams
- 5) Recycle streams are shown with dotted lines

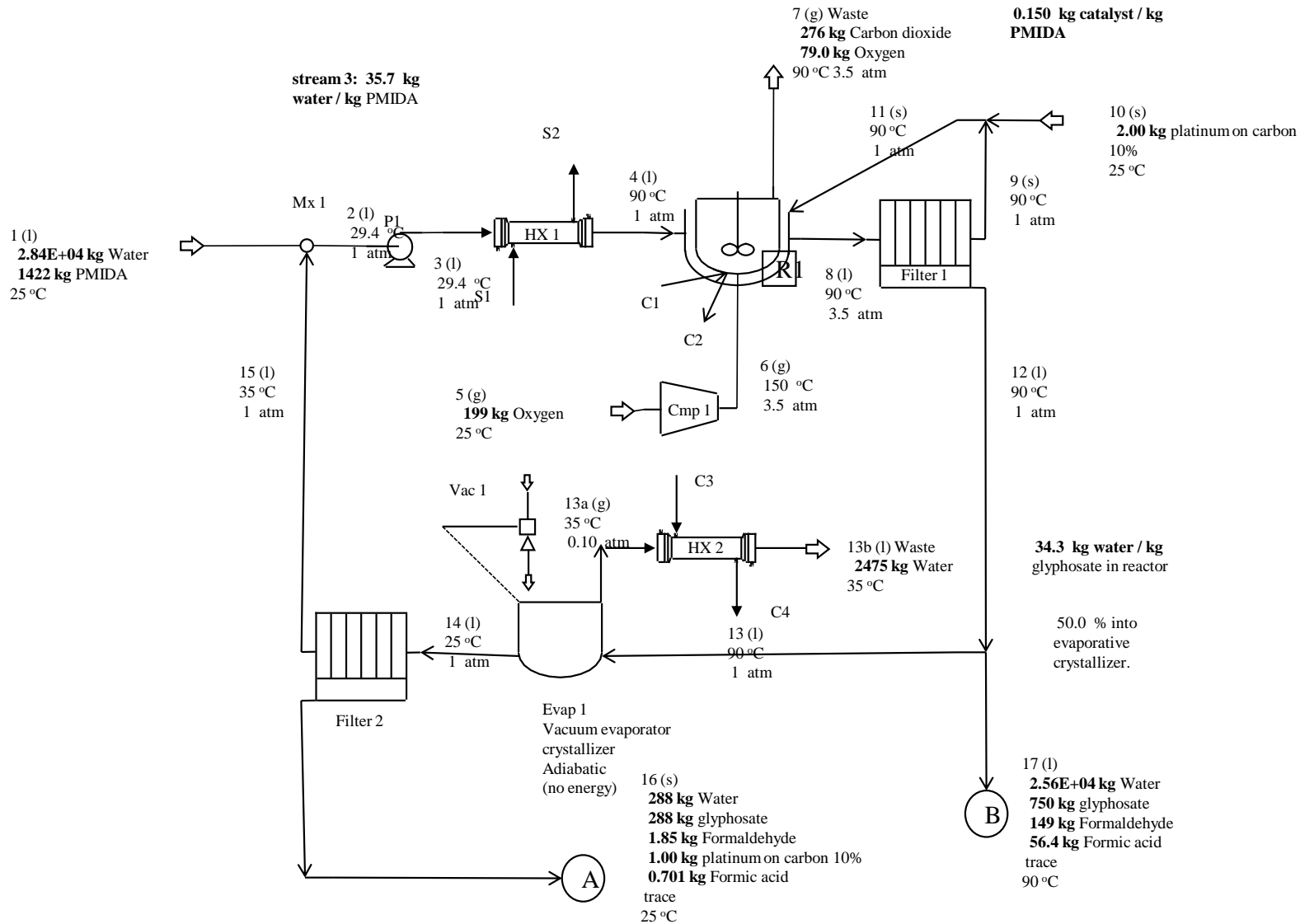
For most streams, the temperature and pressure are shown, if the pressures are greater than 1 atm

