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Toward A Glycerol Based (Bio)refinery: Process Design, Simulation and Assessment of Chemocatalytic Production Paths

Master's thesis in Sustainable Energy Systems

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Department of Energy and Environment
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2017

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Abstract

Acrylic acid is an important organic industrial chemical, widely used as a raw material in various production. Poly-acrylic acids have shown excellent performances for polymeric materials. The global consumption is expected to grow high up to around 8.2 million tonnes by 2020. The conventional way of producing acrylic acid is performed by the catalytic partial oxygenation process of propylene, which is derived from petroleum and natural gas. This process has been highly dependent on fossil fuels for over 40 years.

Under the pressure of 2°C target and volatility of acrylic acid price due to changeable fossil fuels price, alternative methods of producing acrylic acid on industrial scale are required for breaking the "Carbon lock-in". Renewable resources, such as glucose and glycerol, seem to have big potential. In this project, crude glycerol is used as the feeding stock for producing acrylic acid with acrolein as the intermediate product; the crude glycerol is considered as the byproduct of biodiesel production. Two steps of chemical reaction are involved, namely dehydration and oxidation. Each step is assisted by one kind of highly efficient catalyst, which is selected based on former literature results. Purification process is necessary for achieving high purity of acrylic acid. The simulation is performed with software Aspen Plus ®. Simulation results show that 2.48 kg of crude glycerol can be converted to 1 kg of acrylic acid of 99.94% purity. Pinch analysis helps defining the maximum heat recovery target and helps lower the impact of environment and operating cost by 12-14%.

The glycerol based production of acrylic acid is compared with the fossil based production of acrylic acid under EU operating conditions and a glucose based model using sugarcane or corn as feedstock. The comparison mainly suggests that: glycerol based production seems more competitive environmentally and economically than the glucose based one; the environmental impact is heavily influenced by the alternative use of glycerol as a waste from the biodiesel production. In places where crude glycerol can be used as fuel in incineration plants, it may be less environmental friendly to use it for chemical production with the current status of technology; in areas where glycerol can only be treated in conventional waste treatment plants, to use glycerol for value-added production of chemicals (e.g., acrylic acid) seems a very promising method. To this end, further in-depth research is needed towards an integrated (multi-product) glycerol biorefinery.

Keywords: glycerol, acrylic acid, acrolein, dehydration, oxidation, catalyst, Aspen.

Acknowledgements

After having worked in electrical power sector (thermal mechanical part) for several years, industrial chemical production was an untouched area for me. The course "Industrial energy systems" in my first year of master study at Chalmers has inspired me to explore some sparkles in this field.

First of all, I sincerely would like to express my gratitude to my supervisor and examiner, Stavros Papadokonstantakis for providing me this interesting topic and letting me have opportunity of studying in this area. More than that, no matter how busy he was, he always arranged weekly meeting with me for checking my progress and giving me valuable advice and encouraging feedbacks; and he always kept his door open and offered me help. Every time after I discussed with him, I felt having taken a wonderful lecture. I am very grateful for his help guiding me along this project. Ευχαριστώ πολύ!

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Yiyu Ding,
Gothenburg, June 2017

Abbreviation and Symbols

Abbreviation

AA	Acrylic acid
CED	Cumulative energy demand
EI99	Eco-indicator 99
EU	European Union
$FePO_4$	Iron phosphate
GCC	Grand composite curve
Gly	Glycerol
GWP	Global warming potential
HEN	Heat exchanger network
Inc	Incineration
LCA	Life cycle assessment
LHV	Low heating value
NRTL	Non-random two-liquid model
OECD	Organisation for Economic Co-operation and Development
Op. cost	Operating cost
RSTOIC	Stoichiometric reactor
VMo-SiC	Vanadiummolybdenum mixed oxides supported on silicon carbide
WW	Waste water
WWTP	Waste water treatment plant

Chemical compounds

3-HP	3-hydroxypropionic acid
C	Carbon
CO	Carbon monoxide
CO_2	Carbon dioxide
H_2	Hydrogen
H_2O	Water
O_2	Oxygen
N_2	Nitrogen

Latin letters

γ	Heat capacity ratio
t	temperature (°C)
$\Delta\mathrm{T}$	temperature difference (K)
p	pressure
$\Delta\mathrm{H}$	Enthalpy difference

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Introduction

1.1 Background

Acrylic acid, $C_3H_4O_2$, is an important organic industrial chemical, that has widely been used as a raw material in diverse production of coatings, plastics, adhesives, paints. The total global market of acrylic acid is around 5-6 million tonnes between 2013 and 2015. By the end of 2020, it is estimated that the growing consumption will be high up to 8.2 million tonnes with revenue as $18.8 billion [5]. Polyacrylic acids have shown excellent performances for polymeric materials, such as colour stability, resistance of heat, aging and acid, endurability at low temperature. The use for diapers in the form of superabsorbent polymers accounts for more than one-fourth of the total consumption. This segment is the biggest driver in the market of acrylic acid, followed by coatings, sealants, water treatment and other applications [5, 6]. Meanwhile, Asia-Pacific is leading the increasing demand and forecasted to be the most important area of the market by the end of 2020 [5].

Acrylic acid is dominantly produced by the catalytic partial oxygenation process of propylene, which is a by-product of the ethylene attained from petroleum and natural gas cracking, as shown in the following equation [6]:

$$CH_2 = CHCH_3 + \frac{3}{2}O_2 \rightarrow CH_2 = CHCO_2H + H_20 \quad (\Delta H_R = -254.1 kg/mol)$$

The process has been highly reliant on fossil fuels for over four decades and leads to the so-called "Carbon lock-in". Under the high demand of acrylic acid as depicted above and volatility of acrylic acid price due to changeable prices of natural gas and crude oil, alternative synthesis methods have been studied and examined. Additionally, to find a production method based on renewable feedstock to replace the conventional production process can have significant environmental benefits, e.g., for limiting the global warming under 2 °C target [7].

1.2 Purpose

Renewable sources, such as corn, sugar and glycerol, have gained attention on the research of alternative ways for producing acrylic acid.

Sugarcane and corn have been regarded as the two most favorable renewable raw materials in the biofuel market for synthesizing ethanol fuel, thanks to their high energy content and large amount of plantation, especially in the United States and Brazil [8]. Meanwhile, glucose being extracted from the two resources can be fermented into 3-hydroxypropionic acid (3-HP), which can be further dehydrated into acrylic acid [9]. Whereas plantation of corn and sugar has been restricted geographically and seasonally, price of the raw material can be unpredictable. An environmental concern is that it can lead to (indirect) land use change and competition for food, and have severe effect on biodiversity [8].

As for glycerol, it is typically acquired from plant and animal sources, also as a by-product from synthesis of biodiesel. Figure 1.1 illustrates that the biodiesel production is growing steadily and forecasts show that it may reach to approximately 37 million metric tons in 2020 from the report of OECD [1]. Meanwhile, there is a variety of research and application of converting waste biomass, waste cooking oils and grease into biodiesel, which makes biodiesel and glycerol greener [10, 11, 12, 13]. Therefore, availability of glycerol also benefits from the widely expanding industry of biodiesel; price of crude glycerol can be as low as 100-150 USD/ ton [14]. Plenty of research has been performed in order to consume the oversupply of glycerol to form commodity chemicals [15, 16, 17], one of which is to utilize glycerol as an alternative method to produce acrylic acid, especially on the fruitful findings on improving performance of catalysts.

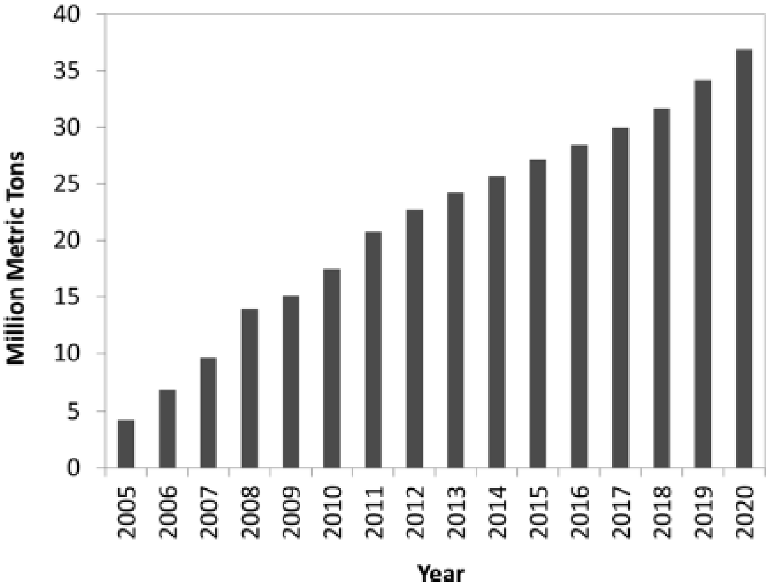

Figure 1.1: Annual production of biodiesel [1]

Figure 1.2 presents the overview of glycerol valorization processes, diverse value-added commodities can be acquired from glycerol via different chemical reaction routes. For example, environmental and economic assessment of generation of dihydroxyacetone and lactic acid from glycerol have been analyzed in [18, 19].

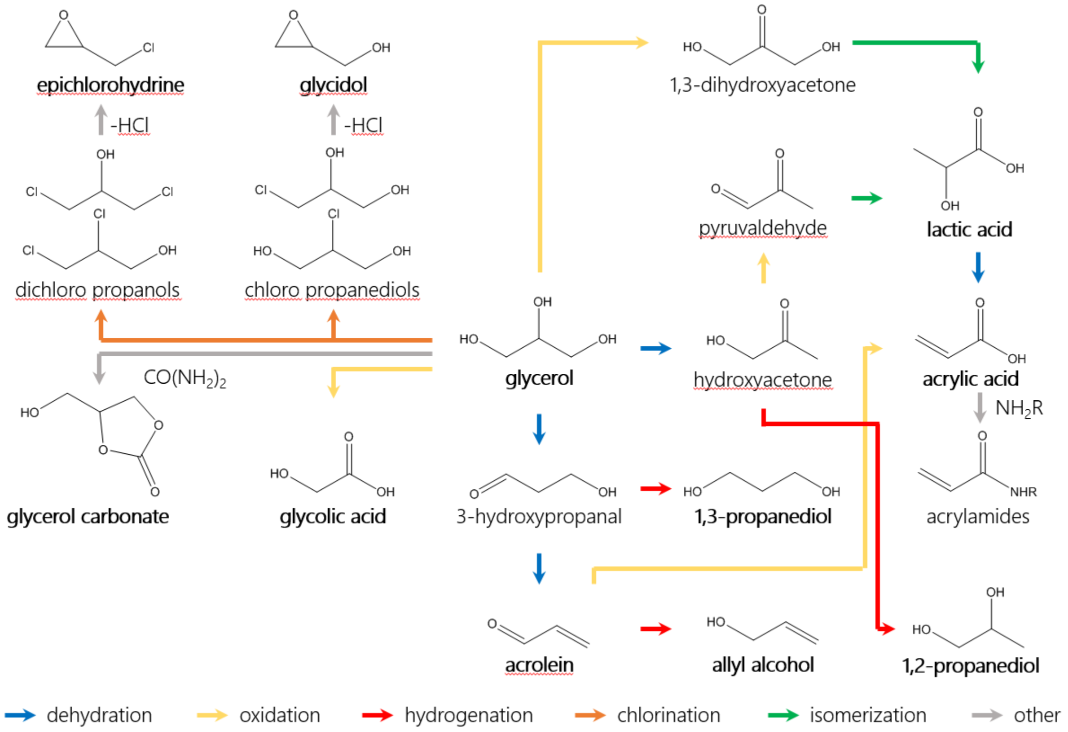

Figure 1.2: Overview of glycerol valorization processes [2]

Herein, examining the process of glycerol based biorefinery for producing acrylic acid (via acrolein as the intermediate) on an industrial scale, from aspect of technology feasibility to life cycle and operating cost, is the main target of this thesis.

2

Theory

In order to better compare and find out if the glycerol or glucose platform might be more attractive for acrylic acid production under EU operating condition and markets, the project of "*Renewable Acrylic Acid*" performed by a research group from University of Pennsylvania [9] is utilized as the benchmark model in this project. This benchmark model was reassessed for EU operating conditions, energy utility, markets, etc. The techno-economic and environmental assessment of these two systems supported by two different types of biomass feedstock are compared and discussed. This chapter mainly describes the main chemical reactions of the two systems.

2.1 Glucose based system

The overall chemical reaction routes fed by glucose are as follows:

$$glucose \rightarrow 3 - hydroxypropionic\ acid(3 - HP) \rightarrow acrylic\ acid$$

$$(CH)_5(OH)_5CH_2 \rightarrow 2(CH)_2CO(OH)_2 \rightarrow 2CH_2 = CHCOOH + H_2O$$

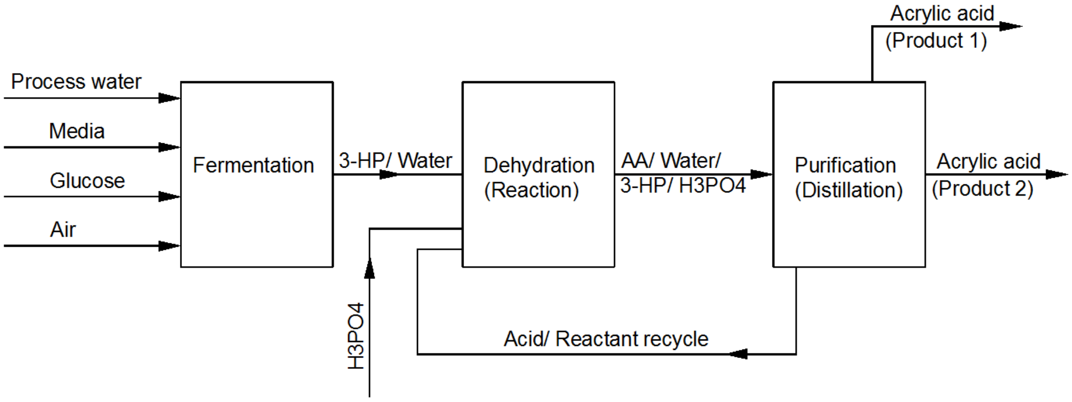

Figure 2.1: Overall flowchart of glucose based model

The general process diagram is simplified in Figure 2.1, which includes three major sections: fermentation, dehydration and distillation.

- **Fermentation:** Glucose can be extracted from sugarcane or corn in processing plants. In the simulation, it can be assumed as pure glucose feed ready for being fermented into 3-HP with air and water using *E.Coli*.

