# Production of dl-Methionine

## Background

Dl-methionine is an amino acid, which is used as a nutritional supplement. It is not synthesized in the human body. The goal of this project is to safely and efficiently design a grass roots facility that is capable of producing 1,000 metric tons of dl-methionine per year from acrolein.

## Process Description

Figure 1 shows a BFD for the overall batch process. The feed stream, consisting of acrolein, methyl mercaptan, methanol, hydrocyanic acid, and ammonium carbonate must be made up off site. This feed stream, Stream 1, is fed to an isothermal batch reactor, R-101. The reaction takes place at 80°C and 405 kPa for 1.5 hours. The methanol in the reactor acts as a reaction medium and does not take part in the reaction. After the reaction is complete, the acrolein, methyl mercaptan, hydrocyanic acid, water, and methanol are vaporized along with the products of ammonium carbonate decomposition, ammonia, carbon dioxide, and water. The products are then sent, at atmospheric pressure, to a partial condenser, E-102, where the gases are vented, Stream 4, and sent to waste treatment, and the methanol, ammonia, and water, Stream 5, are sent to a recovery reactor, R-102. A 50 wt.% NaOH solution, Stream 3, is added, and it is then heated to 160°C under pressure for 1.5 hours to form the salt of dl-methionine. After completion of the reaction, the mixture is heated, and the ammonia and carbon dioxide that are formed during the reaction are vented in Stream 7 and sent to waste treatment. The dl-methionine in solution is sent to V-102 and cooled to 80°C for 0.5

hours. The batch from the cooling vessel is then sent, via Stream 8, to a decolorization vessel, V-201. The decolorization vessel removes any organic impurities such as residual hydantoin from the dl-salt. A filter after the charcoal decolorization vessel, F-201, removes any carbon particles washed out of the unit. The mixture is then sent to a neutralization reactor, R-201, where the dl-salt is neutralized to dl-methionine and precipitated. A high concentration of HCl, Stream 10, is added to reduce the pH below 2.28, allowing for complete precipitation of the dl-methionine but keeping NaCl and water in solution. The dl-methionine molecule with the attached HCl molecule, Stream 11, is then filtered in F-202 from the hydrochloric acid, water, and sodium chloride and sent to an evaporator, E-201, where the HCl is evaporated to purify the dl-methionine.

**Necessary Information and Simulation Hints**

This process assumes a 90% conversion of the acrolein. The following reaction is the initial reaction for the production of dl-methionine, which leads to the formation of the hydantoin ring in R-101:

$$\underset{\text{acrolein}}{C_3H_4O} + HCN + \underset{\substack{\text{methyl}\\\text{mercaptan}}}{CH_3SH} + \frac{5}{2}(NH_4{}^+)_2CO_3 \rightarrow \underset{\text{hydantoin}}{C_6H_{10}N_2SO_2} + \frac{3}{2}H_2CO_3 + 4NH_3 + 2H_2O$$

Addition of 50 wt.% sodium hydroxide in R-102 leads to the formation of dl-salt which occurs by the following reaction:

$$\underset{\text{hydantoin}}{C_6H_{10}N_2SO_2} + H_2O + NaOH \rightarrow \underset{\text{dl - salt}}{C_5H_{10}NSO_2Na} + NH_3 + CO_2$$

Addition of HCl in R-201 allows for complete precipitation of the dl-methionine with the following reactions:

$$\underset{\text{dl - salt}}{C_5H_{10}NSO_2Na} + 2HCl \rightarrow \underset{\text{dl - methionine}}{C_4H_{12}SNO_2} + NaCl + Cl^-$$

$$NaOH + HCl \rightarrow NaCl + H_2O$$

**Equipment Summary**

| | |
|---|---|
| E-101 | Reactor Cooler |
| E-102 | Partial Condenser |
| E-103 | Reactor Heater |
| E-104 | Heat Exchanger |
| E-201 | Heat Exchanger |
| F-101 | Carbon Filter |
| F-101 | Waste Filter |
| P-101A/B | Heat Exchanger Pump |
| P-102A/B | Partial Condenser Pump |
| P-103A/B | Heat Exchanger Pump |
| P-104A/B | Heat Exchanger Pump |
| R-101 | Isothermal Batch Reactor |
| R-102 | Isothermal Batch Reactor |
| R-101 | Neutralization Reactor |
| V-101 | Evaporation Vessel |
| V-102 | Cooling Vessel |
| V-201 | Decolorization Vessel |
| V-202 | Evaporation Vessel |