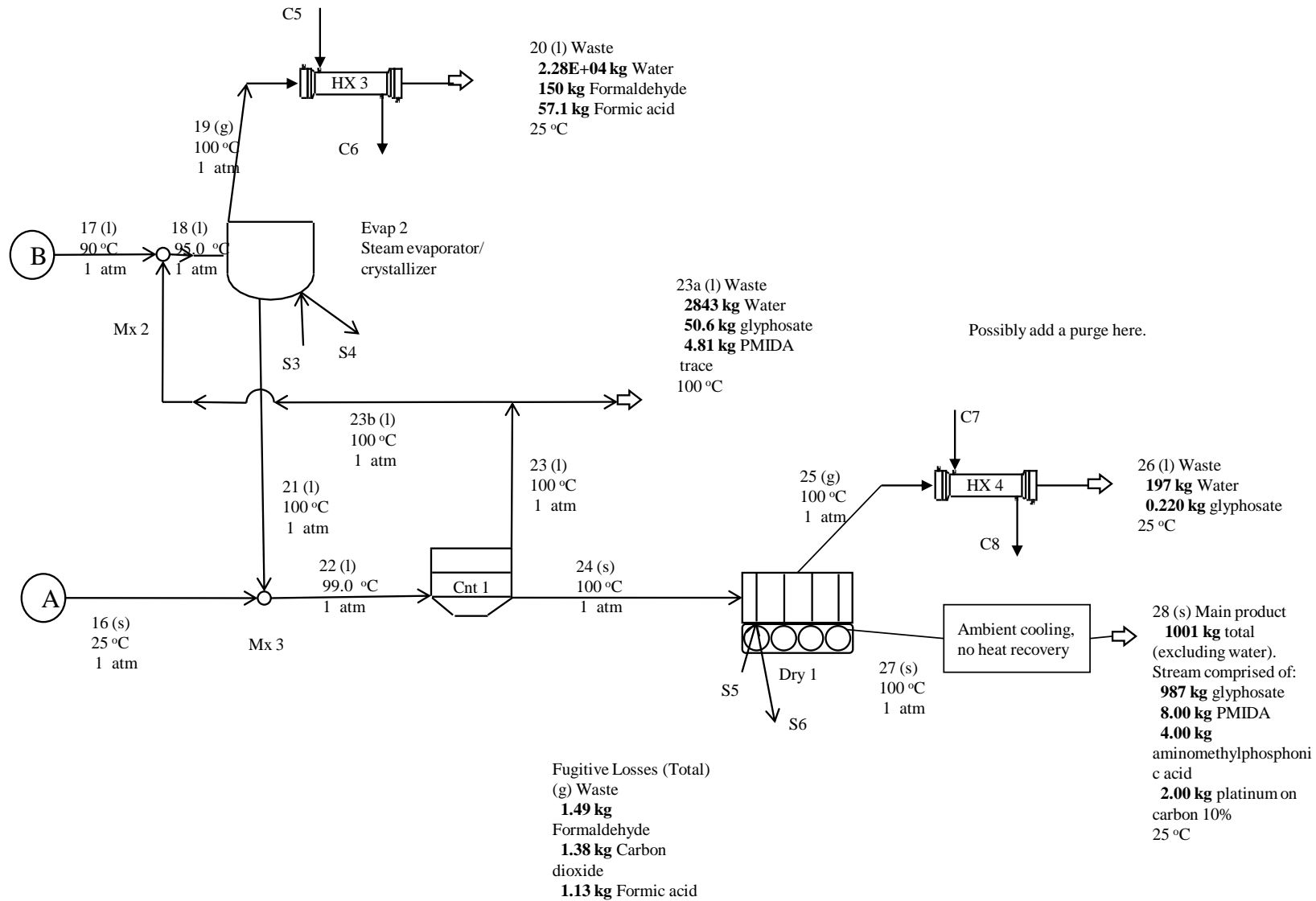


# Process Diagram or Boundary of LCI

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:





# 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  | PMIDA  | Oxygen | aminomethylphosphonic acid | Formaldehyde | Formic acid | Carbon dioxide | glyphosate | platinum on carbon 10% |
|-------|----------|------------------------------|----------|------|--------------|------------|--|--------|--------|----------------------------|--------------|-------------|----------------|------------|------------------------|
| Input |          | 1                            | 25.0     | 1.00 | l            | 2.98E+04   | 2.84E+04                                       | 1422   |        |                            |              |             |                |            |                        |
|       |          | Stream 15:Recycle input      |          |      |              | 2.35E+04   | 2.28E+04                                       | 13.7   | 0      | 6.60                       | 146          | 55.7        |                | 462        |                        |
|       |          | Stream 15:Recycle calculated |          |      |              | 2.35E+04   | 2.28E+04                                       | 13.8   | 0      | 6.66                       | 147          | 55.7        | 0              | 462        | 0                      |
|       |          | Stream 15:Recycle residue    |          |      |              | -0.274     | 0.194  | -0.101 | 0      | -0.0576                    | -0.292       | 0.0275      | 0              | -0.0448    | 0                      |
|       |          | 2                            | 29.4     | 1.00 | l            | 5.33E+04   | 5.12E+04                                       | 1435   | 0      | 6.60                       | 146          | 55.7        | 0              | 462        | 0                      |
|       |          | 3                            | 29.4     | 1.00 | l            | 5.33E+04   | 5.12E+04                                       | 1435   | 0      | 6.60                       | 146          | 55.7        | 0              | 462        | 0                      |
|       |          | 4                            | 90.0     | 1.00 | l            | 5.33E+04   | 5.12E+04                                       | 1435   | 0      | 6.60                       | 146          | 55.7        | 0              | 462        | 0                      |
| Input |          | 5                            | 25.0     | 1.00 | g            | 199        |  |        | 199    |                            |              |             |                |            |                        |
|       |          | 6                            | 150      | 3.50 | g            | 199        |  |        | 199    |                            |              |             |                |            |                        |
|       |          | Stream 11:Recycle input      |          |      |              | 428        | 213  |        |        |                            |              |             |                |            | 215                    |
|       |          | Stream 11:Recycle calculated |          |      |              | 429        | 213  | 0      | 0      | 0                          | 0            | 0           | 0              | 0          | 215                    |
|       |          | Stream 11:Recycle residue    |          |      |              | -0.321     | -0.321   | 0      | 0      | 0                          | 0            | 0           | 0              | 0          | 0                      |
| R1    | 1408     | kg                           |          |      | PMIDA        | :          | is converted in rxn ( 98.1 % of reactor input) |        |        |                            |              |             |                |            |                        |
|       | 37.2     | kg                           |          |      | Formaldehyde | :          | is converted in rxn ( 25.4 % of reactor input) |        |        |                            |              |             |                |            |                        |
|       | 10.5     | kg                           |          |      | glyphosate   | :          | is converted in rxn ( 2.27 % of reactor input) |        |        |                            |              |             |                |            |                        |
|       |          | Input to reactor             |          |      | :            | 5.39E+04   | 5.14E+04                                       | 1435   | 199    | 6.60                       | 146          | 55.7        | 0              | 462        | 215                    |

