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SUBJECT: Final Design Report Submission- Oxalic Acid Production (CHBE 220 and CHBE 201)

Dear Dr. Verrett and Mr. Schoen:

In response to your request for a design report as the final written assignment for CHBE 220 and CHBE 201, we have prepared the enclosed the report titled Oxalic Acid Production.

The design for producing oxalic acid by oxidizing glucose with nitric acid is outlined. Oxalic acid produced is separated from unused reactants, nitric oxide and water using a crystallizer and centrifuge. Energy consumption for cooling the reactor outlet stream is calculated. The process flow diagram, stream table and control loops for the production process are presented.

If you require further information, please call us at (604) 822-2211 or email at

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Respectfully,

Team 14
OXALIC ACID
CORPORATION

Team 14, Alex Cho, Harry Pandher, Jordyn Knock, Vivian Su

Enclosure: Design report on oxalic acid production

Oxalic Acid Production

Submitted to: Prof. Jonathan Verrett & Prof. Mike Schoen

Submitted by: Alex Cho, Harry Pandher, Jordyn Knock, Vivian Su

Courses: CHBE 220 & CHBE 201

Date: December 9, 2024

Executive Summary

A client in Weifang city in Shandong, China wants to produce 50,000 tonnes of oxalic acid annually with a purity of 99.9%. China is the world's leading oxalic acid producer; oxalic acid is used as a cleaning agent and reducing agent. The global market for oxalic acid is estimated to be 1.57 billion and expected to increase annually. [1] The gross economic potential for this process is estimated to be \$7.4 million US dollars annually.

Oxidation of carbohydrates is the recommended process because it does not require the use of high pressurized and high temperature equipment. Oxidation of carbohydrates produces oxalic acid with a theoretical yield of 64%. Nitric acid and glucose react and produce nitric oxide, water and crude oxalic acid, which is cooled, separated and purified. Constant airflow into the reactor removes the gaseous nitric oxide. Excess nitric acid is recycled back to the reactor.

The liquid product stream contains oxalic acid, water, and unreacted nitric acid. The unreacted reactants are separated and recycled back into the reactor. Oxalic acid solution is cooled to crystallize the oxalic acid. The mixture is centrifuged to separate the oxalic acid crystals from the liquid solution. Oxalic acid is further purified to attain a purity of greater than 99%.

Energy transfer takes place before the output stream from the reactor enters the crystallizer. The outlet stream is cooled with cooling water in a heat exchanger, which decreases its temperature from 70°C to 50°C. This cooling separates oxalic acid from the crude slurry.

The total cooling utility required for this stream is 0.562 GJ/hr. The cost of cooling water is \$0.212/hr or \$1700/yr assuming 8,000 hours of operation. The amount of cooling water required for this process is 26.5 tonnes/hr.

The control strategy focuses on controlling the temperature and liquid level of the reactor. Temperature control ensures the reactor is not overheated or over pressurized. The flow controller ensures the liquid in the reactor does not overflow.

Recommendation

Oxidizing carbohydrates is recommended for producing 50,000 tonnes annually of oxalic acid for the plant located in Weifang, China. The process poses minimal environmental risks, the nitric oxide by-products are recovered and recycled in the process making it more sustainable. The simplicity of the one-step process, mild reaction conditions, and profitability are favourable.

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List of Abbreviations

	Definition
PFD	Process Flow Diagram
$C_6H_{12}O_6$	Glucose
$(COOH)_2$	Oxalic Acid
H_2O	Water
HNO_3	Nitric Acid
NO	Nitric Oxide

1.0 Introduction for Design Report on Producing Oxalic Acid

1.1 Background

A project for producing oxalic acid is proposed to a client at a site near Weifang city in Shandong, China. Geographical conditions, synthesis pathway, and economic potential of oxalic acid manufacturing are discussed, and an input/output diagram and a table of common compound properties and prices are provided. Sample calculations are in Appendix A.

1.2 Purpose

Our client wants to produce 50,000 tonnes of 99% purity oxalic acid dihydrate (see Figure 1) annually at a chemical complex in Weifang city in Shandong, China. The temperature at the site varies from -7 °C in the winter to 32 °C in the summer and is rarely below -12 °C or above 37 °C [2].

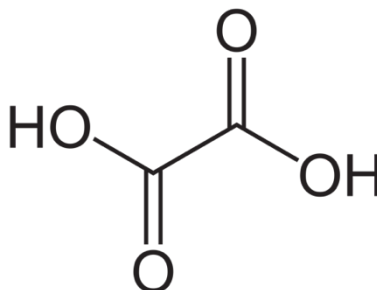


Figure 1: Structure of Oxalic Acid [3]

1.3 Significance

Oxalic acid is used to isolate rare-earth elements, bleach textiles, tan leather and polish marble [4]. Notably, its use in isolating rare-Earth elements is critical in clean energy technologies and gives this product potential for growth. China dominates oxalic acid production, generating approximately 100,000 tons per year [3]. Oxalic acid is not flammable below 400°C. It is toxic to fish and bacteria [4]. One method for producing oxalic acid (COOH)₂ is by oxidizing glucose (C₆H₁₂O₆) with nitric acid in a one-step process,

which is shown in reaction (1) [5]. The oxidation occurs in the presence of vanadium pentoxide and iron (III) salts. [5] Molecular weights and prices for these compounds are shown in Table 1.