- **Dehydration:** The 3-HP stream is sent to the reactor, where 3-HP is converted into acrylic acid with the assistance of the catalyst phosphoric acid. The subsequent reactive distillation tower promotes further conversion of the unreacted 3-HP by removing excess water in the product flow.
- **Distillation:** The resulting product flow is further distilled and partially recycled back to the reactor in order to achieve the almost complete yield of acrylic acid. Most of the catalyst can be recycled back to the reactor with small amount being purged and make-up fresh catalyst fed in simultaneously.

2.2 Glycerol based system

From Figure 1.2, two main chemical reaction processes are required to produce acrylic acid with acrolein as the intermediate product, namely dehydration and oxidation. Figure 2.2 simply illustrates the overall conceptual diagram of glycerol based model. The raw material is crude glycerol, and the purity of final product, acrylic acid, is required to be high above 99.9 % as the benchmark model. The whole model is made up by pre-treatment of crude glycerol, dehydration and oxidation with purification. After purification, each organic/ anorganic waste stream shall be checked in order to decide the way of waste treatment for lowering their environmental impact.

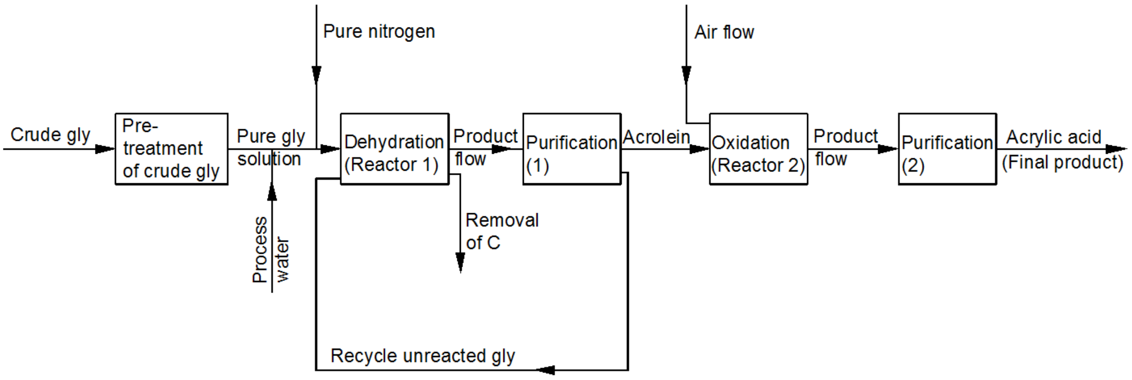

Figure 2.2: Overall flowchart of glycerol based model

2.2.1 Dehydration

Within the aspect of chemistry and biological research, dehydration refers to a chemical reaction leading to loss(es) of water molecule(s) under the aid of catalysts accelerating the whole reaction without changing the reaction mechanisms. Brønsted acid catalyst usually assists the reaction by improving the poor leaving group, hydroxyl group (-OH) into the better leaving group ($\breve{}OH_2^+$) via protonation.

There are two-step losses of water during dehydration to form acrolein as the wanted product, shown in the following equations:
Step 1: $glycerol \rightarrow 3 - hydroxypropanal + H_2O$
Step 2: $3 - hydroxypropanal \rightarrow acrolein + H_2O$

3-hydroxypropanal, which is produced after the first loss of water, is not easy to be detected mainly because the following reaction is too fast and 3-hydroxypropanal is quite unstable. Also, retroaldol effect can induce 3-hydroxypropanal to form acetaldehyde and formaldehyde, which may further lead to many other by-products as well [3, 20].

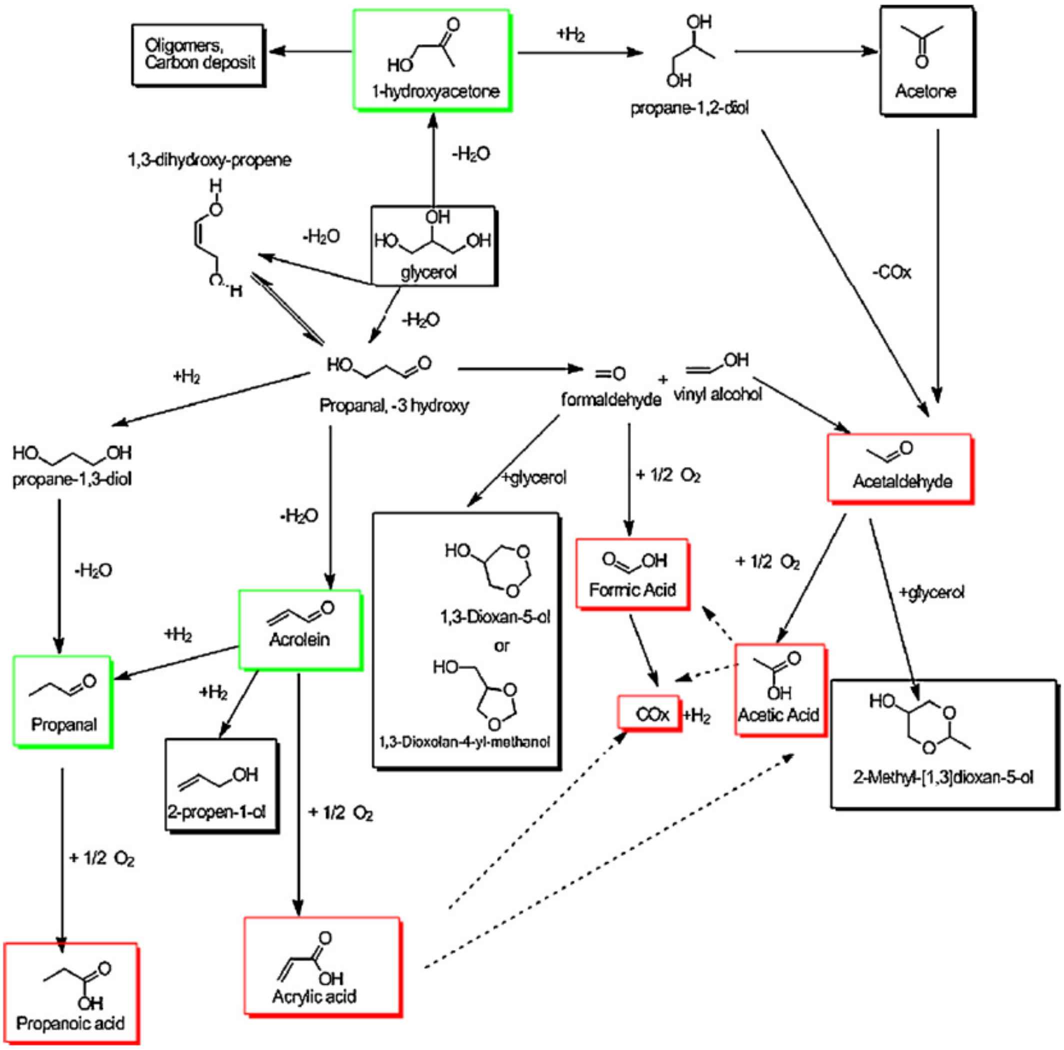

Figure 2.3: Proposed mechanism of (oxy)dehydration of glycerol. Surrounded products were detected. Oxygen helps the formation of products in red on detriment of products in green. [3]

Figure 2.3 exhibits almost all the possible reaction routes during dehydration of glycerol. Based on the laboratory result [3], the following reactions happened in dehydration when catalyst $FePO_4$ is chosen with nitrogen as carrier gas. The main product is acrolein, there are diverse by-products detected, such as acetaldehyde, propanal, formic acid; formation of CO_x, solid carbon deposited on the catalyst and unknown products account for missing carbon.

$$C_3H_8O_3 \rightarrow C_3H_4O + 2H_20 \tag{2.1}$$

(glycerol) (acrolein)

$$C_3H_8O_3 + H_2 \rightarrow C_3H_6O + 2H_20 \tag{2.2}$$

(glycerol) (propanal)

$$C_3H_8O_3 + H_2 \rightarrow C_3H_6O + 2H_20 \tag{2.3}$$

(glycerol) (acetone)

$$C_3H_8O_3 + H_2 \rightarrow C_3H_6O + 2H_20 \tag{2.4}$$

(glycerol) (allyl alcohol)

$$C_3H_8O_3 \rightarrow CH_2O + H_20 + C_2H_4O \tag{2.5}$$

(glycerol) (formaldehyde) (acetaldehyde)

$$C_3H_8O_3 + H_2 + 0.5O_2 \rightarrow C_3H_6O_2 + 2H_20 \tag{2.6}$$

(glycerol) (propanoic acid)

$$C_3H_8O_3 + 0.5O_2 \rightarrow C_3H_4O_2 + 2H_2O \tag{2.7}$$

(glycerol) (acrylic acid)

$$C_3H_8O_3 + 0.5O_2 \rightarrow CO_2 + H_2 + C_2H_4O + H_2O \tag{2.8}$$

(glycerol) (acetaldehyde)

$$C_3H_8O_3 \rightarrow CO + H_2 + C_2H_4O + H_2O \tag{2.9}$$

(glycerol) (acetaldehyde)

$$C_3H_8O_3 + 0.5O_2 \rightarrow CH_2O_2 + H_2O + C_2H_4O \tag{2.10}$$

(glycerol) (formic acid) (acetaldehyde)

$$C_3H_8O_3 \rightarrow 3C + 3H_2O + H_2 \tag{2.11}$$

(glycerol)

$$C_3H_8O_3 \rightarrow C_3H_6O_2 + H_2O \tag{2.12}$$

(glycerol) (1-hydroxyacetone)

The conversion of glycerol and yield of each product are calculated by:

$$glycerol\ conversion\ (\%) = \frac{total\ moles\ of\ carbon\ in\ all\ detected\ products}{moles\ of\ carbon\ in\ reacted\ glycerol} \times 100$$

$$product\ selectivity\ (\%) = \frac{moles\ of\ carbon}{moles\ of\ glycerol\ in\ the\ feed} \times 100$$

$$product\ yield = glycerol\ conversion \times product\ selectivity$$

It can be seen that oxygen is needed for synthesis of several by-products, such as formic acid, propanoic acid, acrylic acid and CO_2. Although there is no oxygen in the feeding stream, all the required oxygen is assumed to be released from the catalyst, $FePO_4$. Maximum 20 % of the catalyst oxygen can be considered to take place in the reactions; this value was estimated by the catalyst team of ETH. Oxygen flow acquired from the catalyst can be roughly calculated as:

$$O_2\ flow = \frac{weight\ of\ FePO_4 \times oxygen\ released\ from\ catalyst \times 4}{151 g/mol \times 2 \times duration\ hours}.$$

Duration refers to continuance of the reaction in batch conditions. The limited oxygen flow constraints the production yield of these hydro-oxidized by-products. The assumed conversion of glycerol and yield of each product is listed in Appendix A.1

Meanwhile, hydrogen shall be involved in the generation of propanal, acetone, 2-propen-1-ol and propanoic acid. Hydrogen can be produced through intermediates, formic acid and propane-1,2-diol [1] ; the reactions are simplified as Equation 2.8 and Equation 2.9. The actual mechanism routes are as follows:
via formic acid:

$$glycerol \rightarrow 3 - hydroxypropanal + H_2O \rightarrow formaldehyde + vinyl\ alcohol,$$

$$formaldehyde + 0.5O_2 \rightarrow formic\ acid \rightarrow H_2 + CO_2;$$

via propane-1,2-diol:

$$glycerol \rightarrow 1 - hydroxyacetone + H_2O,$$

$$hydroxyacetone + H_2 \rightarrow propane - 1,2 - diol,$$

$$propane - 1,2 - diol \rightarrow CO + 2H_2 + acetaldehyde.$$

---

[1] At present fossil fuels is still contributing most of hydrogen production by means of steam reforming of methane extracted from natural gas and gasification of coal. This conventional generation of hydrogen at industrial scale is much like that of acrylic acid, which is desperately necessary to be broke. Although fraction contributed by biomass and water electrolysis is small, to use biomass (such as glycerol) and formic acid is regarded as renewable chemical synthesis approach for producing hydrogen [21, 22, 23].

2.2.2 Oxidation

Oxidation refers to any chemical reaction with involvement of the electrons transfer. After losing electrons, the matter can be defined as being oxidized.

Based on the Liu et al. [20], besides the main route of acrolein to acrylic acid, there are also other reactions involved, mainly caused by some by-products during the former dehydration process (such as acetone, acetaldehyde, hydroxyacetone) which cannot be separated or removed completely after purification, and are thus sent to oxidation reactor along with acroelin. The following reactions can happen.

$$C_3H_4O + 0.5O_2 \rightarrow C_3H_4O_2 \tag{2.13}$$

(acrolein) (acrylic acid)

$$C_2H_4O + 0.5O_2 \rightarrow C_2H_4O_2 \tag{2.14}$$

(acetaldehyde) (acetic aicd)

$$C_3H_6O + 2O_2 \rightarrow C_2H_4O_2 + CO_2 + H_2O \tag{2.15}$$

(acetone) (acetic aicd)

$$CH_2O_2 \rightarrow CO_2 + H_2 \tag{2.16}$$

(formic acid)

$$CO + 0.5O_2 \rightarrow CO_2 \tag{2.17}$$

$$C_3H_6O_2 + H_2 + 2O_2 \rightarrow C_2H_4O_2 + CO_2 + 2H_2O \tag{2.18}$$

(1-hydroxyacetone) (acetic aicd)

3

Methods

This chapter describes the methodology about the simulation and calculation of the process models for producing acrylic acid from glucose and glycerol, respectively. The simulation models are built up in software Aspen Plus ® V8.8. The main principles and assumptions of pinch analysis for heat integration are also explained at the end of this chapter.

3.1 General method settings in Aspen Plus®

Thermophysical properties in the simulation are calculated using the NRTL method (non-random two-liquid model). It is a state-of-art activity coefficient model and applicable to handle polar and non-polar compounds by providing a broad electrolyte thermodynamic configuration. The NRTL method is suitable to manage the chemical system of the acidic reaction involving ideal gases, organics mix with the presence of water within this project [24, 25].

For the removal of unwanted substances from flow streams, distillation is an important method of purification to achieve required high purities of final products. Distillation columns of RadFrac equilibrium stage model equipped with condenser and reboilers are chosen for the purification [26]. The actual absorption and distillation are affected by process kinetics. However, the process kinetics are neglected at this stage, since no capital cost assessment is performed. Thus, this shortcut and rigorous methods is sufficient to design the near steady-state operation process [27, 25, 26]. Both dehydration and oxidation reaction taking place in reactors are modeled by stoichiometric reactor (RSTOIC) in Aspen Plus®.