**Stream Tables**

| Stream | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| Temperature (°C) | 25.0 | 80.0 | 80.0 | 30.0 | 30.0 | 160.0 | 80.0 | 80.0 |
| Pressure (kPa) | 405.0 | 101.0 | 405.0 | 101.0 | 101.0 | 101.0 | 405.0 | 101.0 |
| Total Flow (kmol/hr) | 63.1 | 71.4 | 12.0 | 8.5 | 64.3 | 3.7 | 15.5 | 6.8 |
| Component Flows (kmol/hr) | | | | | | | | |
| Acrolein | 2.07 | 0.21 | -- | 0.21 | -- | -- | -- | -- |
| Methyl Mercaptan | 2.07 | 0.21 | -- | 0.21 | -- | -- | -- | -- |
| Hydrogen Cyanide | 2.07 | 0.21 | -- | 0.21 | -- | -- | -- | -- |
| Ammonium Carbonate | 5.18 | 0.52 | -- | -- | -- | -- | -- | -- |
| Methanol | 51.8 | 51.8 | -- | 0.62 | 51.2 | -- | -- | -- |
| Hydantoin | -- | 1.68 | -- | -- | 1.68 | -- | 1.68 | 1.68 |
| Water | -- | 6.52 | 8.28 | 0.56 | 6.48 | -- | 6.42 | 3.21 |
| Carbon Dioxide | -- | 2.79 | -- | 3.31 | -- | 1.86 | 1.86 | -- |
| Ammonia | -- | 7.45 | -- | 3.42 | 4.55 | 1.86 | 1.86 | -- |
| Dl-salt | -- | -- | -- | -- | -- | -- | 1.86 | 0.93 |
| Dl-methionine | -- | -- | -- | -- | -- | -- | -- | -- |
| Hydrochloric Acid | -- | -- | -- | -- | -- | -- | -- | -- |
| Sodium Chloride | -- | -- | -- | -- | -- | -- | -- | -- |
| Sodium Hydroxide | -- | -- | 3.73 | -- | -- | 1.87 | -- | 0.93 |

| Stream | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|
| Temperature (°C) | 80.0 | 25.0 | 80.0 | 80.0 | 80.0 | 80.0 | 80.0 |
| Pressure (kPa) | 101.0 | 101.0 | 101.0 | 101.0 | 101.0 | 101.0 | 101.0 |
| Total Flow (kmol/hr) | 5.1 | 9.5 | 14.6 | 12.7 | 1.9 | 0.9 | 0.9 |
| Component Flows (kmol/hr) | | | | | | | |
| Acrolein | -- | -- | -- | -- | -- | -- | -- |
| Methyl Mercaptan | -- | -- | -- | -- | -- | -- | -- |
| Hydrogen Cyanide | -- | -- | -- | -- | -- | -- | -- |
| Ammonium Carbonate | -- | -- | -- | -- | -- | -- | -- |
| Methanol | -- | -- | -- | -- | -- | -- | -- |
| Hydantoin | -- | -- | -- | -- | -- | -- | -- |
| Water | 3.21 | 6.72 | 10.9 | 10.9 | -- | -- | -- |
| Carbon Dioxide | -- | -- | -- | -- | -- | -- | -- |
| Ammonia | -- | -- | -- | -- | -- | -- | -- |
| Dl-salt | 0.93 | -- | -- | -- | -- | -- | -- |
| Dl-methionine | -- | -- | 0.93 | -- | 0.93 | 0.93 | -- |
| Hydrochloric Acid | -- | 2.8 | 0.93 | -- | 0.93 | -- | 0.93 |
| Sodium Chloride | -- | -- | 1.86 | 1.86 | -- | -- | -- |
| Sodium Hydroxide | 0.93 | -- | -- | -- | -- | -- | -- |