The gross economic potential for the process is estimated to be \$7.4 million USD based on the prices shown in Table 1 and the input output flows. The calculations are shown in Figure A.2.3 in Appendix A.2.

Table 1: Properties and prices for relevant compounds in oxalic acid manufacturing

Name	Formula	Molecular Weight (g/mol)	Price (\$USD/tonne)
Glucose	$\text{C}_6\text{H}_{12}\text{O}_6$	180.16	576.00 [6]
Nitric Acid	HNO_3	63.01	305.00 [7]
Water	H_2O	18.02	0.00
Oxalic acid	$(\text{COOH})_2$	90.03	779.00 [8]

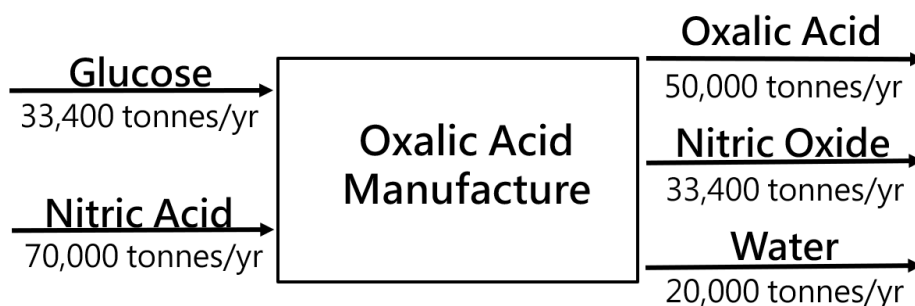


Figure 2: Input-output diagram for the reactor

1.4 Overview

Section 2 describes three reaction pathways for producing oxalic acid and the reasons for recommending oxidizing carbohydrates. Section 3 describes the separation process and the product stream flowrate. Section 4 describes the energy transfer for cooling the product stream and its utilities and cost estimates. Section 5 describes the overall process. Section 6 describes the control loops for the reactor.

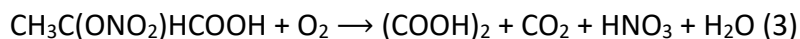
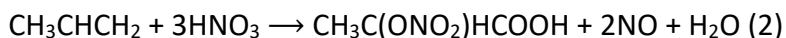
2.0 REACTION PATHWAYS

2.1 Introduction

Three reaction pathways for producing oxalic acid are described in terms of their yield, cost, and process. The oxidation of carbohydrates is recommended. Oxidation of propene, ethylene glycol, and carbohydrates are outlined.

2.2 Reaction Pathway 1: Oxidizing Propene

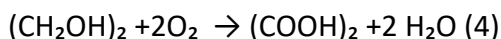
Oxidizing propene is a two-step process. Propene is reacted with nitric acid at a temperature between 10-40°C, shown in equation (2). The intermediates are reacted with oxygen at 45-100°C in the presence of a catalyst (salts or compounds containing Fe, Al, Cr, Sn, Bi, or I), shown in equation (3). Oxalic acid is formed, separated by crystallization, and filtered. [5]



Oxidizing propene is not economically favorable. The gross economic potential is estimated at −\$12.9 million USD based on the prices shown in Table A.1.1 in Appendix A.1 and calculations shown in Figure A.2.1 in Appendix A.2.

2.3 Reaction Pathway 2: Oxidizing Ethylene Glycol

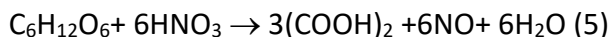
Oxidizing ethylene glycol with nitric acid is a one-step process that gives a high yield as shown in equation (4). An oxidizing mixture of 30-40% sulfuric acid and 20-25% nitric acid is mixed with ethylene glycol, in the presence of pentoxide and iron (III) salts at 50-70°C under atmospheric pressure. CO₂ is the only side product. After cooling and recrystallization, oxalic acid dihydrate with >99% purity is obtained. Nitric acid is almost entirely recovered during the process. [5]



The gross economic potential is estimated at \$8.1 million USD based on the prices in Table A.1.2 in Appendix A.1 and calculations shown in Figure A.2.2 in Appendix A.2.

2.4 Reaction pathway 3: Oxidizing Carbohydrates

Oxidizing carbohydrates such as glucose, sucrose, starch, dextrin, and cellulose with nitric acid produces oxalic acid [9]. In the case of glucose, the process involves a single-step reaction conducted at approximately 70°C [5]. The oxidation of glucose is shown in reaction (5).



Nitric acid (65%) is added slowly to the glucose in the reactor and stirred vigorously to make crude oxalic acid. 50% sulfuric acid, vanadium pentoxide and iron (III) sulfate are used as catalysts in the reactor to increase reaction efficiency and produce higher yields of oxalic acid. Air is blown into the reactor to remove excess nitric oxide and keep the reactor cool. The nitric oxide gas produced is absorbed, oxidized, and recycled. 65% of the theoretical yield is obtained [5].

The gross economic potential of this process is \$7.4 million USD based on the prices in Table A.1.3 in Appendix A.1 and the cost calculations in Figure A.2.3 Appendix A.2.