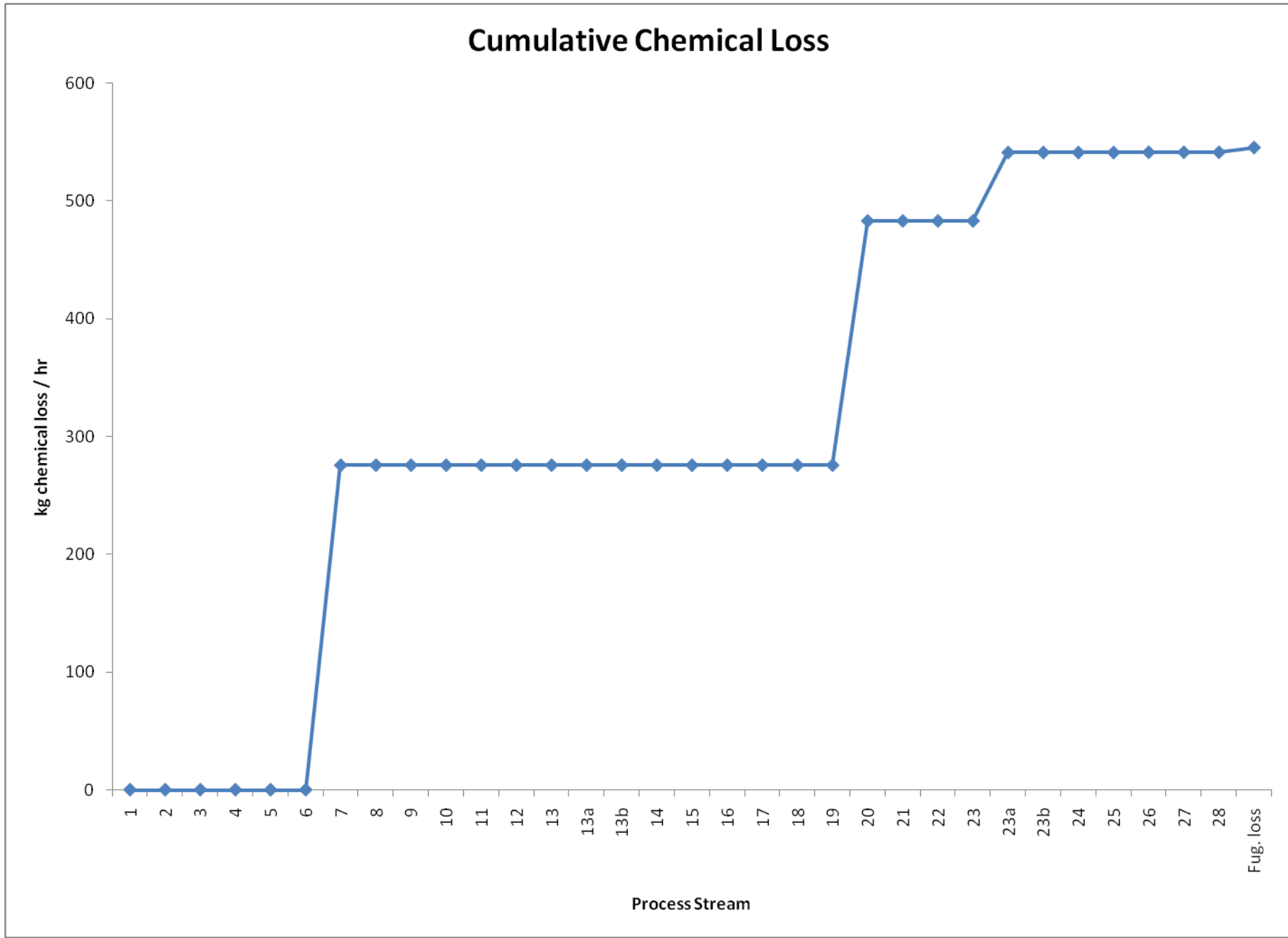
|                | Comments | Streams                    | Temp [C] | P     | Phase | Total Flow | Water    | PMIDA | Oxygen  | aminomethylphosphonic acid | Formaldehyde | Formic acid | Carbon dioxide | glyphosate | platinum on carbon 10% |
|----------------|----------|----------------------------|----------|-------|-------|------------|----------|-------|---------|----------------------------|--------------|-------------|----------------|------------|------------------------|
|                |          | R1 Reaction Coefficient 1  |          |       | :     |            |          | -1.00 | -0.500  |                            | 1.00         |             | 1.00           | 1.00       |                        |
|                |          | R1 Conversion 1 [kg/hr]    |          |       | :     | 0          |          | -1408 | -99.2   |                            | 186          |             | 273            | 1048       |                        |
|                |          | R1 Conversion 1 [kgmol/hr] |          |       | :     | 6.20       |          | -6.20 | -3.10   |                            | 6.20         |             | 6.20           | 6.20       |                        |
|                |          | R1 Reaction Coefficient 2  |          |       | :     |            |          |       | -0.500  |                            | -1.00        | 1.00        |                |            |                        |
|                |          | R1 Conversion 2 [kg/hr]    |          |       | :     |            |          |       | -19.8   |                            | -37.2        | 57.0        |                |            |                        |
|                |          | R1 Conversion 2 [kgmol/hr] |          |       | :     | 1.24       |          |       | -0.620  |                            | -1.24        | 1.24        |                |            |                        |
|                |          | R1 Reaction Coefficient 3  |          |       | :     |            |          |       | -0.500  | 1.00                       | 1.00         |             | 1.00           | -1.00      |                        |
|                |          | R1 Conversion 3 [kg/hr]    |          |       | :     | 0          |          |       | -0.992  | 6.88                       | 1.86         |             | 2.73           | -10.5      |                        |
|                |          | R1 Conversion 3 [kgmol/hr] |          |       | :     |            |          |       | -0.0310 | 0.0620                     | 0.0620       |             | 0.0620         | -0.0620    |                        |
|                |          | Flow out of reactor        |          |       | :     | 5.39E+04   | 5.14E+04 | 27.9  | 79.0    | 13.5                       | 297          | 113         | 276            | 1500       | 215                    |
|                |          | Primary product            |          |       | :     | glyphosate |          |       |         |                            |              |             |                |            |                        |
|                |          | Total conversion           |          |       | :     |            | 0        | 99.0  | 60.3    | NA                         | NA           | NA          | NA             | NA         | 0                      |
|                |          | Per pass conversion        |          |       | :     |            | 0        | 98.1  | 60.3    | NA                         | NA           | NA          | NA             | NA         | 0                      |