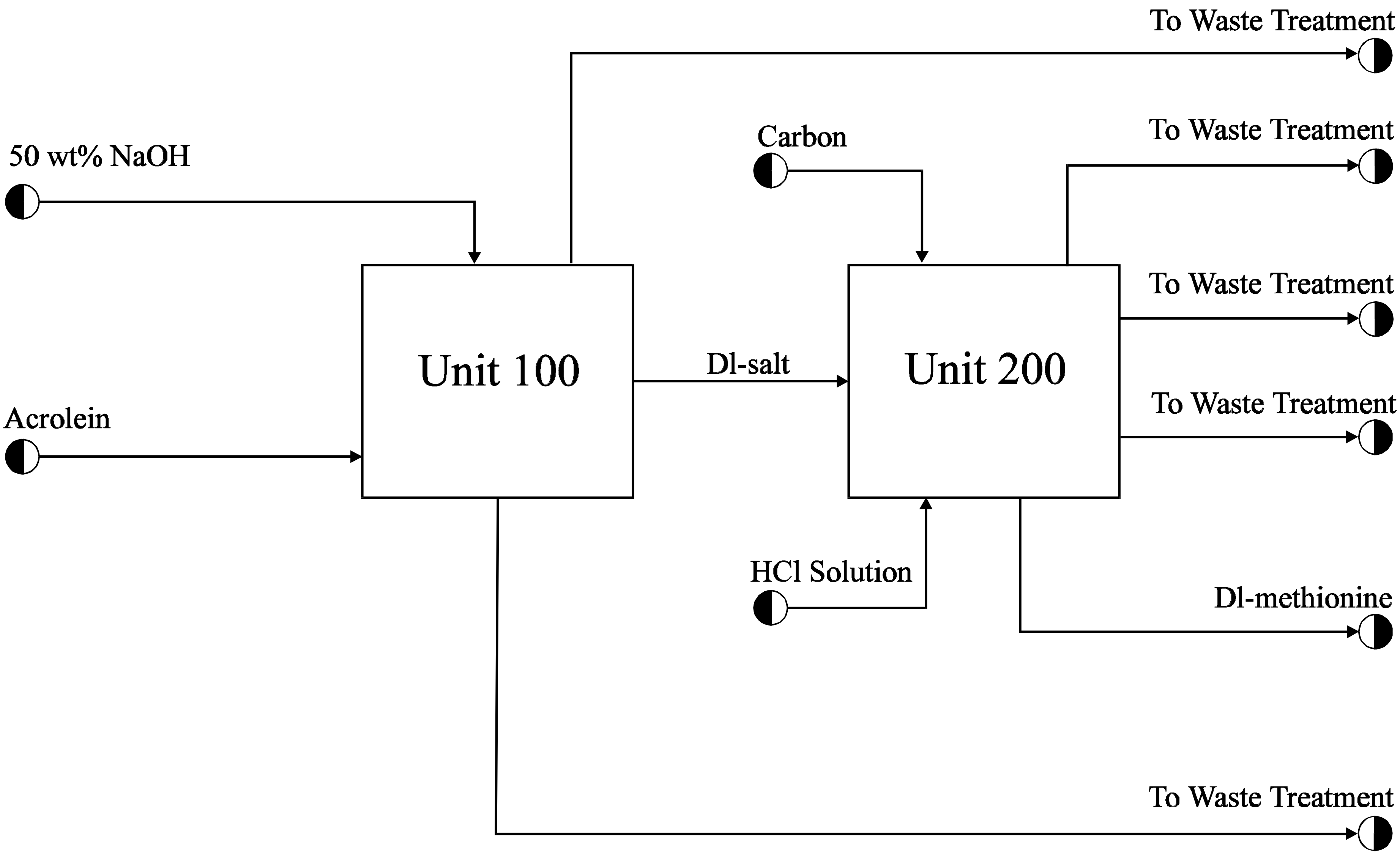


Figure 1: BFD for Overall Process