2.5 Recommended pathway

Oxidizing carbohydrates is recommended for the reaction pathway because of its profitability, the simplicity of the one-step process, and the mild reaction conditions. The nitric oxide byproduct is recycled, which makes this reaction pathway economical and environmental.

3.0 Separation Technique

3.1 Introduction

A separation strategy for the manufacturing of oxalic acid is described. A material balance for the flow of materials entering the separation unit is provided based on the reaction and anticipated product flow rate.

3.2 Reaction pathway

The oxidation of carbohydrates method is used to produce oxalic acid. The one-step reaction is shown below (1):



65% nitric acid (HNO_3) and glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) react with 50% sulfuric acid (H_2SO_4), vanadium pentoxide (V_2O_5) and iron (III) sulfate ($\text{Fe}_2(\text{SO}_4)_3$) catalysts at 70°C . The reaction is exothermic, so air is blown into the reactor to cool the reactor and remove the nitric oxide (NO) gas. The nitric oxide is absorbed, oxidized, and recycled. The product stream is an aqueous solution of crude oxalic acid and unreacted reactants. The unreacted glucose concentration is negligible because it is the limiting reagent. The unreacted nitric acid concentration is not negligible. [5]

3.3 Separation strategy

The crude oxalic acid is crystallized and centrifuged. It is purified by dissolving in hot water, filtering in a grease separator, recrystallizing, centrifuging, and drying. This separation process obtains 65% of the theoretical yield. [5]

Chemical plants commonly operate 8,000 hours annually. Applying this operational capacity, the flow of oxalic acid is 6.25 tonnes/hr based on the production of 50,000 tonnes annually. The mass balance based on this flow rate in the reactor results in the values shown in Appendix B.

Some relevant physical properties for each compound in the separation process are shown below in Table 2.

Table 2: Relevant properties of compounds in the separation process

Compound	Formula	Melting Point (°C)	Boiling point (°C)	Density (kg/l)
Nitric Acid	HNO ₃	-42 [10]	83 [10]	1.51 [10]
Water	H ₂ O	0	100	1
Oxalic acid	(COOH) ₂	187 [11]	365.1 [11]	1.90 [11]

3.4 Crystallization

Nitric acid and water exit the reactor at a temperature between 65-70 °C.

Separation guidelines recommend crystallizing the oxalic acid to separate it from the liquid solution. [12] Reactor effluent containing crude oxalic acid, water, and nitric acid is cooled to 50 °C to crystallize the oxalic acid [13].

3.5 Centrifugation

After crystallization, the mixture is centrifuged. Centrifugation separates dense oxalic acid crystals from the less dense liquid solution.

Oxalic acid is then further purified. This sequence—first crystallization, then centrifugation—ensures that the oxalic acid is isolated effectively, creating a final product with a purity greater than 99%. [5]

4.0 Energy Balance

4.1 Introduction

Energy transfer in oxalic production downstream of the reactor, before the crystallizer, is outlined. The best utility to cool the product stream composed of nitric acid (HNO_3), water (H_2O) and oxalic acid (COOH)₂ is cooling water. Values for energy exchanged for cooling, total cost and amount of utility are outlined.

4.2 Energy transfer: cooling the stream before separation

Energy transfer occurs on the stream between the reactor and the crystallizer. The stream exiting the reactor is cooled from 70°C to 50°C with cooling water [13]. Cooling the solution decreases the solubility of oxalic acid, and forms crystals. The flow rate of the compounds to the crystallizer are shown in Table 3 and the calculation are in Appendix C.

Table 3: Flow rate of compounds to the crystallizer

Compound	Formula	Molecular Weight (g/mol)	Flow to crystallizer (tonnes/hr)	Flow to crystallizer (tonmol/hr)
Nitric Acid	HNO_3	63.01	8.748	0.058
Water	H_2O	18.02	2.502	0.1388
Oxalic acid	$(\text{COOH})_2$	90.03	6.25	0.0689

4.3 Utility stream, heating capacities and operating costs

Cooling water is the best utility to cool the process stream. The water enters at 20°C and leaves at 25°C. The temperature difference between the process stream and the cooling water is more than 10°C, providing a sufficient driving force for energy transfer.

Heat capacities for components are displayed in Table 4. These values reflect heat capacities at 298K for nitric acid and water and at 463K for oxalic acid. Heat capacity values corresponding to the temperature of nitric acid and oxalic are not found. Heat

capacity for water is kept constant because of the low temperature change. Calculations for amount of utility required for cooling is presented in Appendix C.

The total cooling utility required for this stream is 0.562 GJ/hr (Appendix C.2). The cost of cooling water is \$0.212/hr or \$1700/yr assuming 8,000 hours of operation (Appendix C.3). The amount of cooling water required for this process is 26.5 tonnes/hr (Appendix C.3).

Table 4: Heat capacities required to calculate utility cost

Compound	Formula	Heat Capacity (J/mol*K)
Nitric Acid	HNO ₃	110.68 at 298K [14]
Water	H ₂ O	76.39 at 298K [14]
Oxalic acid	(COOH) ₂	159.61 at 463K [14]

5.0 PROCESS DESCRIPTION AND FLOW DIAGRAM (PFD)

5.1 Introduction

Oxidizing carbohydrates is recommended for producing oxalic acid ((COOH)₂). Appendix D shows the PFD with the reactor (R-100), crystallizer (V-100), and centrifuge (C-100). The process flow diagram (PFD) and stream table (Appendix D.1) provide key information for three major process steps: oxidizing glucose (C₆H₁₂O₆) to produce (COOH)₂ and water (H₂O), crystallizing (COOH)₂, and centrifuging the mixture to separate the (COOH)₂ solids from the liquid.