|                |          | Total yield from reactor   |          |       | :     |            |          | 99.0  | 81.8    |                            | NA           |             | NA             | NA         |                        |
| Waste          |          | 7                          | 90.0     | 3.50  | g     | -355       |          |       | -79.0   |                            |              |             | -276           |            |                        |
|                |          | 8                          | 90.0     | 3.50  | l     | 5.36E+04   | 5.14E+04 | 27.9  | 0       | 13.5                       | 297          | 113         | 0              | 1500       | 215                    |
|                |          | 9                          | 90.0     | 1.00  | s     | 427        | 213      |       |         |                            |              |             |                |            | 213                    |
| Input          |          | 10                         | 25.0     | 1.00  | s     | 2.00       |          |       |         |                            |              |             |                |            | 2.00                   |
|                |          | 11                         | 90.0     | 1.00  | s     | 429        | 213      | 0     | 0       | 0                          | 0            | 0           | 0              | 0          | 215                    |
|                |          | 12                         | 90.0     | 1.00  | l     | 5.31E+04   | 5.12E+04 | 27.9  | 0       | 13.5                       | 297          | 113         | 0              | 1500       | 2.00                   |
|                | 0.500    | 13                         | 90.0     | 1.00  | l     | 2.66E+04   | 2.56E+04 | 13.9  | 0       | 6.74                       | 149          | 56.4        | 0              | 750        | 1.00                   |
| Waste          |          | 13a                        | 35.0     | 0.100 | g     | -2475      | -2475    |       |         |                            |              |             |                |            |                        |
|                |          | 13b                        | 35.0     | 1.00  | l     | 2475       | 2475     |       |         |                            |              |             |                |            |                        |
|                |          | 14                         | 25.0     | 1.00  | l     | 2.41E+04   | 2.31E+04 | 13.9  | 0       | 6.74                       | 149          | 56.4        | 0              | 750        | 1.00                   |
|                |          | 15                         | 35.0     | 1.00  | l     | 2.35E+04   | 2.28E+04 | 13.8  | 0       | 6.66                       | 147          | 55.7        | 0              | 462        | 0                      |
| Display in PFD |          | 16                         | 25.0     | 1.00  | s     | 579        | 288      | 0.173 | 0       | 0.0839                     | 1.85         | 0.701       | 0              | 288        | 1.00                   |
| Display in PFD |          | 17                         | 90.0     | 1.00  | l     | 2.66E+04   | 2.56E+04 | 13.9  | 0       | 6.74                       | 149          | 56.4        | 0              | 750        | 1.00                   |
|                |          | Stream 23b:Recycle input   |          |       |       | 2.61E+04   | 2.56E+04 | 42.0  | 0       | 22.2                       | 1.00         | 1.00        | 0              | 455        | 0                      |