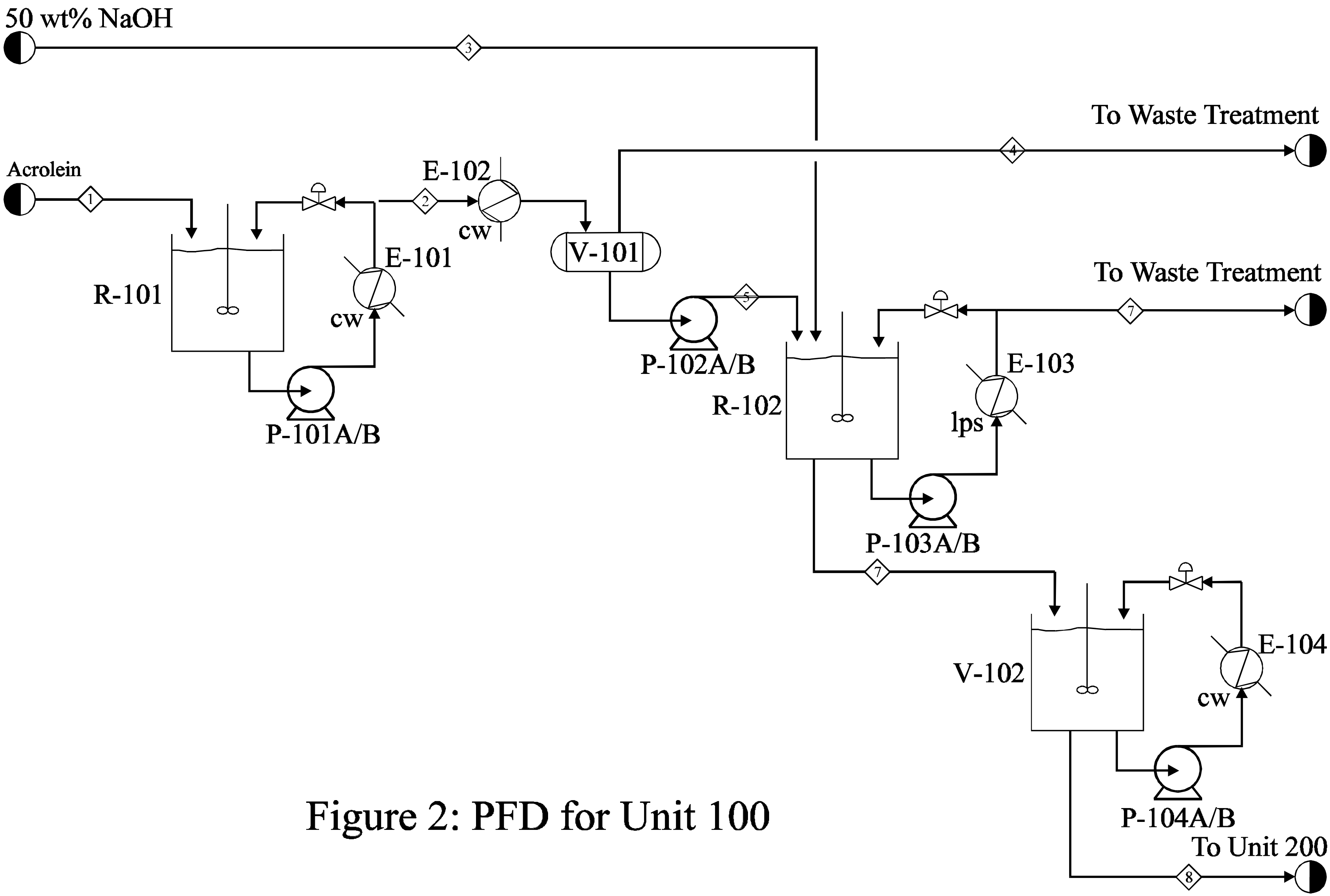


Figure 2: PFD for Unit 100