5.2 Oxidizing glucose to produce oxalic acid (R-100)

A solution of 65% nitric acid (HNO₃) is slowly added to glucose (C₆H₁₂O₆) in R-100 and stirred vigorously to make crude (COOH)₂. A solution of 50% sulfuric acid, vanadium pentoxide and iron (III) sulfate are used as catalysts in R-100 to increase the reaction efficiency and produce more (COOH)₂ [5]. The reaction occurs at 70°C and is maintained by a stream of cooled air that blows into R-100. Liquid H₂O and aqueous (COOH)₂ are produced. Excess liquid HNO₃ exits R-100 and is recycled.

5.3 Crystallizing crude oxalic acid (V-100)

H₂O, (COOH)₂ and HNO₃ are cooled to 50°C with cooling water (CW) in E-100 and further cooled within the crystallizer (V-100). 50°C is the starting point for crystallizing (COOH)₂ [15]. Cooling the slurry decreases the solubility of (COOH)₂ and it forms solid crystals [15]. Solid (COOH)₂ crystals are easier to isolate with centrifuging.

5.4 Centrifuging oxalic acid crystals (C-100)

H₂O, HNO₃, and (COOH)₂ crystals enter the centrifuge (C-100). The density of (COOH)₂ crystals is 1.9 g/mL [16] while the densities of H₂O and HNO₃ are 1 g/mL and 1.5 g/mL [17], respectively. The difference in density separates the (COOH)₂ crystals from the liquid as it is centrifuged, and they are recycled back into R-100. The (COOH)₂ crystals enter stream 6 for further separation.

6.0 CONTROL STRATEGY

6.1 Introduction

Control strategies for reactor (R-100) in the oxalic acid manufacturing process are described. The control strategies manipulate the level and temperature in the reactor. Level control ensures R-100 does not exceed liquid capacity and temperature control ensures vapour-liquid equilibrium is maintained and nitric oxide is separated.

6.2 Unit controlling level

Glucose and nitric acid produce nitric oxide vapour, liquid oxalic acid and water in R-100. The liquid level transmitter (LT-100) in R-101 sends a signal to a liquid level controller (LC-100) which opens or closes the control valve (CV-100). CV-100 is opened if the liquid level in R-100 is too high, and it flows out of R-100 into the crystallizer. CV-100 is closed if the liquid in the reactor is too low and restores the level. Refer to Appendix E for details.

6.3 Unit controlling temperature

Nitric oxide vapour is produced and heats R-100. The temperature in the column is measured at the top of the column with a temperature transmitter (TT-101). It relays a signal to a temperature controller (TC-101) which opens or closes a control valve (CV-101). CV-101 controls the flow of nitric oxide vapour exiting R-100. CV-101 opens if the temperature is too high in the column to release the nitric oxide. CV-101 closes if the temperature in the column is too low, to avoid slowing down the reaction. Refer to Appendix E for details.

The reactor's level and temperature are controlled by the two distinct control loops described.

7.0 Findings and Recommendations

This report outlines the process to produce 50,000 tonnes of oxalic acid annually in a plant located in Weifang, China. Our team aims to capitalize on the growing demand for oxalic acid as an environmentally friendly solution to commercial cleaning.

We are recommending the oxidation of carbohydrates for oxalic acid production. This pathway has a favorable economic outlook and low environmental impact. It requires no high pressurized and high temperature equipment. To minimize costs our team chose to oxidize glucose as the preferred carbohydrate.

There are two control loops in R-100: one overseeing the reactor's temperature, and the other managing the liquid level in the reactor.

Our findings are

- Carbohydrates are oxidized with nitric acid while air removes the formed nitric oxide gas.
- Produced nitric oxide gas is absorbed and kept from being released into the atmosphere.
- Two separation units operate in parallel – crystallization and centrifugation – to separate oxalic acid from crude slurry.
- The separation strategy is repeated, and the product is purified to obtain oxalic acid with a >99% purity.
- Cooling water cools the product stream leaving the reactor.
- Nitric acid is recycled back into the reactor.

Our recommendations

- This process can be modified to oxidize the most available/cost effective carbohydrate such as agricultural corn waste.
- Recycle the cooling water utility to lower cost.

Additional information can be found in the appendices.