|              | Comments | Streams                                    | Temp [C] | P    | Phase | Total Flow | Water     | PMIDA | Oxygen | aminomethylphosphonic acid | Formaldehyde | Formic acid | Carbon dioxide | glyphosate | platinum on carbon 10% |
|--------------|----------|--|----------|------|-------|------------|-----------|-------|--------|----------------------------|--------------|-------------|----------------|------------|------------------------|
|              | 1001     | Stream 23b:Recycle calculated              |          |      |       | 2.61E+04   | 2.56E+04  | 43.3  | 0      | 22.5                       | 0.900        | 0.900       | 0              | 455        | 0                      |
|              |          | Stream 23b:Recycle residue                 |          |      |       | -0.0901    | 1.29      | -1.31 | 0      | -0.323                     | 0.100        | 0.1000      | 0              | 0.0500     | 0                      |
|              |          | 18   | 95.0     | 1.00 | l     | 5.27E+04   | 5.12E+04  | 55.9  | 0      | 28.9                       | 150          | 57.4        | 0              | 1205       | 1.00                   |
|              |          | 19   | 100      | 1.00 | g     | 2.30E+04   | 2.28E+04  |       |        |                            | 150          | 57.1        | 0              |            |                        |
| Waste        |          | 20   | 25.0     | 1.00 | l     | -2.30E+04  | -2.28E+04 | 0     | 0      | 0                          | -150         | -57.1       | 0              | 0          | 0                      |
|              |          | 21   | 100      | 1.00 | l     | 2.96E+04   | 2.83E+04  | 55.9  | 0      | 28.9                       | -0.848       | 0.299       | 0              | 1205       | 1.00                   |
|              |          | 22   | 99.0     | 1.00 | l     | 3.02E+04   | 2.86E+04  | 56.1  | 0      | 29.0                       | 1.000        | 1.00        | 0              | 1492       | 2.00                   |
|              |          | 23   | 100      | 1.00 | l     | 2.90E+04   | 2.84E+04  | 48.1  | 0      | 25.0                       | 1.000        | 1.00        | 0              | 506        | 0                      |
| Waste        | 0.100    | 23a  | 100      | 1.00 | l     | -2902      | -2843     | -4.81 | 0      | -2.50                      | -0.1000      | -0.100      | 0              | -50.6      | 0                      |
|              |          | 23b  | 100      | 1.00 | l     | 2.61E+04   | 2.56E+04  | 43.3  | 0      | 22.5                       | 0.900        | 0.900       | 0              | 455        | 0                      |
|              |          | 24   | 100      | 1.00 | s     | 1198       | 197       | 8.00  |        | 4.00                       |              |             |                | 987        | 2.00                   |
|              |          | 25   | 100      | 1.00 | g     | 198        | 197       | 0     | 0      | 0                          | 0            | 0           | 0              | 0.220      | 0                      |
| Waste        |          | 26   | 25.0     | 1.00 | l     | -198       | -197      |       |        |                            |              |             |                | -0.220     |                        |
|              |          | 27   | 100      | 1.00 | s     | 1001       | 0         | 8.00  | 0      | 4.00                       | 0            | 0           | 0              | 987        | 2.00                   |
| Main product |          | 28   | 25.0     | 1.00 | s     | -1001      | 0         | -8.00 | 0      | -4.00                      | 0            | 0           | 0              | -987       | -2.00                  |
|              |          | Product purity (%)                         |          |      | :     | 98.6       |           |       |        |                            |              |             |                |            |                        |
|              |          | Main product                               |          |      | :     | glyphosate |           |       |        |                            |              |             |                |            |                        |
|              |          | Overall Rxn coefficients                   |          |      | :     |            |           | -1.00 | -0.500 |                            | 1.00         |             | 1.00           | 1.00       |                        |
|              |          | Total yield of process (from reactant)     |          |      | :     |            |           | 93.2  | 46.9   |                            | NA           |             | NA             | NA         |                        |
| Waste        |          | Fugitive Losses (Total)                    |          |      | g     | -3.99      | 0         | 0     | 0      | 0                          | -1.49        | -1.13       | -1.38          | 0          | 0                      |
|              |          | Input Sum                                  |          |      | :     | 3.00E+04   | 2.84E+04  | 1422  | 199    | 0                          | 0            | 0           | 0              | 0          | 2.00                   |
|              |          | Fugitive Replacement of Reactants          |          |      | :     | 0          |           | 0     | 0      |                            |              |             |                |            |                        |
|              |          | Total Input (Input + Fugitive Replacement) |          |      | :     | 3.00E+04   | 2.84E+04  | 1422  | 199    | 0                          | 0            | 0           | 0              | 0          | 2.00                   |
|              |          | Product Sum                                |          |      | :     | 1001       | 0         | 8.00  | 0      | 4.00                       | 0            | 0           | 0              | 987        | 2.00                   |
|              |          | Main product flow                          |          |      | :     | 1001       | 0         | 8.00  | 0      | 4.00                       | 0            | 0           | 0              | 987        | 2.00                   |