3.2 Simulation of Benchmark model

The general conceptual model fed by glucose is simplified in Figure 2.1 containing three process as introduced in the theory chapter: fermentation, dehydration and purification. Since *E.Coli* requires a time period for fermentation from media, batch process simulation software, such as SuperPro Designer ® or Aspen Batch Process Developer® shall be used to handle the scheduling approach. Due to the limited time of this thesis, simulation of the benchmark model starts from pure 3-HP water solution after sterilizing and centrifuging off the biomass. Figure 3.1 and Figure 3.2 present the set up of the benchmark model. The input flow data is taken from Cie et al. [9], the production target is to produce 21.7 t/hr of acrylic acid (99.99% wt). Treatment of waste water is also considered.

After being sterilized and centrifuged, the 3-HP water solution is heated for removing large amount of water through a 5-stage multi-effective evaporation flash vessels, as shown in Figure 3.1. Figure 3.2 describes the conversion into acrylic acid and purification of acrylic acid. The concentrated 3-HP stream is pumped into the reactor (R-101), where approximately 30% of 3-HP is converted into acrylic acid with the catalyst phosphoric acid. The subsequent reactive distillation tower (D-101) promotes further conversion of the unreacted 3-HP and removes excess water in the overhead product flow as well. A trace amount of CO_2 is applied to D-101 for the prevention of decarboxylation reactions. The resulting product flow (mainly acrylic acid with water, unreacted 3-HP and the catalyst) is further distillated in two distillation towers (D-102 and D-103). The overhead product flow (99.99% wt of acrylic acid) of D-102 is collected with the overhead product flow (99.99% wt of acrylic acid) of D-103 for the final product stream. Bottom flow of D-103 contains almost all the catalyst, most of which is recycled back to R-101 with unreacted 3-HP and acrylic acid that cannot be separated into the final product stream. A small amount of catalyst is purged (SD-122) and the same amount of fresh make-up catalyst is fed in (SR-102) simultaneously. All the removed water and the purged catalyst are mixed, cooled and sent to waste water treatment plant.

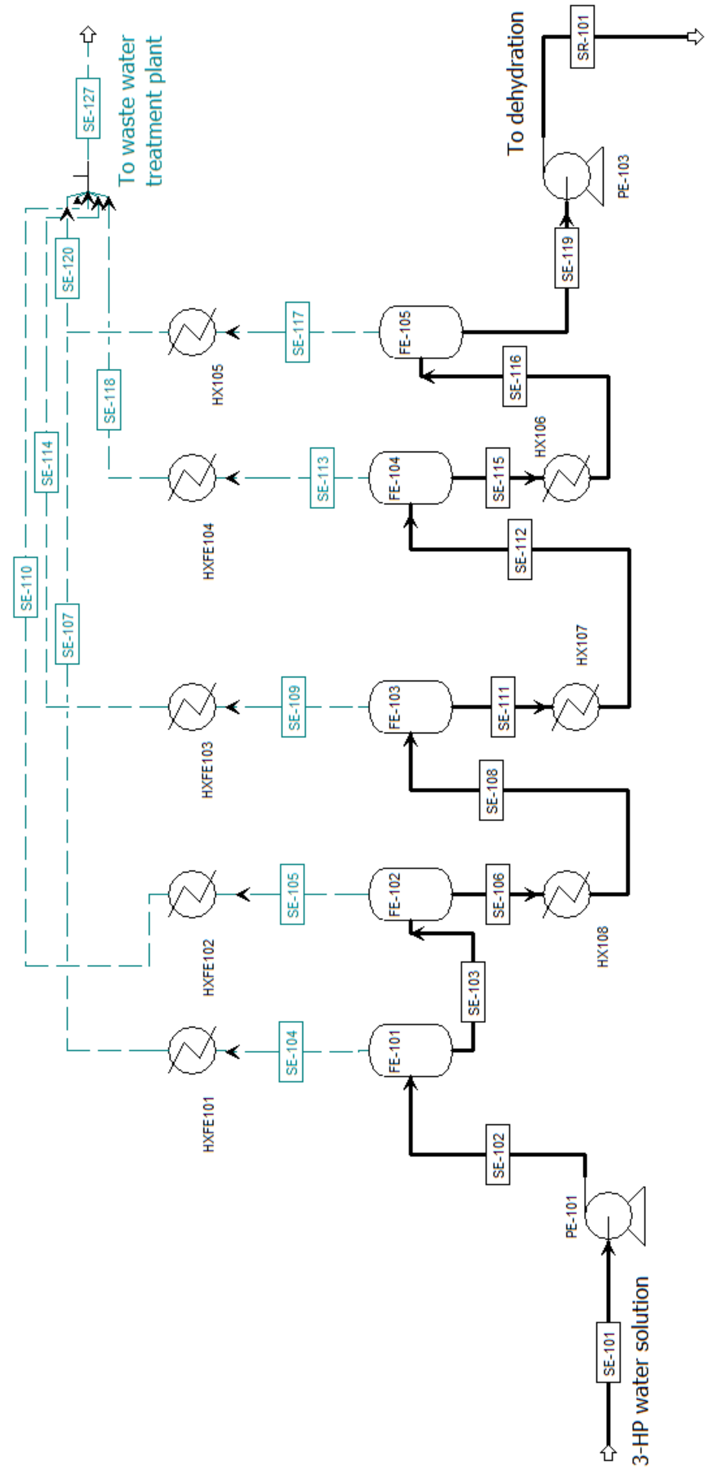

Figure 3.1: Flowsheet of multi-effect evaporation of glucose based model. The explanation of the stream and process unit acronyms can be found in Appendix A.6, A.8, and A.9.

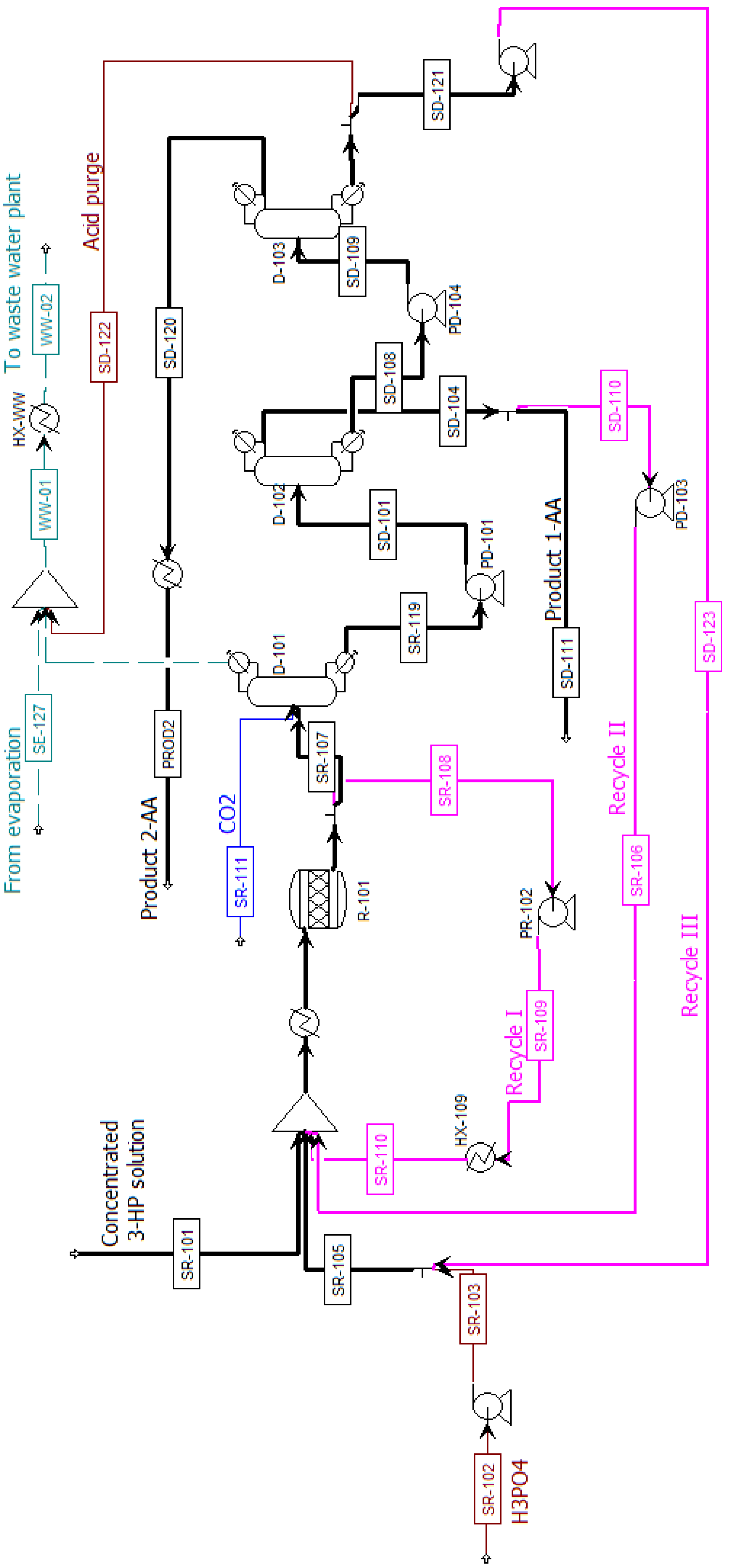

Figure 3.2: Flowsheet of dehydration and purification of glucose based model. The explanation of the stream and process unit acronyms can be found in Appendix A.6, A.9, A.10 and A.11.

3.3 Simulation of Glycerol based model

The overall conceptual diagram of glycerol based model is simply shown in Figure 2.2 including pre-treatment, dehydration (purification) and oxidation (purification). Additionally, pumps and fans are considered for compensation of potential piping pressure losses. The simulation flowsheets are shown below.

3.3.1 Simulation of Pre-treatment of crude glycerol

Crude glycerol is commonly composed by around 80 % of glycerol with small amount of water, fatty acid, ash and methanol. The impurities are expected to be removed through heating, evaporation and separator as much as possible in order to reach higher conversion of glycerol in next phase. The acquired pure glycerol is diluted with process water up to 40 wt% of glycerol. The process layout of the crude glycerol pretreatment is presented in Figure 3.3.

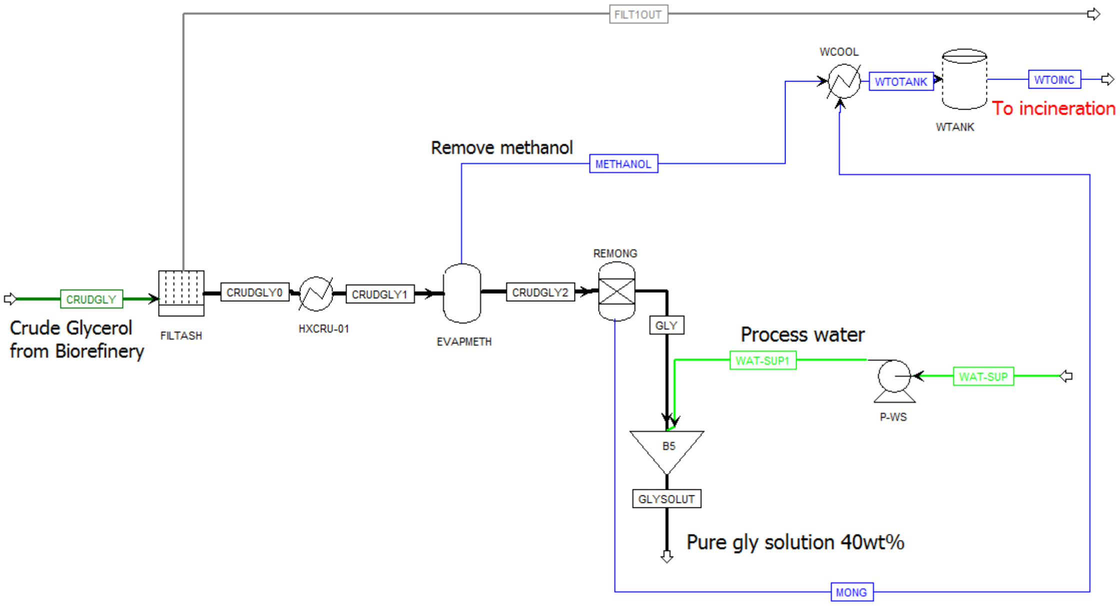

Figure 3.3: Flowsheet of the simulation of pre-treatment of crude glycerol from biorefinery. The explanation of the stream and process unit acronyms can be found in Appendix A.7 and A.12.

3.3.2 Simulation of Dehydration process

Next step is to dehydrate the glycerol. After taking data from J.Deleplanque et al.[3], the glycerol solution is set to be heated up to 280 °C and introduced to Reactor 1 by pure nitrogen as carrier gas. The reason of adopting two heaters is that heaters can be fueled by different heating utilities separated by temperature levels. More specifically, it seems more economical to import low pressure and medium pressure steam to heat up to 200 °C at first; this can be followed by a furnace fueled by natural gas to heat up to 280 °C. In other words, it is assumed that if high pressure steam is generated in the plant, this is first expanded in steam turbines to produce electricity and medium to low pressure steam, which is then used for heating purposes.

Since 3-hydroxypropanal is hardly being traced, the main dehydration process has been compacted as $glycerol \rightarrow acrolein + 2H_2O$. It has been tested that acrolein yield by using $FePO_4$ as catalyst drops from above 90% at first time of test sharply down to 66% after using it 4 times under batch operation conditions [28]. There are not many studies focusing on the regeneration ability of this catalyst yet [28, 29, 20], and $FePO_4$ can be easily purchased on the market [30]. Additionally, results of some laboratory experiment for testing catalyst performance of converting glycerol into acrolein are gathered after 70 hours [19, 20]. Hence, the catalyst $FePO_4$ is assumed to get changed completely every 70 hours without regeneration in this simulation.

Acidity of catalyst helps the dehydration process by improving selectivity of glycerol to acrolein, it also causes coke formation and deposit on the catalyst, which deactivates the catalyst at some extent and explains the decrease of catalyst performance as well. Meanwhile, hydrogen can come out with coke formation from glycerol, as shown in Equation 2.11. For simplicity, solid carbon is assumed to be removed through the block "Separator", without rigorous modelling of this separation process.