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Appendices

Appendix A: Economics and input-output diagram calculations

Appendix A.1: Prices of compounds for all reaction pathways

Table A.1.1: Common properties for compounds in oxidizing propene

Name	Formula	Molecular Weight (g/mol)	Price (\$USD/tonne)
Propene	$\text{CH}_3\text{CH}=\text{CH}_2$	42.081	865.00 [18]
Nitric Acid	HNO_3	63.01	305.00 [7]
Oxygen	O_2	31.99	335.00 [19]
Oxalic acid	$(\text{COOH})_2$	90.03	779.00 [8]
Carbon Dioxide	CO_2	44.01	256.00 [20]
Nitric oxide	NO	30.01	270.00 [7]

Table A.1.2: Common properties for compounds in oxidizing ethylene glycol

Name	Formula	Molecular Weight (g/mol)	Price (\$USD/tonne)
Ethylene Glycol	$(\text{CH}_2\text{OH})_2$	62.07	534.00 [21]
Oxygen	O_2	31.99	350.00 [22]
Water	H_2O	18.02	0.00
Oxalic acid	$(\text{COOH})_2$	90.03	779.00 [8]

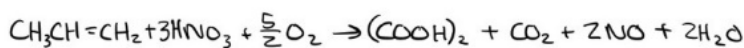
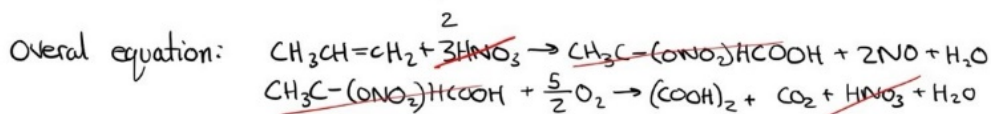
Table A.1.3: Common properties for compounds in oxidizing carbohydrates

Name	Formula	Molecular Weight (g/mol)	Price (\$USD/tonne)
Glucose	$C_6H_{12}O_6$	180.15	576.00 [6]
Nitric Acid	HNO_3	63.01	305.00 [7]
Water	H_2O	18.02	0.00
Oxalic acid	$(COOH)_2$	90.03	779.00 [8]
Nitric Oxide	NO	30.01	270.00 [7]

Appendix A.2: GEP calculations for all reaction pathways

A.2.1 Calculations for oxidizing propene.

Want to make 50 000 tonnes/year



Ratio \rightarrow 1 : 3 : $\frac{5}{2}$: 1 : 1 : 2 : 2

$$(\text{COOH})_2: 50\,000 \frac{\text{tonnes}}{\text{year}} \times \frac{1 \text{ tonne-mol}}{90.3 \text{ tonne}} = 555.37 \text{ tonne-mol/yr}$$

$$\text{CH}_3\text{CH}=\text{CH}_2: 555.37 \frac{\text{tonne-mol}}{\text{yr}} \times \frac{1}{1} \times \frac{42.08 \text{ tonne}}{\text{tonne-mol}} = 23370.52 \frac{\text{tonne}}{\text{yr}}$$

$$\text{HNO}_3: 555.37 \frac{\text{tonne-mol}}{\text{yr}} \times \frac{3}{1} \times \frac{63.01 \text{ tonne}}{\text{tonne-mol}} = 104981.59 \frac{\text{tonne}}{\text{yr}}$$

$$\text{O}_2: 555.37 \frac{\text{tonne-mol}}{\text{yr}} \times \frac{5}{2} \times \frac{31.99 \text{ tonne}}{\text{tonne-mol}} = 44415.72 \frac{\text{tonne}}{\text{yr}}$$

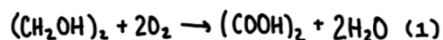
$$\text{CO}_2: 555.37 \frac{\text{tonne-mol}}{\text{yr}} \times \frac{1}{1} \times \frac{44.01 \text{ tonne}}{\text{tonne-mol}} = 24441.83 \frac{\text{tonne}}{\text{yr}}$$

$$\text{NO}: 555.37 \frac{\text{tonne-mol}}{\text{yr}} \times \frac{2}{1} \times \frac{30.01 \text{ tonne}}{\text{tonne-mol}} = 33333.31 \frac{\text{tonne}}{\text{yr}}$$

GEP = Value of products - cost of feeds

$$\begin{aligned} &= \left(50\,000 \frac{\text{tonne}}{\text{yr}} \cdot \frac{779\$}{\text{tonne}} + 24\,441.83 \frac{\text{tonne}}{\text{yr}} \cdot \frac{256\$}{\text{tonne}} + 33\,333.31 \frac{\text{tonne}}{\text{yr}} \cdot \frac{270\$}{\text{tonne}} \right) \\ &- \left(23\,370.52 \frac{\text{tonne}}{\text{yr}} \cdot \frac{865\$}{\text{tonne}} + 104\,981.59 \frac{\text{tonne}}{\text{yr}} \cdot \frac{305\$}{\text{tonne}} + 44\,415.72 \frac{\text{tonne}}{\text{yr}} \cdot \frac{335\$}{\text{tonne}} \right) \\ &= \$-12907048.77/\text{yr} \end{aligned}$$

A.2.2 Calculations for oxidizing ethylene glycol.



1 : 2 : 1 : 2 ← ratio between compounds

oxalic acid : $(\text{COOH})_2 = 50,000 \text{ tonnes/yr}$

① $(\text{COOH})_2 = 50,000 \text{ tonnes/yr} \div 90.03 \text{ tonnes/tonne-mol} = 555.37 \text{ tonne-mol/yr}$
(molecular weight)

② using the 1:1 ratio from $(\text{CH}_2\text{OH})_2$ to $(\text{COOH})_2$:

$$(\text{CH}_2\text{OH})_2/\text{yr} = 555.37 \text{ tonne-mol/yr} \cdot 62.07 \text{ tonnes/tonne-mol} = 34480 \text{ tonnes/yr}$$