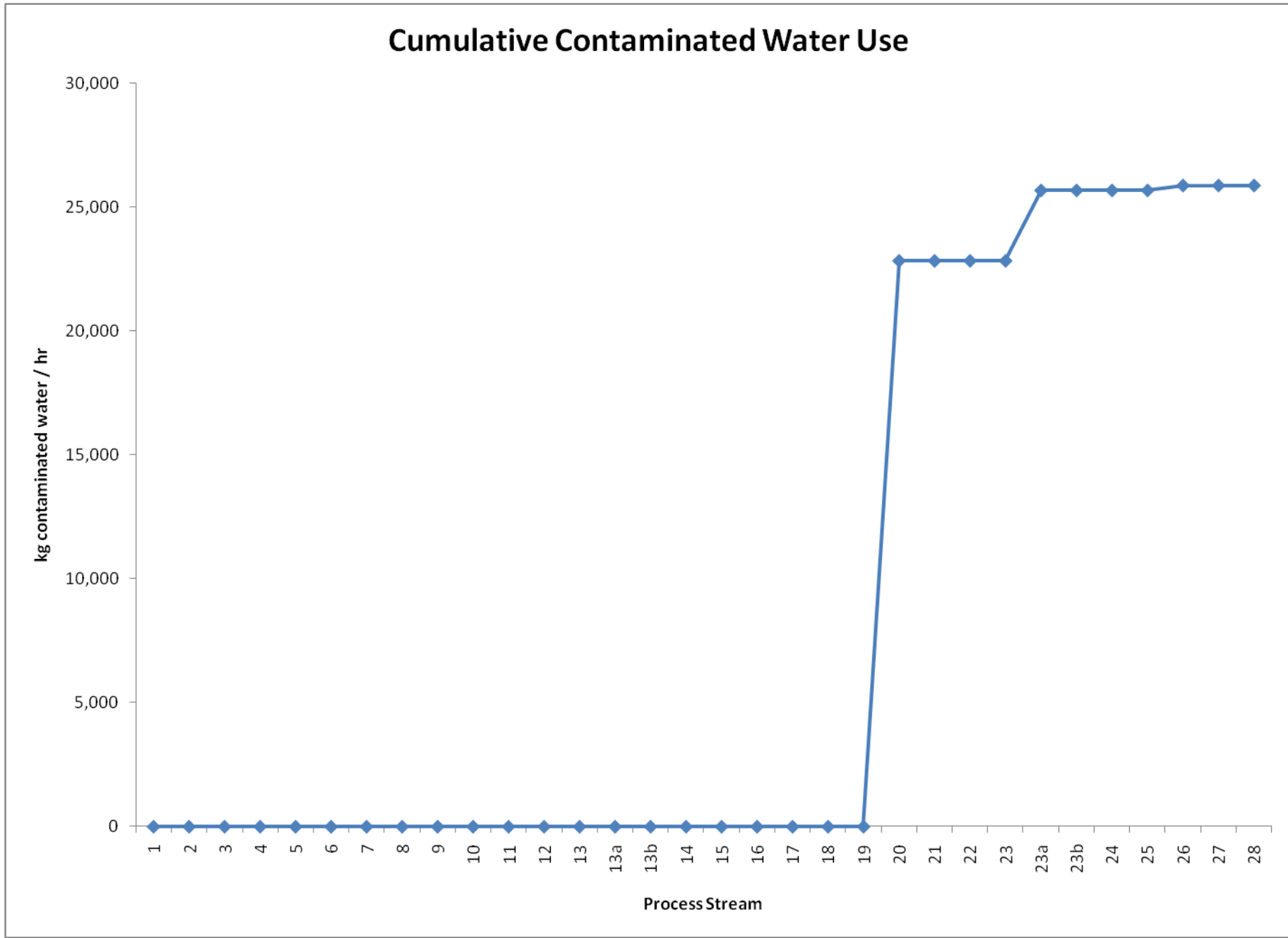
| Comments | Streams                                  | Temp [C] | P | Phase | Total Flow | Water | PMIDA | Oxygen | aminomethylphosphonic acid | Formaldehyde | Formic acid | Carbon dioxide | glyphosate | platinum on carbon 10% |
|----------|--|----------|---|-------|------------|-------|-------|--------|----------------------------|--------------|-------------|----------------|------------|------------------------|
|          | Net Input (in - out, omitting fugitives) |          |   | :     | 0.905      |       |       |        |                            |              |             |                |            |                        |