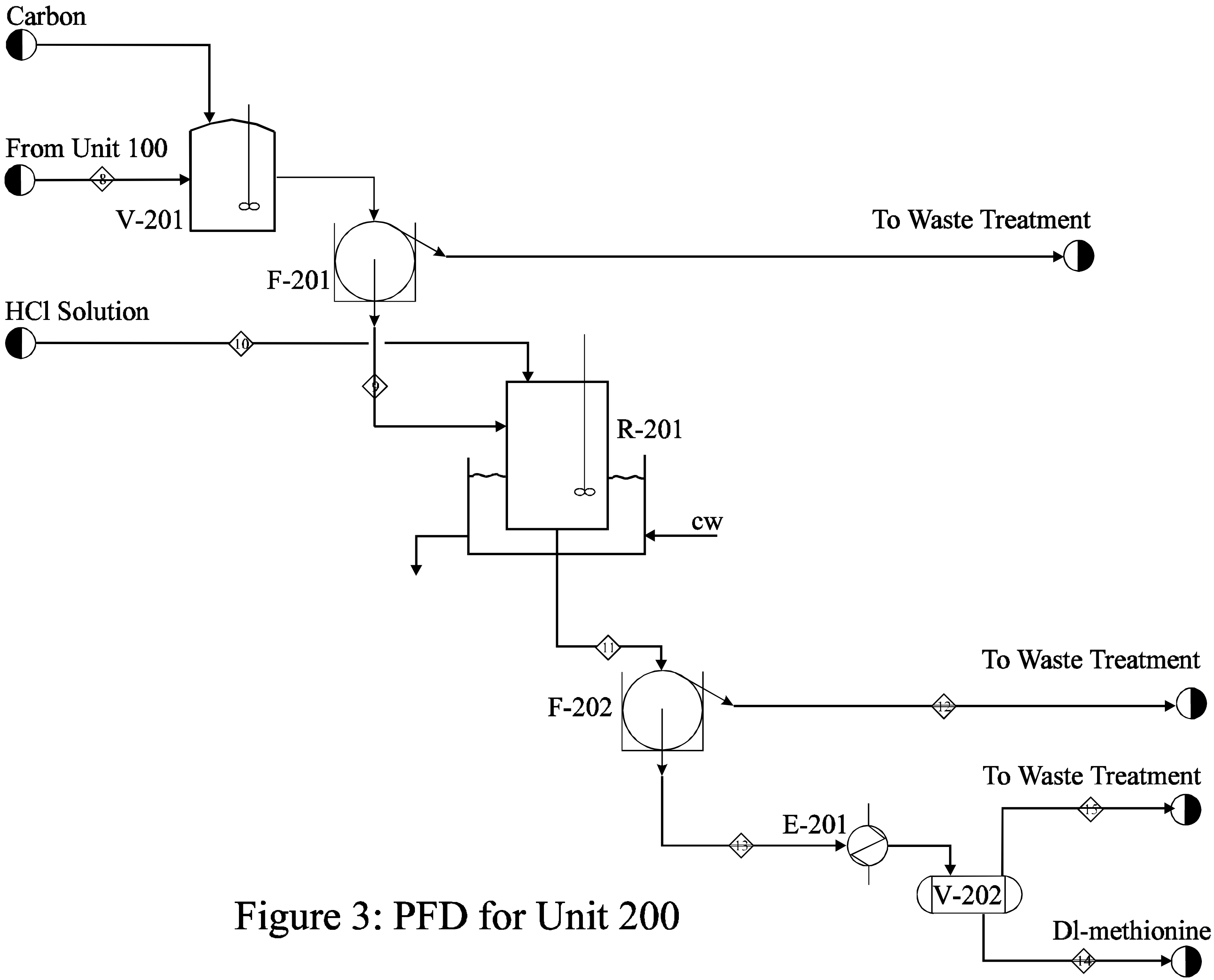


Figure 3: PFD for Unit 200