③ using the 2:1 ratio from O_2 to $(\text{COOH})_2$:

$$\text{O}_2/\text{yr} = 2 \cdot 555.37 \text{ tonne-mol/yr} \cdot 31.99 \text{ tonnes/tonne-mol} = 35535 \text{ tonnes/yr}$$

④ using the 2:1 ratio from H_2O to $(\text{COOH})_2$:

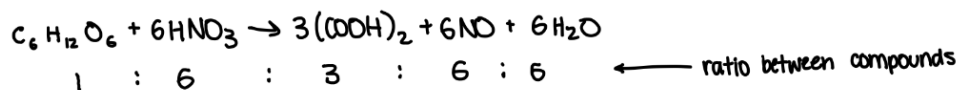
$$\text{H}_2\text{O}/\text{yr} = 2 \cdot 555.37 \text{ tonne-mol/yr} \cdot 18.02 \text{ tonnes/tonne-mol} = 20015 \text{ tonnes/yr}$$

GSP = value of products - value of feeds

$$= 50,000 \text{ tonnes/yr} \cdot \$779/\text{tonne} + 20,015 \text{ tonnes/yr} \cdot \$0/\text{tonne} - 34,480 \text{ tonnes/yr} \cdot \$534/\text{tonne} \\ - 35,535 \text{ tonnes/yr} \cdot \$350/\text{tonne}$$

$$= \$8,100,420/\text{yr}$$

A.2.3 Calculations for oxidizing carbohydrates



oxalic acid : $(\text{COOH})_2 = 50,000 \text{ tonnes/yr}$

① $(\text{COOH})_2 = 50,000 \text{ tonnes/yr} \div 90.03 \text{ tonnes/tonne-mol} = 555.37 \text{ tonne-mol/yr}$
(molecular weight)

② using the 1:3 ratio from $\text{C}_6\text{H}_{12}\text{O}_6$ to $(\text{COOH})_2$:

$$\text{C}_6\text{H}_{12}\text{O}_6/\text{yr} = \frac{555.37 \text{ tonne-mol/yr} \cdot 180.15 \text{ tonnes/tonne-mol}}{3} = 33350 \text{ tonnes/yr}$$

③ using the 6:3 ratio from HNO_3 to $(\text{COOH})_2$:

$$\text{HNO}_3/\text{yr} = \frac{6 \cdot 555.37 \text{ tonne-mol/yr} \cdot 63.01 \text{ tonnes/tonne-mol}}{3} = 70000 \text{ tonnes/yr}$$

④ using the 6:3 ratio from NO to $(\text{COOH})_2$:

$$\text{NO/yr} = \frac{6 \cdot 555.37 \text{ tonne-mol/yr} \cdot 30.01 \text{ /tonne-mol}}{3} = 33335 \text{ tonnes/yr}$$

⑤ using the 6:3 ratio from H_2O to $(\text{COOH})_2$:

$$\text{H}_2\text{O/yr} = \frac{6 \cdot 555.37 \text{ tonne-mol/yr} \cdot 18.02 \text{ tonnes/tonne-mol}}{3} = 20015 \text{ tonnes/yr}$$

GSP = value of products - value of feeds

$$= 50,000 \text{ tonnes/yr} \cdot \$719/\text{tonne} + 20015 \text{ tonnes/yr} \cdot \$0/\text{tonne} + 33335 \text{ tonnes/yr} \cdot \$270/\text{tonne} \\ - 33350 \text{ tonnes/yr} \cdot \$576/\text{tonne} - 70,000 \text{ tonnes/yr} \cdot \$305/\text{tonne}$$

$$= \$7,390,850/\text{yr}$$

Appendix B: Separation sample calculations

FLOW INTO/OUT OF CRYSTALLIZER:

Oxalic acid: $(\text{COOH})_2 = \underline{6.25 \text{ tonnes/hr}}$

$$\text{H}_2\text{O} = \frac{6.25 \text{ tonnes/hr}}{90.03 \text{ tonnes/tonne-mol}} \cdot \frac{6}{3} \cdot 18.02 \text{ tonnes/tonne-mol} = \underline{2.502 \text{ tonnes/hr}}$$

*oxalic acid flow out of reactor
molecular weight of oxalic acid*
 *$(\text{COOH})_2$ to compound
ratio*
molecular weight of compound

$\text{HNO}_3 =$ limiting reagent: $\text{C}_6\text{H}_{12}\text{O}_6$
excess reagent: HNO_3

$$\overset{\text{glucose}}{33350 \text{ tonnes/yr}} \left(\frac{6 \text{ mol HNO}_3}{1 \text{ mol gluc}} \right) \left(\frac{63.01 \text{ tonnes}}{1 \text{ mol HNO}_3} \right) = 69968 \text{ tonnes of HNO}_3 \text{ used}$$

tonnes
tonne-mol
tonne

EXCESS = $70,000 - 69968 = 32 \text{ tonnes/yr}$

$\text{HNO}_3: 32 \text{ tonnes/yr} \left(\frac{1000}{365 \times 24} \right) = \underline{3.65 \text{ tonnes/hr}}$