In order to acquire pure acrolein, which is the most volatile component in this system, both flash and distillation units are combined for purification, as presented in Figure 3.5. The products flow with unreacted glycerol and gases (i.e., N_2, H_2) are cooled down to 15°C in cooler HX-PR-11 for condensing part of vapor. Pressurized flash is needed to remove gases and trap acrolein in liquid phase for further separation. Since the cooled stream is mixed gas/liquid (mainly due to large amount of inert gas being involved), the temperature increase of the two-phase flow is largely different after being pressurized. As for liquid, the increase can be neglected, while for vapor, the increase can be calculated as: $T_{02} - T_{01} = \frac{T_{01}}{\eta}\left[\left(\frac{p_{02}}{p_{01}}\right)^{\frac{\gamma-1}{\gamma}} - 1\right]$ [31]. In Aspen Plus this can be modelled as follows. The flash vessel F-01 is used to split the stream into vapor and liquid at 1 bar and 15 °C. Afterwards, the vapor and the liquid is pressurized to 9 bar through a compressor and a pump, respectively, and then mixed again in flash vessel F-02 for removing gases. The left acrolein and other by-products (all in liquid phase) is sent to distillation column D-01 for further separation. The separated acrolein (in vapor phase at this point) flows into the oxidation section.

For increasing total efficiency and lowering the cost of raw material and environmental impact as well, recycle of unreacted glycerol back to Reactor 1 is considered. Figure 3.4 and 3.5 describe explicitly the flowsheet in dehydration.

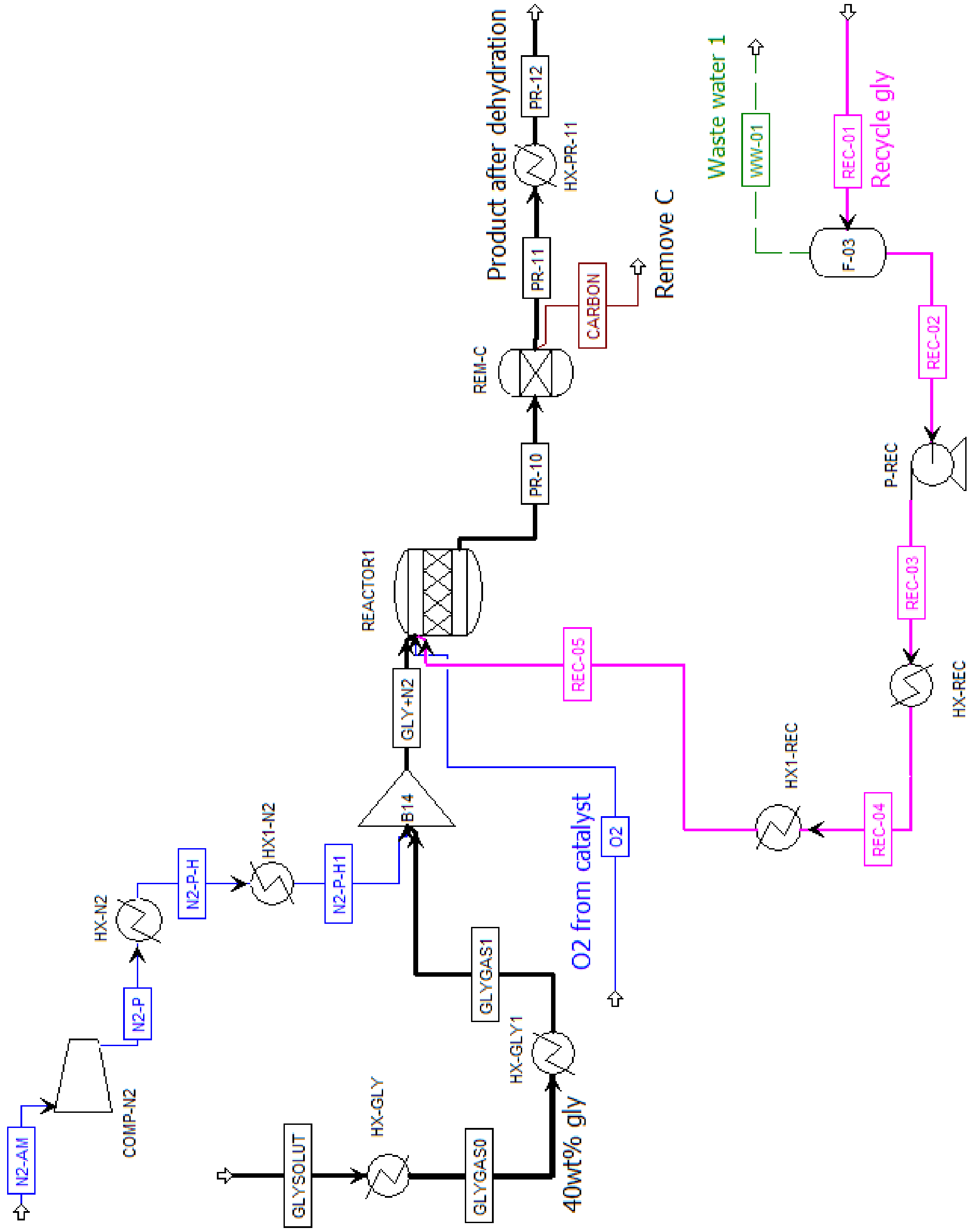

Figure 3.4: Flowsheet of the simulation of dehydration of pure glycerol solution. The explanation of the stream and process unit acronyms can be found in Appendix A.7, A.13 and A.14.

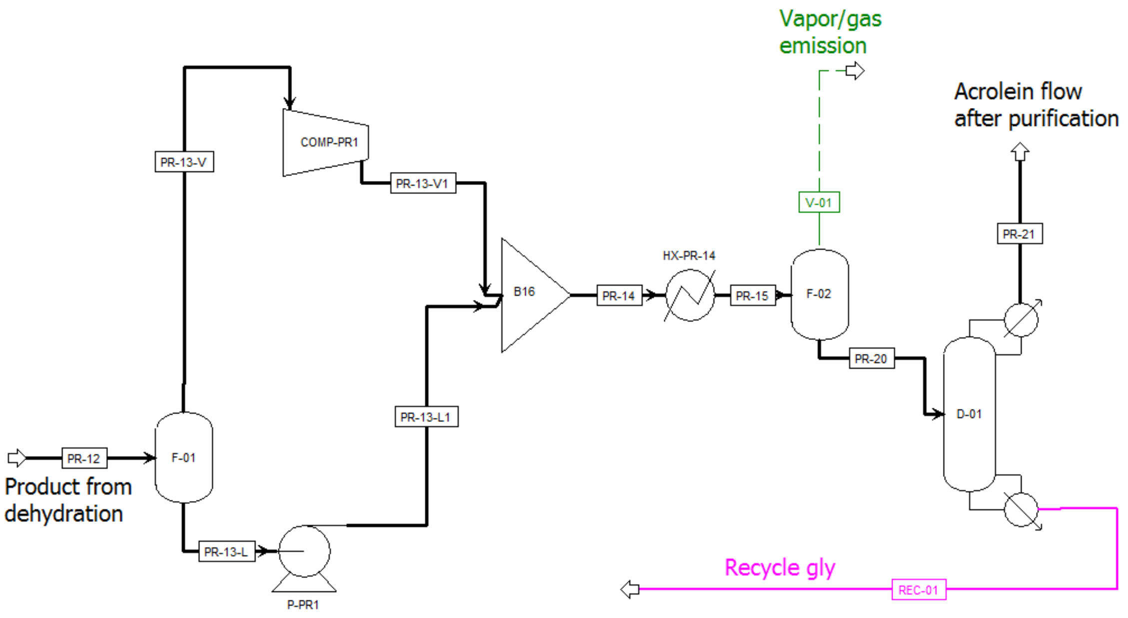

Figure 3.5: Flowsheet of the simulation of purification of dehydration product flow. The explanation of the stream and process unit acronyms can be found in Appendix A.7, A.13 and A.14.

Assumptions in dehydration process

- Reaction conditions: t=280 °C, p=1 bar.
- Catalyst: $FePO_4$ synthesized by hydrothermal method supported on silica sand with whole replacement every 70 hours.
- Reactor model in Aspen Plus $^{®}$: Stoichiometric reactor.
- Composition of crude glycerol by mass weight: Glycerol/H_2O/Fat acid/Methanol/Ash:0.765/ 0.060/ 0.097/ 0.033/ 0.045.
- Feeding stream and carrier gas is scaled-up linearly according to literature data [3].
- Conversion of glycerol: 83.5%; Selectivity of acrolein: 85.5%; Yield of acrolein: 71.4% (yield of other by-products is listed in Appendix A.1).
- Solid carbon dropped on the catalyst: it is assumed to be easily removed (not rigorously modelled) by block "Separator" in Aspen.

3.3.3 Simulation of Oxidation process

The last process step is to oxidize acrolein for producing high purity acrylic acid. Based on the result from Liu et al. [20], acrolein streams and carrier gas, air, have to be heated up to 300 °C at atmospheric pressure before entering Reactor 2. Vanadiummolybdenum mixed oxides supported on silicon carbide (VMo-SiC) has been chosen as catalyst for the reaction. This catalyst has high performance during 70-hour experiment and remain stable at 500°C during coke burning for regeneration [20]. Both nearly complete conversion of acrolein and highest selectivity to acrylic acid can be reached when molar ratio of oxygen/ acrolein is set at 12.5 under the reaction conditions above [20].

The reactor outlet stream is cooled down in two steps, first using cooling water until 15 °C and then a brine solution until 0 °C. After removing the gases such as O_2, N_2, H_2 and CO_2 in the flash vessel F-04, the liquid part is concentrated in two distillation columns D-02 and D-03 to produce pure acrylic acid (> 99.9%). The water streams are sent to conventional waste water treatment plants.

Figure 3.6 and Figure 3.7 present the flowsheets during oxidation and the successive purification in detail.

Assumptions in oxidation process

- Reaction conditions: t=300 °C, p=1 bar.
- Catalyst: V-Mo supported on silica sand with regeneration every 70 hours and whole replacement every 700 hours. Energy for regeneration process is considered.
- Reactor model in Aspen Plus ®: Stoichiometric reactor.
- Air/Acrolein: 62.5/ 1 (mol/mol) (Oxygen/Acrolein: 12.5:1 (mol/mol))
- The conversion of acrolein and acetaldehyde, and yield of each product is calculated on the basis of literature data.
- Yield of acrylic acid from acrolein: 95%. Conversion of other by-products from the dehydration section is listed in Appendix A.2.

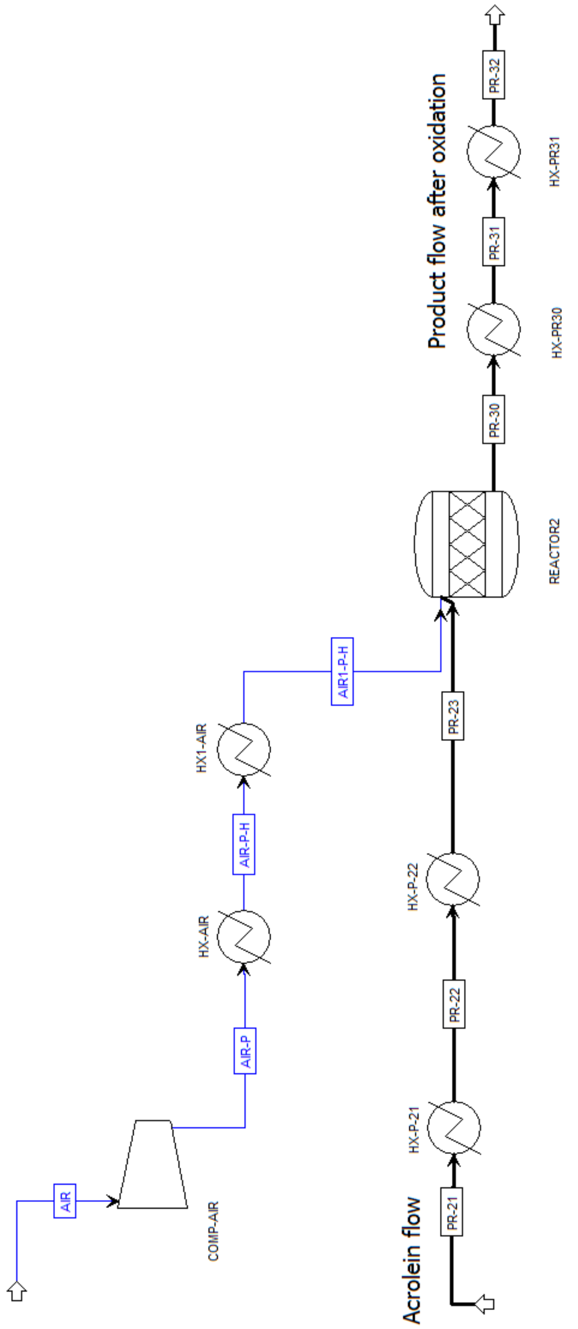

Figure 3.6: Flowsheet of oxidation simulation. The explanation of the stream and process unit acronyms can be found in Appendix A.7, A.15 and A.16.

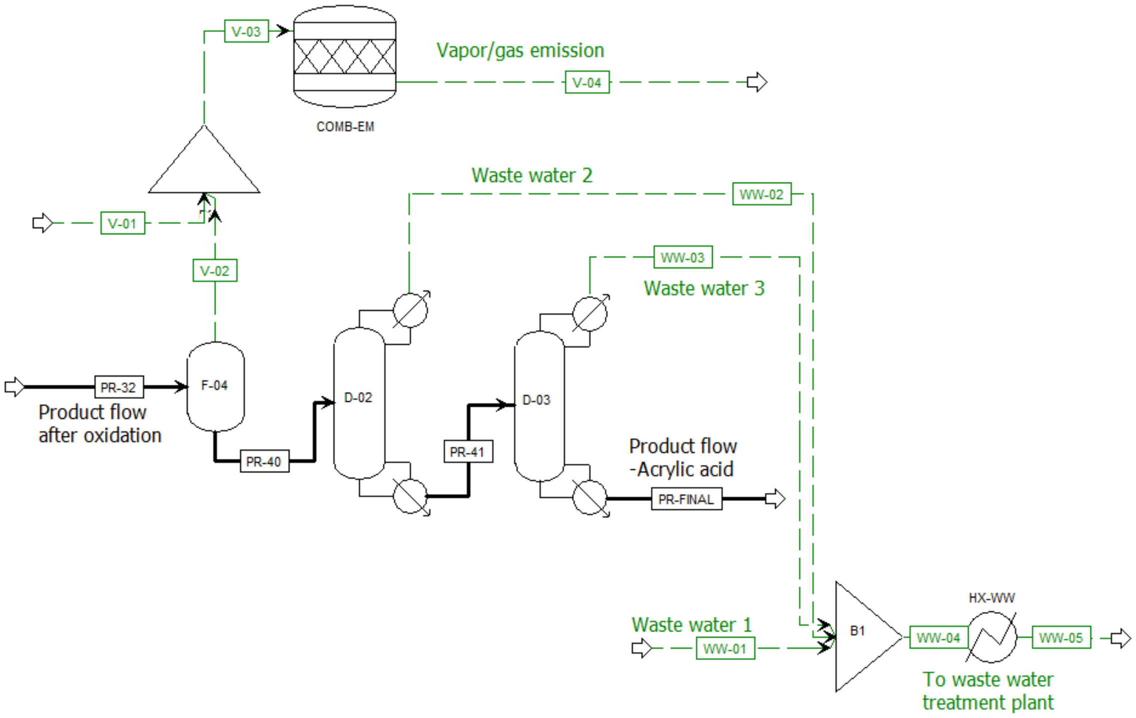

Figure 3.7: Flowsheet of the simulation of purification of oxidation product flow. The explanation of the stream and process unit acronyms can be found in Appendix A.7, A.15 and A.16.