| Type        | Label | Temp, C | P, atm | Phase | Total flow | Steam     | Water     |
|-------------|-------|---------|--------|-------|------------|-----------|-----------|
| Input       | C1    | 20.0    | 1.00   |       | 5615       |           | 5615      |
| Cooling out | C2    | 50.0    | 1.00   |       | -5615      |           | -5615     |
| Input       | C3    | 20.0    | 1.00   |       | 4.04E+04   |           | 4.04E+04  |
| Cooling out | C4    | 50.0    | 1.00   |       | -4.04E+04  |           | -4.04E+04 |
| Input       | C5    | 20.0    | 1.00   |       | 4.88E+04   |           | 4.88E+04  |
| Cooling out | C6    | 50.0    | 1.00   |       | -4.88E+04  |           | -4.88E+04 |
| Input       | C7    | 20.0    | 1.00   |       | 406        |           | 406       |
| Cooling out | C8    | 50.0    | 1.00   |       | -406       |           | -406      |
| Input       | S1    | 207     | 1.00   |       | 8100       | 8100      |           |
| Steam out   | S2    | 207     | 1.00   |       | -8100      | -8100     |           |
| Input       | S3    | 207     | 1.00   |       | 3.20E+04   | 3.20E+04  |           |
| Steam out   | S4    | 207     | 1.00   |       | -3.20E+04  | -3.20E+04 |           |
| Input       | S5    | 207     | 1.00   |       | 261        | 261       |           |
| Steam out   | S6    | 207     | 1.00   |       | -261       | -261      |           |