TOTAL IN/OUT
 $= 12.4 \text{ tonnes/hr}$

Appendix C: Energy balance calculations

C.1 Calculations for flow rate

Flow to crystallizer (tonne-mol/hr)

$$2.65 \frac{\text{tonnes}}{\text{hr}} \left(\frac{\text{ton-mol}}{63.01 \text{ tonnes}} \right) = 0.058 \text{ tonne-mol/hr}$$

$$2.502 \frac{\text{tonnes}}{\text{hr}} \left(\frac{\text{ton-mol}}{18.02 \text{ tonnes}} \right) = 0.1388 \text{ tonne-mol/hr}$$

$$6.25 \frac{\text{tonnes}}{\text{hr}} \left(\frac{\text{ton-mol}}{90.03 \text{ tonnes}} \right) = 0.0694 \text{ tonne-mol/hr}$$

$$\text{TOTAL} = 0.2654 \text{ tonne-mol/hr}$$

C.2 Calculations for energy transfer

$$Q = m \Delta T$$

Nitric Acid:

$$Q = 0.058 \frac{\text{ton-mol}}{\text{hr}} \times \frac{10^6 \text{ mol}}{\text{ton-mol}} \times \frac{110.68 \text{ J}}{\text{mol K}} \times (50 - 70)$$

$$= -126388800 \text{ J/hr}$$

Water:

$$Q = 0.1388 \frac{\text{ton-mol}}{\text{hr}} \times \frac{10^6 \text{ mol}}{\text{ton-mol}} \times \frac{76.39 \text{ J}}{\text{mol K}} \times (50 - 70)$$

$$= -212058640 \text{ J/hr}$$

Oxalic acid:

$$Q = 0.0694 \frac{\text{ton-mol}}{\text{hr}} \times \frac{10^6 \text{ mol}}{\text{ton-mol}} \times \frac{159.61 \text{ J}}{\text{mol K}} \times (50 - 70)$$

$$= -221524800 \text{ J/hr}$$

$$\text{Sum: } Q_T = -561972240 \text{ J/hr}$$

$$= -0.562 \text{ GW/hr}$$

C.3 Calculation for total utilities and costs

cost of utility: cooling water: \$0.378/GJ

$$0.562 \frac{\text{GJ}}{\text{hr}} \times \frac{0.378}{\text{GJ}} = \$0.212/\text{hr}$$

$$0.212 \frac{\$}{\text{hr}} \times \frac{8000 \text{ hr}}{1 \text{ yr}} = \underline{\underline{\$1699.4 / \text{yr}}}$$

Amount of cooling water:

$$-561972240 = \dot{m} \cdot 4.24 \cdot (5)$$

$$C_w @ 25^\circ\text{C} = 76.392 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times \frac{1 \text{ mol}}{18.02 \text{ g}} \\ = 4.24 \frac{\text{J}}{\text{g} \cdot \text{K}}$$

$$\Delta H = 76.39 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times (25 - 20)$$

$$= 381.96 \frac{\text{J}}{\text{mol}}$$

$$\dot{n} = \frac{\dot{Q}}{\Delta H} = \frac{561972240 \text{ J/hr}}{381.96 \text{ J/mol}} = 1471286 \text{ mol/hr}$$

$$1471286 \frac{\text{mol}}{\text{hr}} \times \frac{18.02 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ ton}}{10^6 \text{ g}} = \underline{\underline{26.51 \text{ ton/hr}}}$$