3.4 Pinch analysis

From the flowcharts above, several hot and cold streams with large amount of heat and cold demand are involved in the flow system. Pinch analysis is a well-developed methodology for realizing minimum energy requirement by defining the thermodynamically maximum energy recovery target. This methodology has been widely adopted in industrial chemical plants for optimizing heat recovery, operating conditions and enhancing the whole thermal energy efficiency both for grass-root design and retrofit of heat exchanger network (HEN) [4]. In this project, pinch analysis and simple HEN design is performed by software *Pro_pi2*, which is developed by Department of Energy and Environment at Chalmers University of Technology.

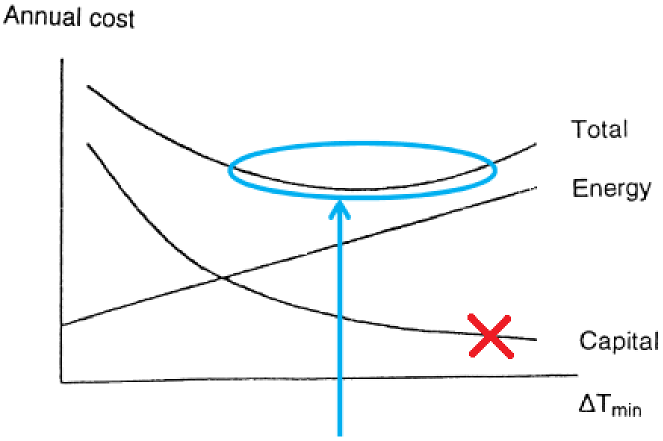

Figure 3.8: Annual cost v.s. ΔT_{min} [4]

Increasing ΔT_{min} pushes up energy costs by increasing driving forces, while lowers capital costs simultaneously [4]. Typically, ΔT_{min} is best chosen in the wide and flat region as pointed by the arrow in Figure 3.8. However, calculation of capital costs is not within the scope of this project. Also, for simplicity, only global temperature difference is used to estimate the energy target, and three levels are selected for sensitivity analysis: ΔT_{min}=10K, ΔT_{min}=20K and ΔT_{min}=40K.

After cascading all the thermal streams (without distillation columns), the grand composite curve (GCC) defines the process pinch point, from which heat sink (above pinch point, absorbing heat) and heat source (below pinch point, releasing heat) can also be defined [4]. Endothermal and exothermal reactors can be also considered in the heat integration, although in some cases for safety and operability reasons this integration potential may be restricted.

Maximum energy recovery target is the difference value between heat demand and minimum heat demand defined by pinch analysis. In practice, 40-70% of this target is expected to be realised (i.e., approximate position of the minimum in Figure 3.8) by adding heat exchangers for optimizing overall thermal efficiency.

3.5 Assessment of techno-economic cost and environmental impacts

Both economic and environmental performance of the two models (benchmark model and glycerol based model) is performed. From economic aspect, only operating cost (Op. cost) is considered in this project expressed per kg of product. Three indicators regarding life-cycle assessment (LCA) are used for assessing environmental and ecological impact from the chemical production, namely cumulative energy demand, eco-indicator 99 and global warming potential.

Cumulative energy demand (CED) is an indicator for assessing the energy intensity during the production life cycle, measured as equivalent mega-joule of energy demand needed to produce 1 kg of product [32, 33]. Global warming potential (GWP) measures the greenhouse gas emission associated with the production of 1 kg of product measured in equivalent CO_2 emission. Several time intervals, such as 20, 100 and 500 years, are usually used for estimation of GWP [34]. Eco-indicator 99 (EI99) expresses the environmental relevance of a product or system in the form of an aggregated figure for producing 1 kg of product. Three kinds of damages are considered in EI99: human health, ecosysem quality and resource depletion [33, 35].

Generally speaking, the higher scores of each indicator means more money is required for running the industrial process and /or less friendly that the process is to the environment.

The substances needed to be summarized in the assessment of benchmark model contain three groups: raw material, utility and waste treatment. Process water, glucose, nutrient feed, CO_2 and phosphoric acid belong to the category of raw material; heat, electricity and cooling water are considered in the category of utility; waste treatment group refers only to waste water treatment. Input data of process water, glucose, nutrient feed, phosphoric acid, heat (for fermentation), and electricity are taken from Cie et al. [9]; result of 3-HP to acrylic acid part is used for input data of heating duties of reboilers, cooling water and waste water treatment. The substances needed to be outlined in the assessment of glycerol based model are also grouped in the three categories. Raw material category includes crude glycerol, catalysts and process water; utilities include heating utility (heat and natural gas), cooling utility (cooling water and cooling medium for cooling down to 0 °C), nitrogen and electricity; lastly, CO_2 emission, catalyst disposal, ash disposal, waste water treatment and incineration of waste vapor/ gases are considered in waste category.

There are two thinking ways of dealing with crude glycerol, one is to use crude glycerol as fuel for incineration and acquire thermal energy, and the other one is to regard glycerol as waste to be treated in conventional waste treatment plants [1]. The former one is commonly seen in developed countries where advanced technologies are

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[1] There are also other alternative ways of treating crude glycerol, e.g., to give it as feed to animals or for landfilling, but these have not been considered in this study.

used for removing the toxic substances from burning waste, such as Sweden, which even imports waste from other countries for running the domestic waste-to-energy power plants [36, 37, 38]; the latter one is mostly adopted in less developed countries with lack of expertise in operating waste incineration plants and other regulation constraints. In this project the crude glycerol is expected to be used for chemical production as the alternative method of the two kinds of treatment above. Herein, two scenarios regarding crude glycerol both for incineration and for being disposed in waste treatment plant are presented and discussed in next chapter. Background data of glycerol for incineration is used in gly-Scenario 1 and that of glycerol for waste water treatment in gly-Scenario 2.

Most of the reference background data of each substance is acquired from ecoinvent[30, 39]; waste water treatment and incineration is calculated with Rerat et al.[40]. Unfortunately, there are still some missing information for the assessment. Background data of catalyst $FePO_4$-H with its supporter and disposal of catalyst V-Mo with its supporter is hardly found. Thus, background data of zeolites including its disposal is used for the estimation.

The detailed background description of each substance is listed in Appendix A.3.

Assumptions in economic cost and environmental impacts assessment

- CED, EI99, GWP and operating cost of crude glycerol used both for incineration and for waste treatment are chosen for the assessment.
- Due to missing information, CED, EI99 and GWP of $FePO_4$ and its disposal is assumed as those of zeolites and its disposal; purchase cost of $FePO_4$ is assumed at its market price \$4.5/kg [30].
- CED, EI99, GWP and purchase cost of V-Mo disposal is assumed as those of zeolites disposal.
- There is no money needed to be paid for disposal of catalyst and ash (from crude glyerol), which only has the environmental concerns.

4

Results

4.1 Simulation results of glycerol based model

4.1.1 Results of key streams

2.48 kg of crude glycerol has been successfully converted into 1 kg of acrylic acid of high purity (99.94%wt). Mole flow of glycerol, acrolein and acrylic acid in the process key streams are listed in Table 4.1. Nearly 2% of glycerol has been lost after preliminary treatment of crude glycerol. Owing to its high boiling temperature (300 °C at 1 bar), almost all the unreacted glycerol has been easily recycled back to Reactor 1. Although acrolein is very volatile and mixed with diverse by-products and inert gases, 92.4% of this main dehydration product has been successfully kept in the flow to Reactor 2. On the other hand, although the highly efficient catalyst has been selected for oxdiation by turning 95% of acrolein into acrylic acid, 12% of acrylic acid is lost to waste streams after two-column purification. This is mainly because of involvement of large amount of water, inert gases and various by-products making this purification step challenging. The composition of the final product stream can be seen in Table 4.2.

Table 4.1: Results of key streams

Step	Component	Name of steam	Flow (kmol/hr)
Pre-treatment	Tot. crude glycerol	$CRUDGLY$	732.3
	Glycerol in crude gly	$CRUDGLY$	467
	Glycerol after treatment	$GLYGAS0$	457
Dehydration	Acrolein	$PR-10$	390.3
	Acrolein after purification	$PR-21$	360.7
Recycle	Unreacted gly	$PR-10$	89.7
	Recycled gly	$REC-05$	89.6
Oxidation	AA	$PR-30$	342.9
	AA-Final	$PR-FINAL$	301.4

Table 4.2: Results of final product stream

Component	Mass fraction (%)
Glycerol	0
Acrolein	0
Acrylic acid	99.94
Water	TRACES
O_2	0
H_2	0
Acetaldehyde	0
Acetone	0
CO_2	0
Allyl alcohol	TRACES
Formic acid	TRACES
Propanoic acid	0.033
Formaldehyde	0
Propanal	0
N_2	0
CO	0
C	0
Hydroxyacetone	TRACES
Acetic acid	0.024
Argon	0
Methanol	TRACES
Ash	0
Fat acid	0

4.1.2 Waste treatment

Table 4.3: Waste emission

	WTOINC	WW-01	WW-02	WW-03	V-01	V-02
Water content (mass %)	21.9	99.1	92.1	95.9	0	0
LHV (MJ/kg)	24.9	0.1	1.6	0.6	1.2	0.1
Total flow (kg/h)	9794	25463	17420	43086	48924	642547
Treatment	Incineration	WW treatment plant			Burning on-site	

In this model, there are totally six vapor streams exhausted from flash vessels and distillation columns, and they need to be treated for lowering the environmental impact instead of being discharged into environment directly. The methanol removal stream during pre-treatment of crude glycerol has a high LHV value and can be incinerated for acquiring thermal energy. Water content in stream WW-01, WW-02 and WW-03 is higher than 90 %, hence, these three streams shall be mixed and cooled down to 15 °C before being sent to waste water treatment plant; the LHV and water content of both stream V-01 and stream V-02 are rather low and are burnt on-site to avoid direct release of organic substances. The results are listed in Table 4.3.

4.1.3 Column design

Table 4.4 presents the main column design parameters. Although no capital cost assessment was performed, the column design follows industrial guidelines with respect to the height/diameter ratio [41]. It can also be easily observed that the reboiler duty accounts for a significant amount of energy consumption. Considering that 21.7 t/hr acrylic aicd is produced, the three reboiler duties sum up to approximate 25 MJ-heat/kg of acrylic acid. This is mainly caused by the tough purification task even reflux ratio is set quite low.

Table 4.4: Column design parameters

	D-01	D-02	D-03
Stages	70	70	70
Diameter (m)	4.82	4.04	8.10
Height (m)	51	51	51
H/D	10.6	12.6	6.3
Tray spacing (m)	0.609	0.609	0.609
Reflux ratio	0.25	1.95	1.18
Reboiler duty (kW)	60327	38010	56976
Reboiler temperature (°C)	101	100	141
Condenser duty (kW)	10532	19990	30719
Condenser temperature (°C)	96	99	100

4.2 Pinch analysis

4.2.1 Grand composite curve

Pinch analysis was performed for three different ΔT_{min} values as presented in Table 4.5. Minimum hot utility increases with increasing driving force as expected, hence, theoretical maximum energy recovery target is set as 154.83 MW at ΔT_{min}=10K, 152.55 MW at ΔT_{min}=20K and 143.64 MW at ΔT_{min}=40K.

Table 4.5: Pinch analysis-Maximum energy target

Scenario	ΔT_{min}=10K	ΔT_{min}=20K	ΔT_{min}=40K
Pinch temperature (°C)	295	290	280
Minimum hot utility (kW)	2285	4570	13476
Minimum cold utility (kW)	139176	141461	150367
Hot demand (kW) (without distillation columns)	157115	157115	157115
Maximum energy recovery target (kW)	154830	152545	143639

Figure 4.1, Figure 4.2 and Figure 4.3 illustrate grand composite curves (GCC) regarding three levels of global temperature difference, only including the process streams without distillation columns, more strictly, these curves will be called as "background grand composite curve" instead. From the three GCCs, there is more than 20MW of available heat at nearly 280 °C (shifted temperature). Interestingly, the temperature of column D-01 and D-02 is 100 °C and that of D-03 is 141 °C, as listed in Table 4.4, which allows the columns to be partially heat integrated to the background process. However, since there is no excess heat at around of the column temperature plus the temperature difference (i.e., 100 °C plus ΔT_{min}=20K), it seems preferable to use the excess high level heat (280 °C) to other process or to the utility system (i.e., in a total site analysis concept) and use low or medium level heat for reboilers of columns. Much of this high level heat comes from exothermal energy released from oxidation reaction; hence, utilizing the exothermal energy in heat integration in a practical way is of high importance for higher thermal efficiency.