# Graph of Cumulative Chemical Losses through Manufacturing Process

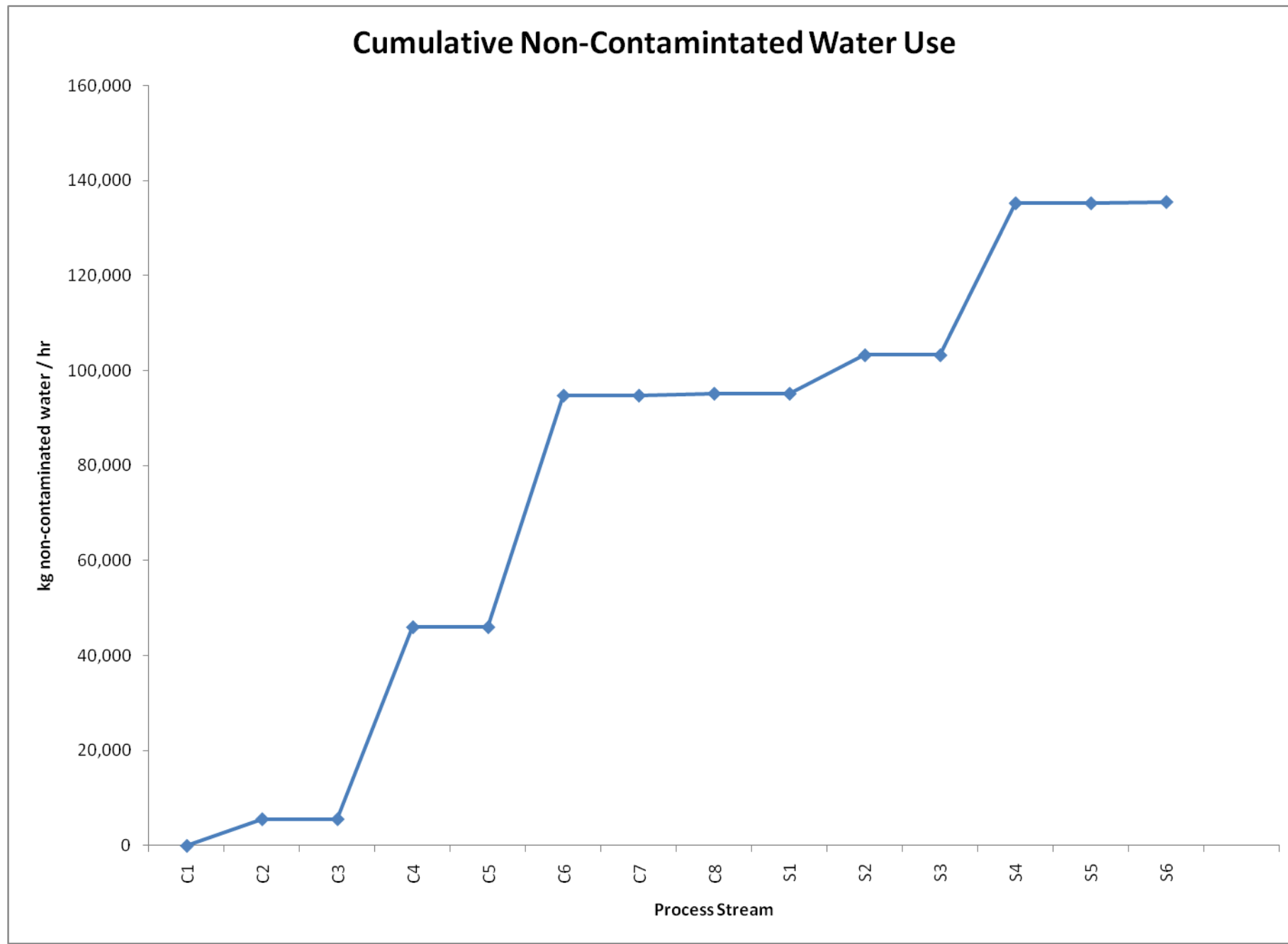


# Graph of Cumulative Contaminated Water Use / Emission through Manufacturing Process





# 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] |
| P1                     | Pump 1               | 3.76                                | 3.76                                     |  | E           | R1                             | Reactor 1   | -824        | -824                            | 90.0                              | 0.250               | -206             | -206  |
| Hx1                    | Heat exchanger 1     | 1.32E+04                            | 1.32E+04                                 | 90.0                                   | S           | Hx2                            | Heat exchanger 2                                    | -5969       | -6793                           | 35.0                              | 0                   | 0                | -206  |
| Cmp1                   | Compressor 1         | 30.8                                | 1.32E+04                                 |  | E           | Hx3                            | Heat exchanger 3                                    | 5.80E+04    | 6.48E+04                        | 100                               | 0.250               | 1.45E+04         | 1.47E+04                                    |
| MxE1                   | Mixer electricity 1  | 236                                 | 1.34E+04                                 |  | E           | Hx4                            | Heat exchanger 4                                    | -501        | 6.53E+04                        | 100                               | 0.250               | -125             | 1.48E+04                                    |
| Vac1                   | Vacuum electricity 1 | 27.2                                | 1.35E+04                                 |  | E           |                                |   |             |                                 |                                   |                     |                  |   |
| Evp2                   | Evaporator 2         | 5.20E+04                            | 6.55E+04                                 | 100                                    | S           |                                |   |             |                                 |                                   |                     |                  |   |
| Cnt1                   | Centrifuge 1         | 202                                 | 6.57E+04                                 |  | E           |                                |   |             |                                 |                                   |                     |                  |   |
| Dry1                   | Dryer 1              | 439                                 | 6.61E+04                                 | 100                                    | S           |                                |   |             |                                 |                                   |                     |                  |   |
|                        | Potential recovery   | -1.48E+04                           | 5.13E+04                                 |  |             |                                |   |             |                                 |                                   |                     |                  |   |
|                        | Net energy           |                                     | 5.13E+04                                 |  |             |                                | Potential recovery:                                 |             |                                 |                                   |                     |                  | -1.48E+04                                   |
|                        | Electricity          | 500                                 | E  | [MJ/hr]                                |             |                                |   |             |                                 |                                   |                     |                  |   |
|                        | DowTherm             | 0                                   | D  | [MJ/hr]                                |             |                                |   |             |                                 |                                   |                     |                  |   |
|                        | Heating steam        | 6.56E+04                            | S  | [MJ/hr]                                |             | Evap 1, adiabatic:             | Evap 1 is adiabatic, and energy should be near zero |             |                                 |                                   |                     |                  |   |
|                        | Direct fuel use      | 0                                   | F  | [MJ/hr]                                |             |                                |   |             |                                 |                                   |                     |                  |   |
|                        | Heating natural gas  | 0                                   | G  | [MJ/hr]                                |             |                                |   |             |                                 |                                   |                     |                  |   |
|                        | Diesel process       | 0                                   | Ds                                       | [MJ/hr]                                |             |                                |   |             |                                 |                                   |                     |                  |   |
|                        | Undefined            | 0                                   | U  | [MJ/hr]                                |             |                                |   |             |                                 |                                   |                     |                  |   |
|                        | Heating coal         | 0                                   | C  | [MJ/hr]                                |             |                                |   |             |                                 |                                   |                     |                  |   |
|                        | Energy input         | 6.61E+04                            |  | [MJ/hr]                                |             |                                |   |             |                                 |                                   |                     |                  |   |

|  |                         |               |  |         |  |  |  |  |  |  |  |  |  |
|--|-------------------------|---------------|--|---------|--|--|--|--|--|--|--|--|--|
|  | requirement             |               |  |         |  |  |  |  |  |  |  |  |  |
|  | Cooling water           | -<br>6.53E+04 |  | [MJ/hr] |  |  |  |  |  |  |  |  |  |
|  | Cooling refrigeration   |               |  | [MJ/hr] |  |  |  |  |  |  |  |  |  |
|  | Potential heat recovery | -<br>1.48E+04 |  | [MJ/hr] |  |  |  |  |  |  |  |  |  |
|  | Net energy              | 5.13E+04      |  | [MJ/hr] |  |  |  |  |  |  |  |  |  |

# Graph of Cumulative Energy Requirements