Appendix D: Process flow diagram

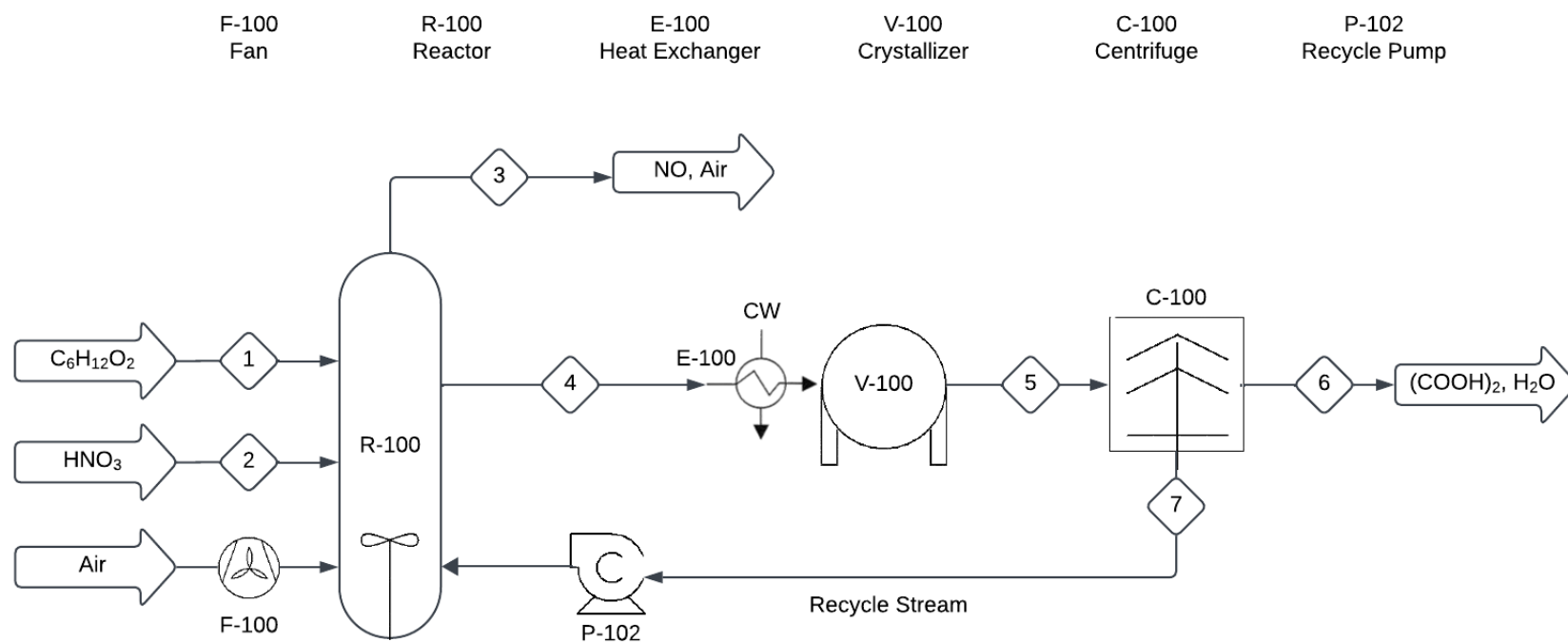


Figure D.1: Process flow diagram for the reactor and the separation process.

Table D.1: Stream table for the reactor, crystallizer and centrifuge in the oxalic acid process.

Stream Number	1	2	3	4	5	6	7
Temperature (°C)	20	20	70	70	50	50	50
Pressure (atm)	1	1	1	1	1	1	1
Vapour Fraction	0	0	1	0	0	0	0
Mass Flowrate (kg/h)	3807	7991	3805	7996	7996	7993	3.65
Mole Flowrate (kmol/h)	21.1	126.8	126.9	190.4	190.4	190.3	0.058
Component Molar Flow (kmol/h)							
Nitric Acid	0	126.8	0	0.058	0.058	0	0.058
Water	0	0	0	126.9	126.9	126.9	0
Oxalic Acid	0	0	0	63.4	63.4	63.4	0
Glucose	21.1	0	0	0	0	0	0
Nitric Oxide	0	0	126.9	0	0	0	0

Appendix E: Control Strategy Process Flow Diagram

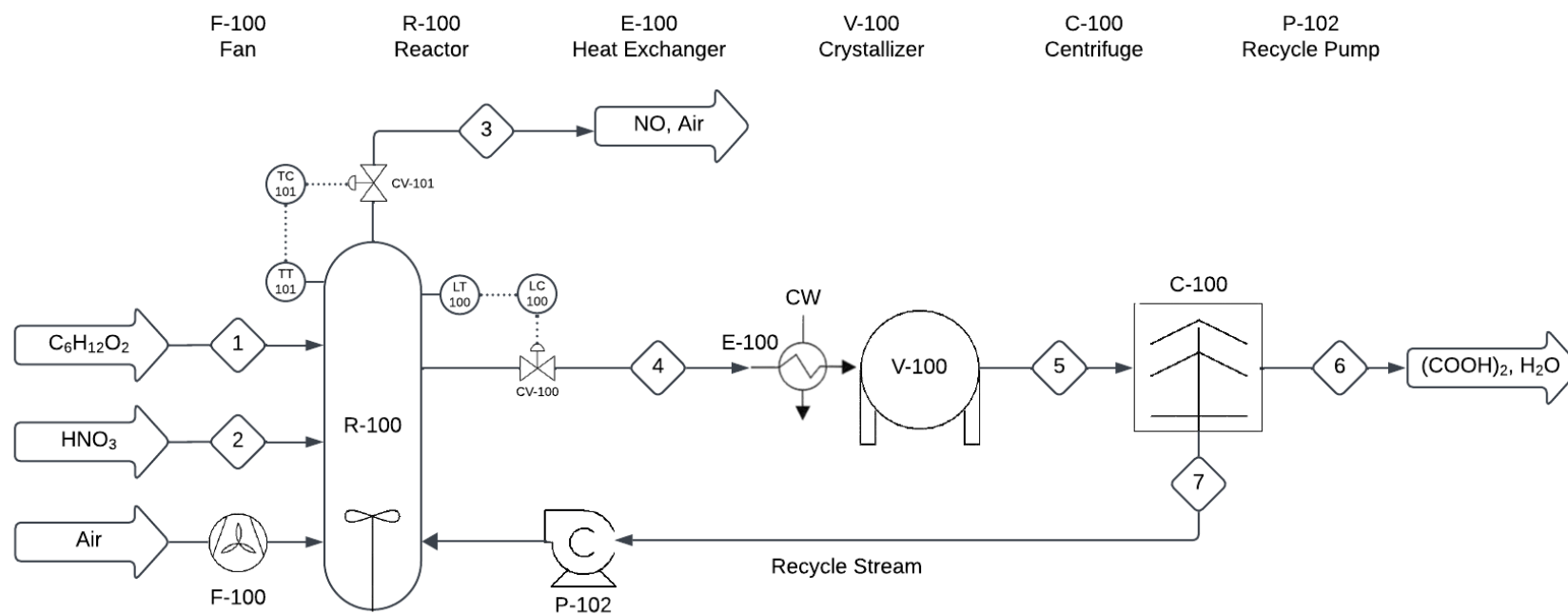


Figure E.1: Process flow diagram with controls for the reactor temperature and liquid level.