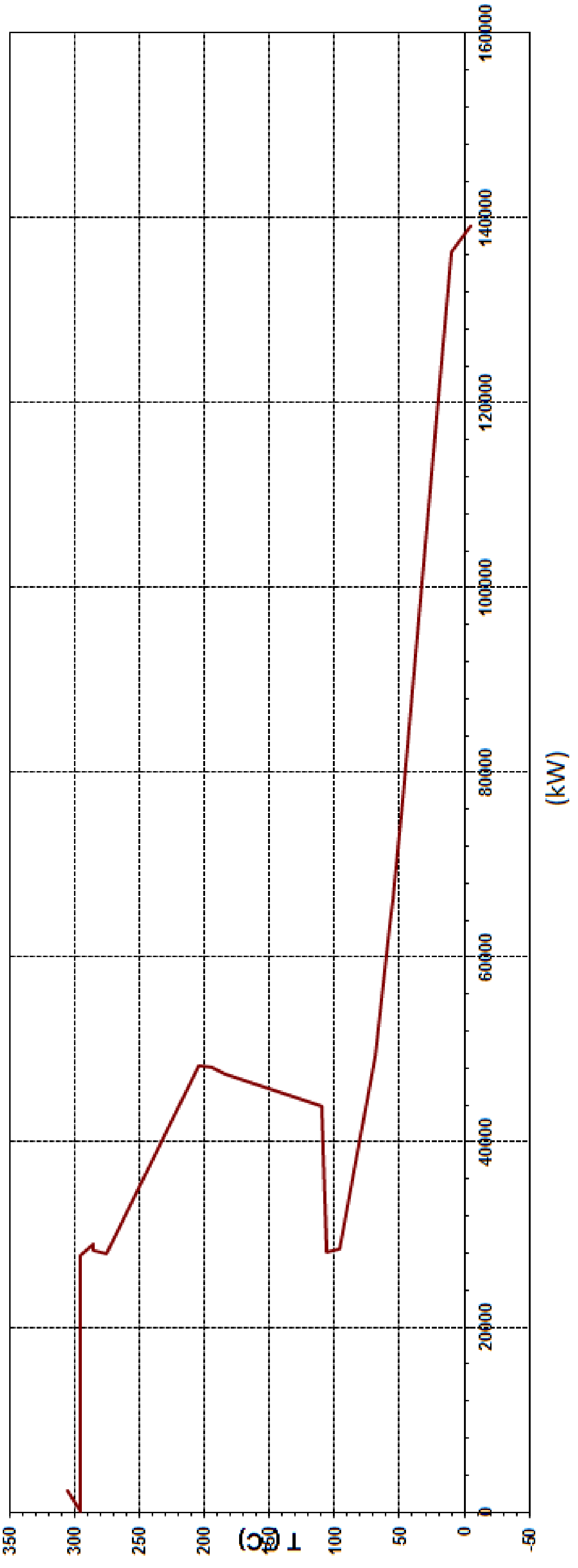

Figure 4.1: Grand composite curve (global ΔT_{min}=10K)

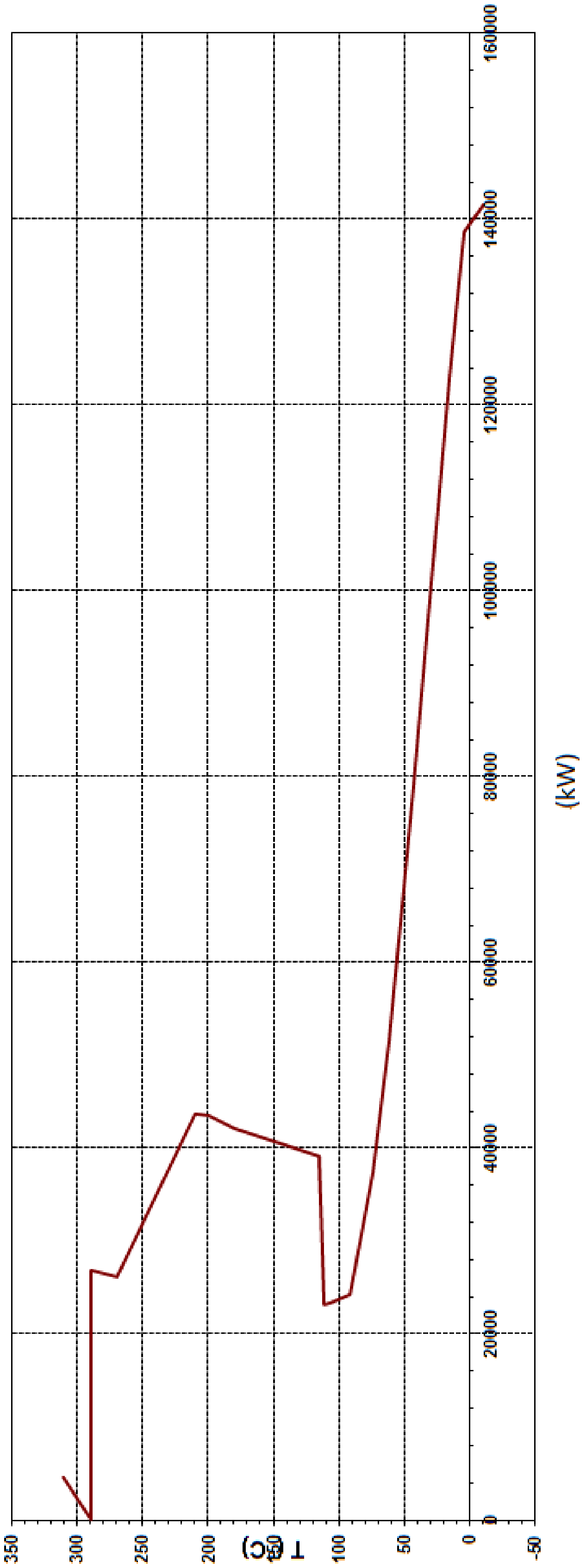

Figure 4.2: Grand composite curve (global ΔT_{min}=20K)

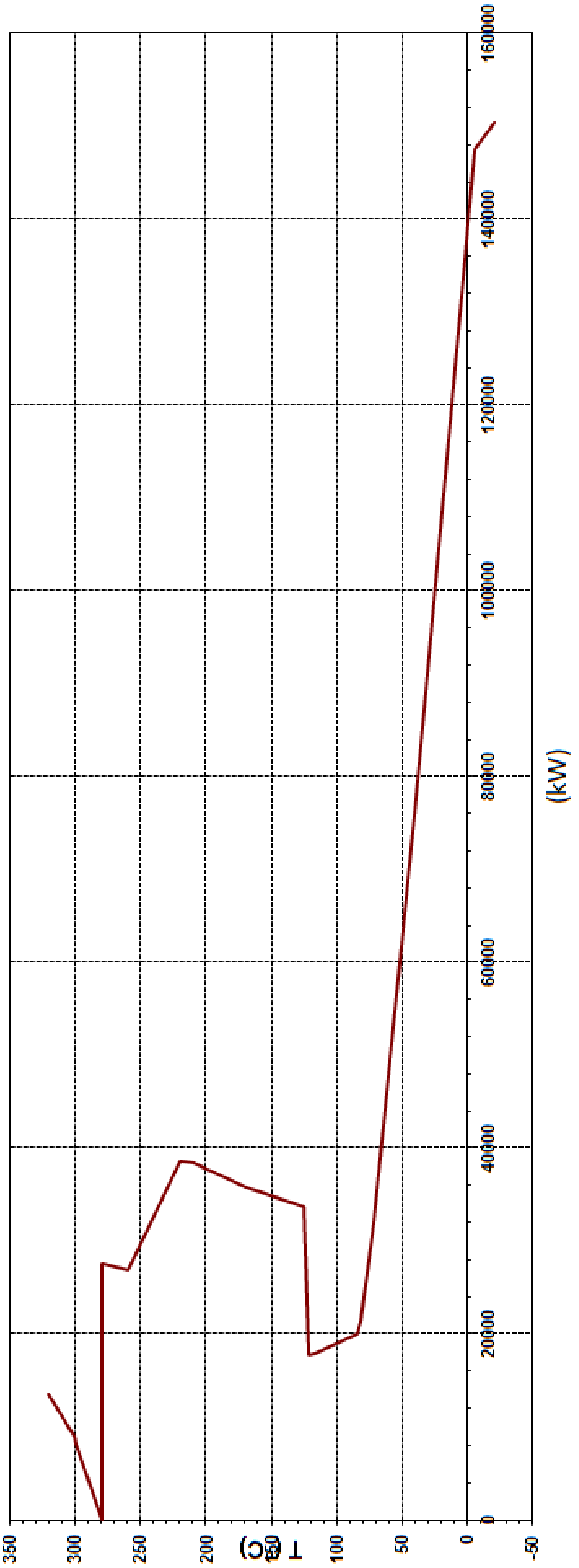

Figure 4.3: Grand composite curve (global ΔT_{min}=40K)

4.2.2 Design of heat exchanger networks

After adopting seven heat exchangers, almost 70% of maximum energy recovery target is reached in all three cases of ΔT_{min}; detailed results are listed in Table 4.6. The HEN is shown in Figure 4.4, Figure 4.5 and Figure 4.6. Among the seven heat exchangers, it can be noticed that there are two heat exchangers are siginificantly larger than others, the exchanger ($Q \approx 55$MW) between stream 3 and stream 8 and the exchanger ($Q \approx 20$MW) between stream 17 and stream 20. There is also a small heat exchanger, which is between stream 6 and stream 16 with only 0.8MW of heat being transferred.

Table 4.6: Pinch analysis-Energy recovery

Scenario	ΔT_{min}=10K	ΔT_{min}=20K	ΔT_{min}=40K
Pinch temperature (°C)	295	290	280
Hot demand (kW)	157115	157115	157115
Maximum energy recovery target (kW)	154830	152545	143639
Number of HEX	7	7	7
Total heat has been recovered (kW)	108869	105702	97603
Heat recovered above 200 °C (kW)	33538	30371	22272
Heat recovered below 200 °C (kW)	75331	75331	75331
New total heat demand above 200 °C (kW) (including regeneration of catalyst)	4344	7511	15610
New total heat demand below 200 °C (kW) (including distillation columns, regeneration of catalyst)	199386	199386	199386

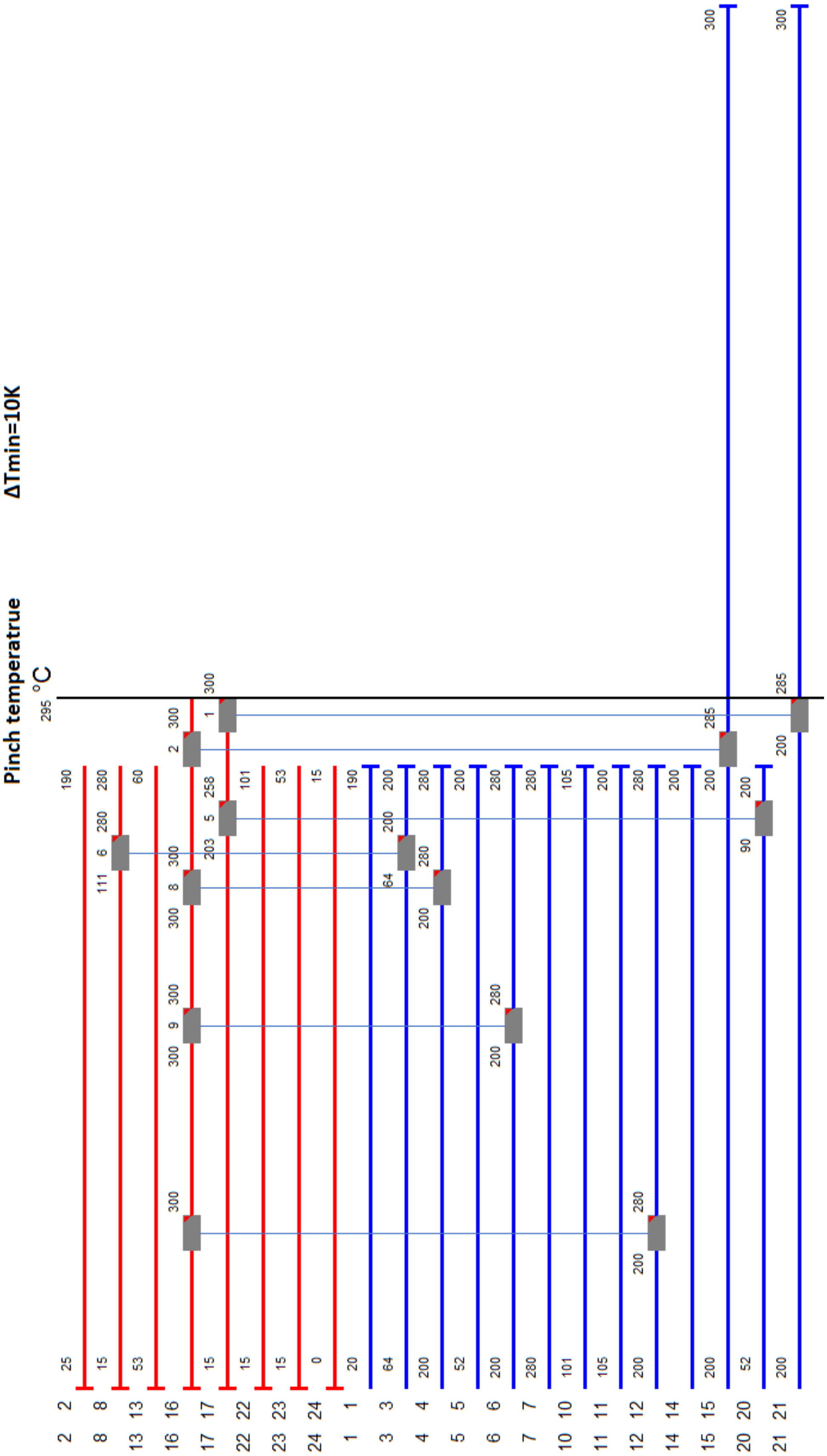

Figure 4.4: Heat exchanger network design (global ΔT_{min}=10K)

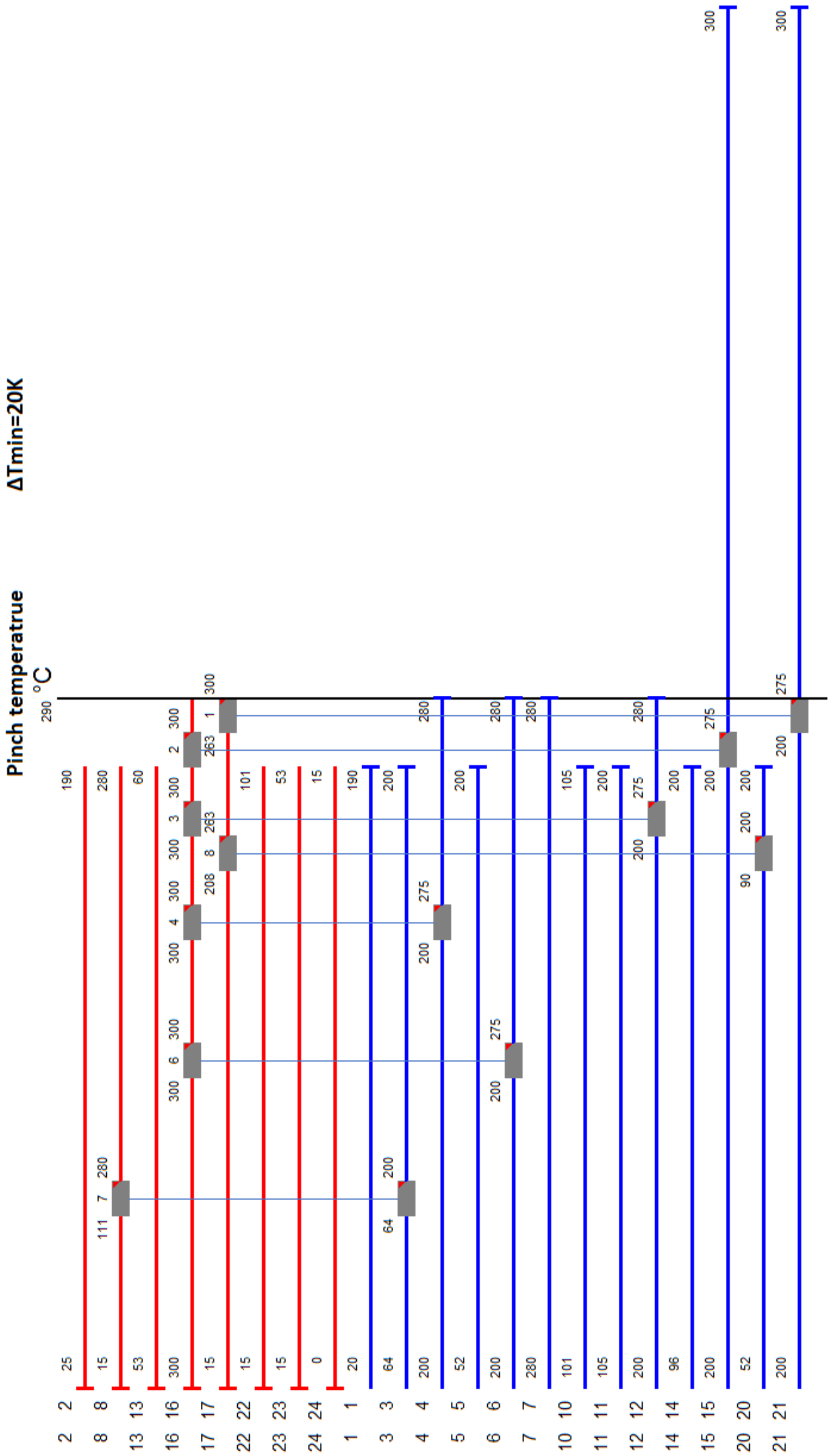

Figure 4.5: Heat exchanger network design (global ΔT_{min}=20K)

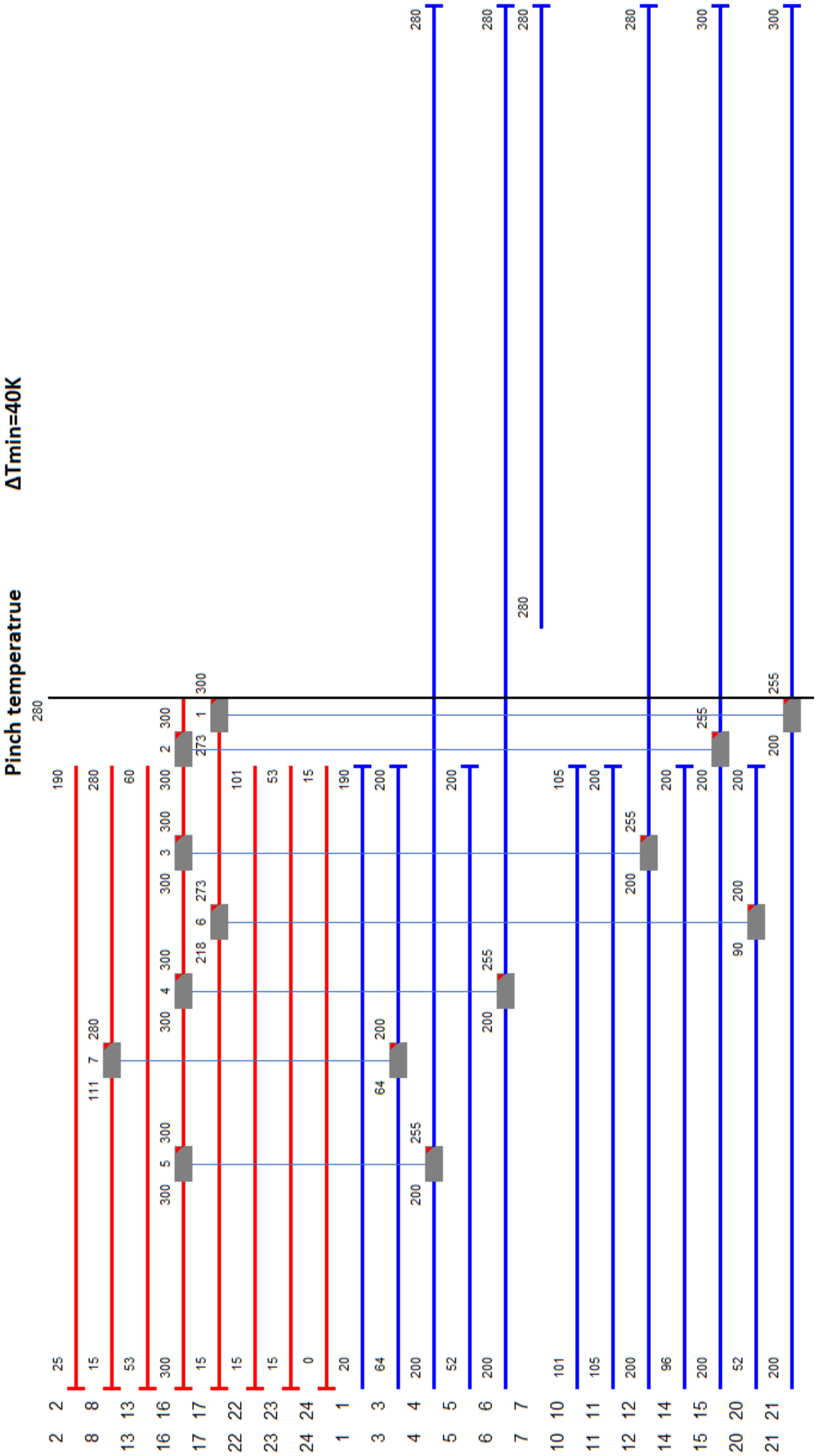

Figure 4.6: Heat exchanger network design (global ΔT_{min}=40K)

4.3 Techno-economic and Environment Analysis

As introduced in Section 3.5, the simulation results are discussed for gly-Scenario 1 (glycerol for incineration) and gly-Scenario 2 (glycerol for waste treatment) based on the two different alternative methods of utilizing glycerol. The assessment of these two glycerol based scenarios are presented explicitly and also compared with benchmark model (based on glucose) and reference level (conventional production based on fossil fuels) in this section.

The contribution from the two steps (dehydration and oxidation including purification) in the non-integrated case (base case) for each performance indicator is presented in Figure 4.7. It can be concluded that most of the environmental impact and operating costs is allocated to the glycerol to acrolein step. This is more evident when the alternative scenario for the fate of glycerol is in waste-to-energy incineration plants. It is important to note that the conventional fossil-based process does not involve the formation of acrolein as an intermediate in the production of acrylic acid.

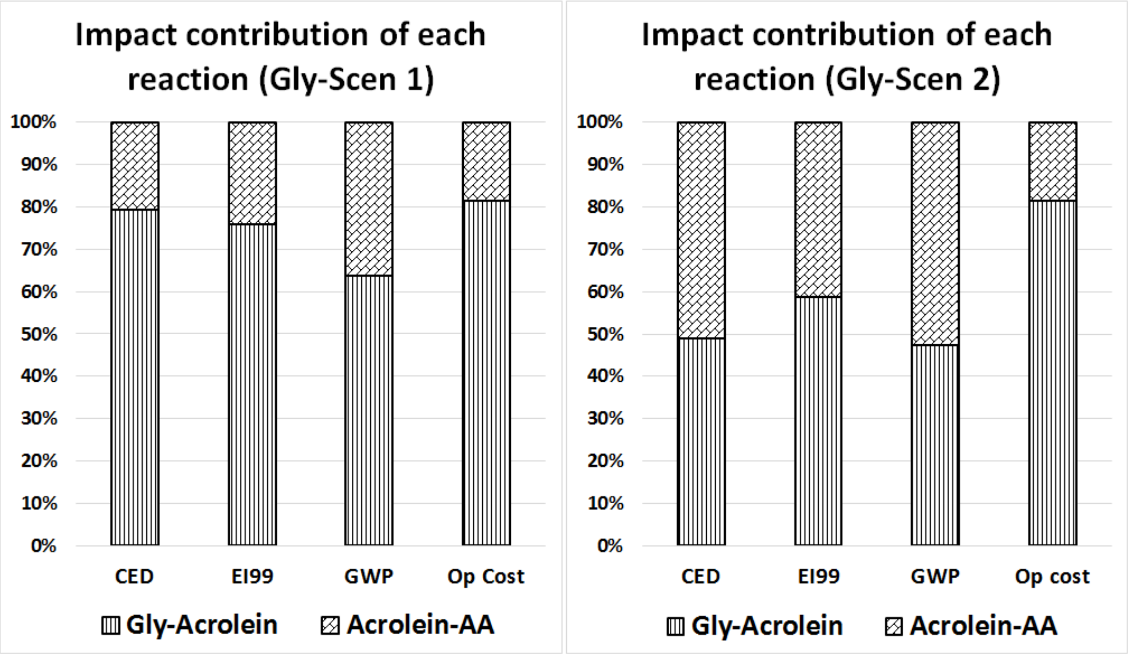

Figure 4.7: Comparison of techno-economic and environmental impact: from glycerol to acrolein v.s. from acrolein to acrylic acid

4.3.1 Results of CED assessment

CED of producing acrylic acid based on glycerol, glucose and fossil fuel are compared in Figure 4.8. Base case refers to the flowsheet without heat integration; while ΔT_{min}=10K, ΔT_{min}=20K and ΔT_{min}=40K are the cases with heat recovery for different ΔT_{min} values, respectively. The two glycerol scenarios are included in each case. RER refers to the conventional production based on fossil fuels under European conditions, and benchmark model refers to the glucose based production as introduced in Section 2.1 and Section 3.2. These arrangements are also applied on the results of EI99 and GWP indicators. In Figure 4.8, with the help of heat recovery, CED can be reduced by around 26 MJ_{-eq} 1 kg of acrylic acid. However, CED results of gly-Scenario 1 are almost double compared to the RER case even after heat recovery. Gly-Scenario 1 is the worst scenario in this indicator, closely followed by the benchmark model. The CED for gly-Scenario 2 is lowest, the value of base case reaching the RER values and being further reduced after adopting heat recovery.

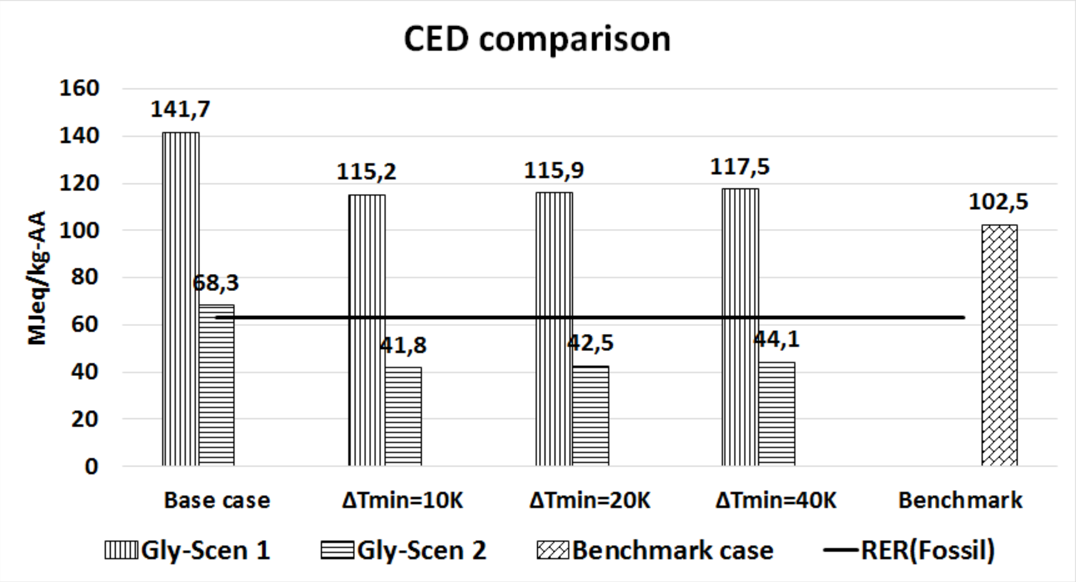

Figure 4.8: CED of producing AA based on glycerol and glucose compared to EU standard production (RER)

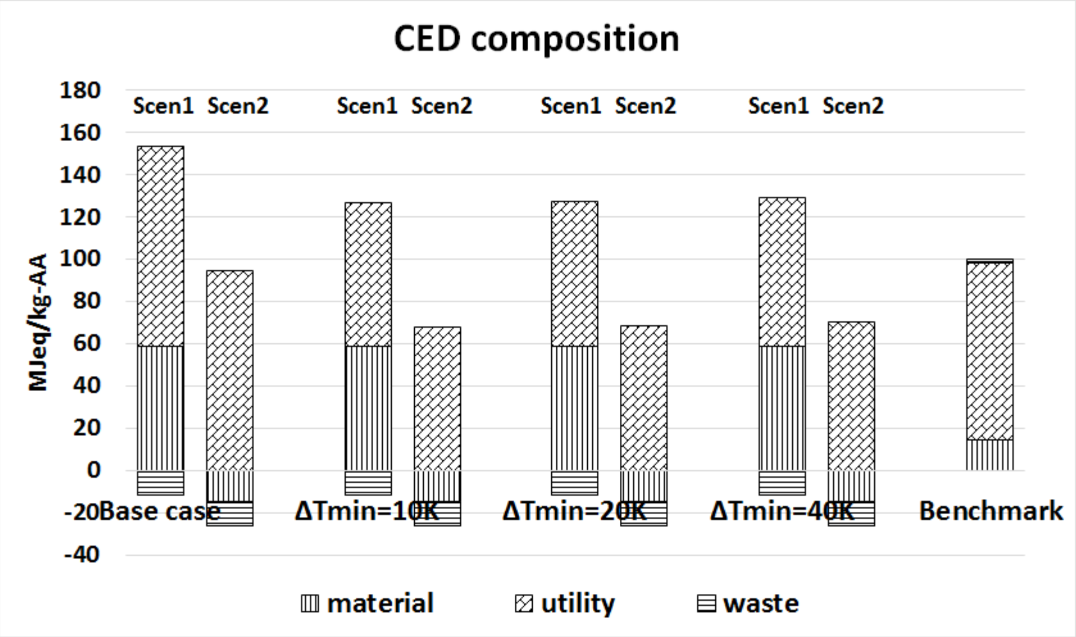

Figure 4.9: CED decomposition to material, utilities and waste impacts

Since conventional production way is not modeled in this project, Figure 4.9 only illustrates the CED composition stacked by three groups (material, utility and waste) for the glucose based model and glycerol based model for the two scenarios. Material and utility are the main contributors. Detailed decomposition of the environmental impacts for utilities,materials and waste impact can be seen in Figure 4.10, Figure 4.11 and Figure 4.12.

Figure 4.10 shows that glycerol and catalysts play the major role in material impact, the only difference being that CED values are positive in gly-Scenario 1 and negative in gly-Scenario 2. As for utility decomposition (Figure 4.11), the difference among all the glycerol based models only relates with the adoption of heat integration. From Figure 4.11, it can be seen that heat and nitrogen account for most of utility CED values. Heat demand can be lowered by one third with heat recovery and much less natural gas is needed with smaller temperature difference. Electricity use does not account for much energy demand and energy demand of cooling is nearly zero. In the waste decomposition (Figure 4.12), results of all the glycerol based models are the same. The thermal energy released from burning methanol removal of crude glycerol is more than energy demand for handling catalyst disposal, ash disposal and waste water, reducing the total CED number.

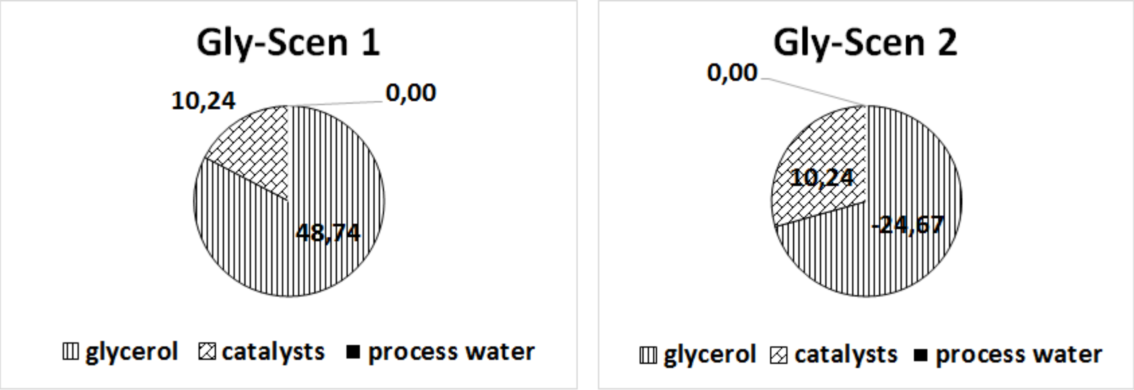

Figure 4.10: CED: Material decomposition of two glycerol based scenarios (Unit: MJ$_{\text{-eq}}$/kg-AA)

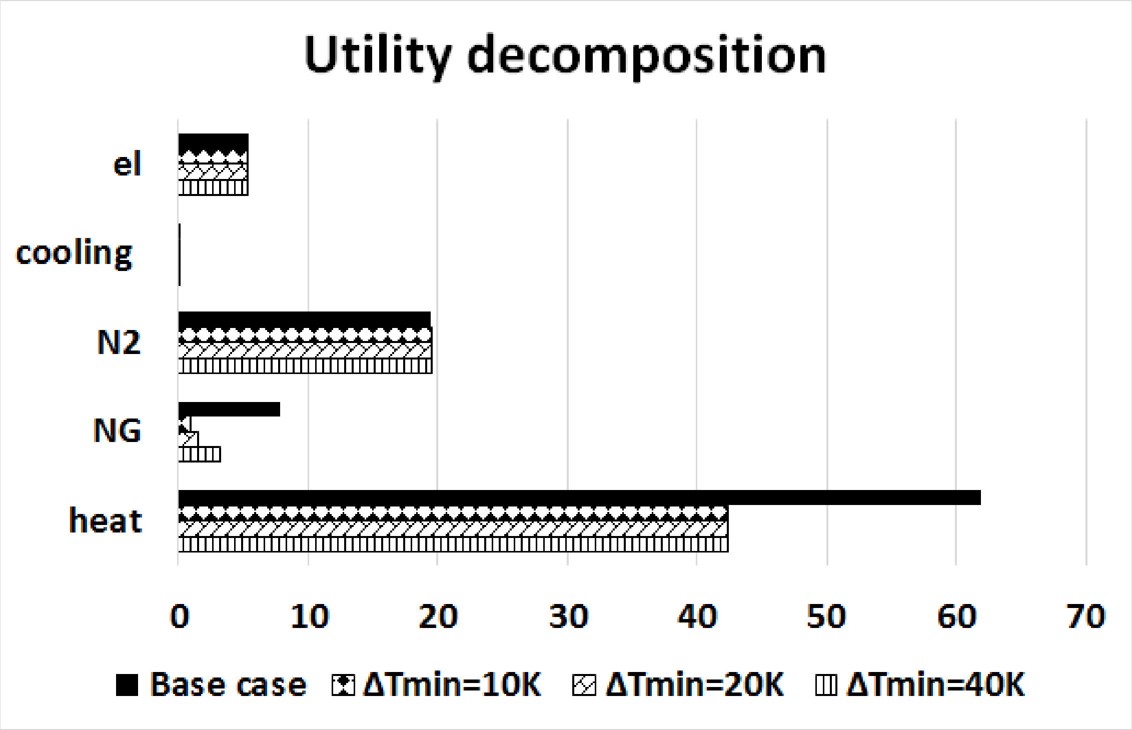

Figure 4.11: CED: Utility decomposition from glycerol to produce acrylic acid of two glycerol based scenarios (Unit: $MJ_{\text{-eq}}$/kg-AA)

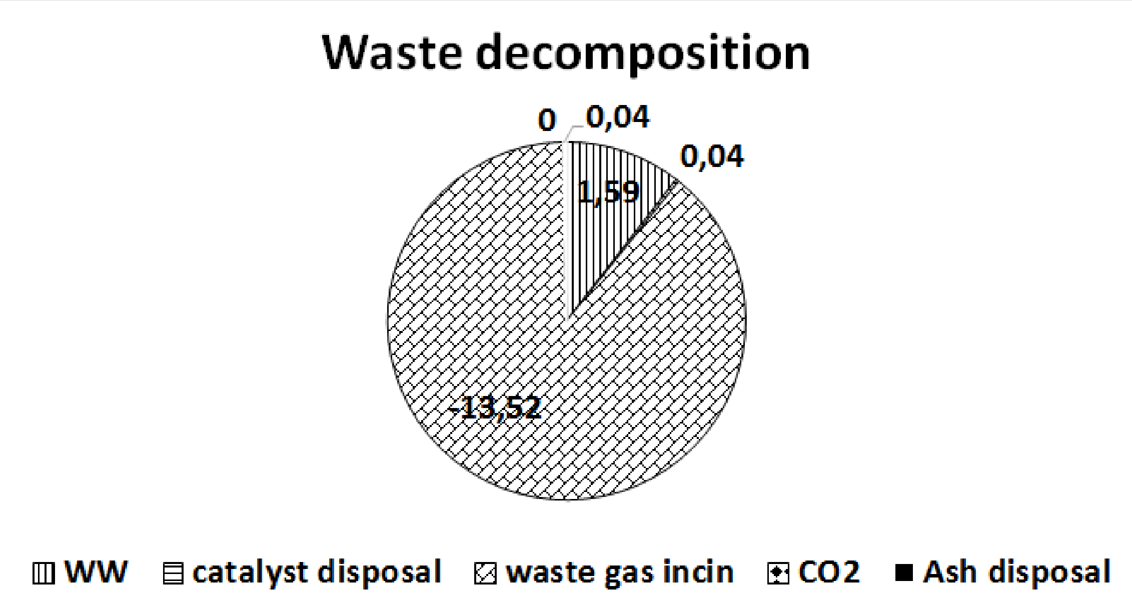

Figure 4.12: CED: Waste decomposition from glycerol to produce acrylic acid of two glycerol based scenarios (Unit: $MJ_{\text{-eq}}$/kg-AA)

4.3.2 Results of EI99 and GWP assessment

EI99 and GWP are the two indicators focusing on the environmental damages from the chemical production process, and the results of the two aspects are discussed together in this part.

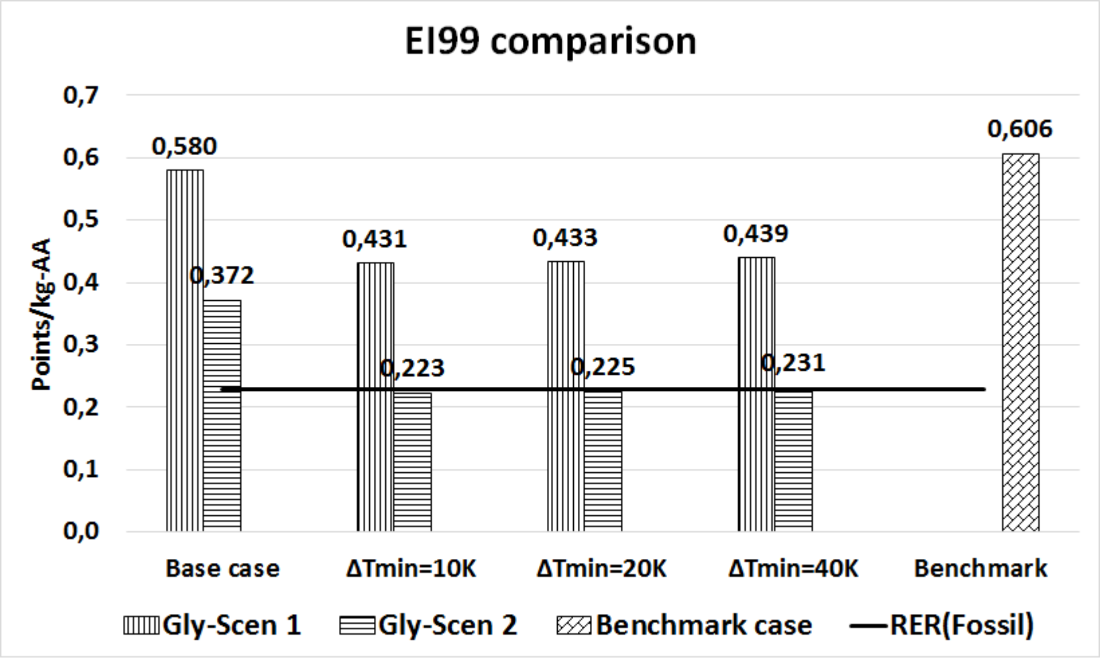

Figure 4.13: EI99 of producing AA based on glycerol and glucose compared to EU standard production (RER)

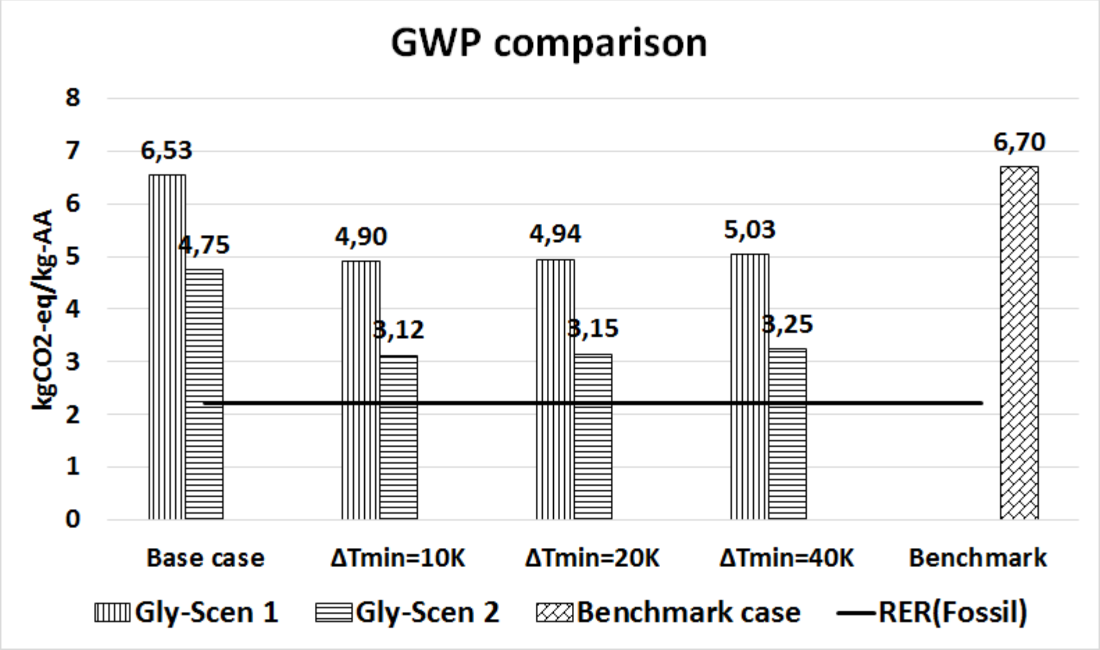

Figure 4.14: GWP of producing AA based on glycerol and glucose compared to EU standard production (RER)

Figure 4.13 and Figure 4.14 exhibit that benchmark model becomes the worst scenario for both indicators, the results of benchmark model being more than double the RER case. Gly-Scenario 2 is much more environmentally friendly than gly-Scenario 1. In EI99 indicator, results of gly-Scenario 2 are almost half of gly-Scenario 1 with the help of heat recovery and are competitive to the RER case, much like the result of CED indicator. As for GWP indicator, although heat recovery helps lowering the GWP values significantly, the impacts are still worse than the RER case.

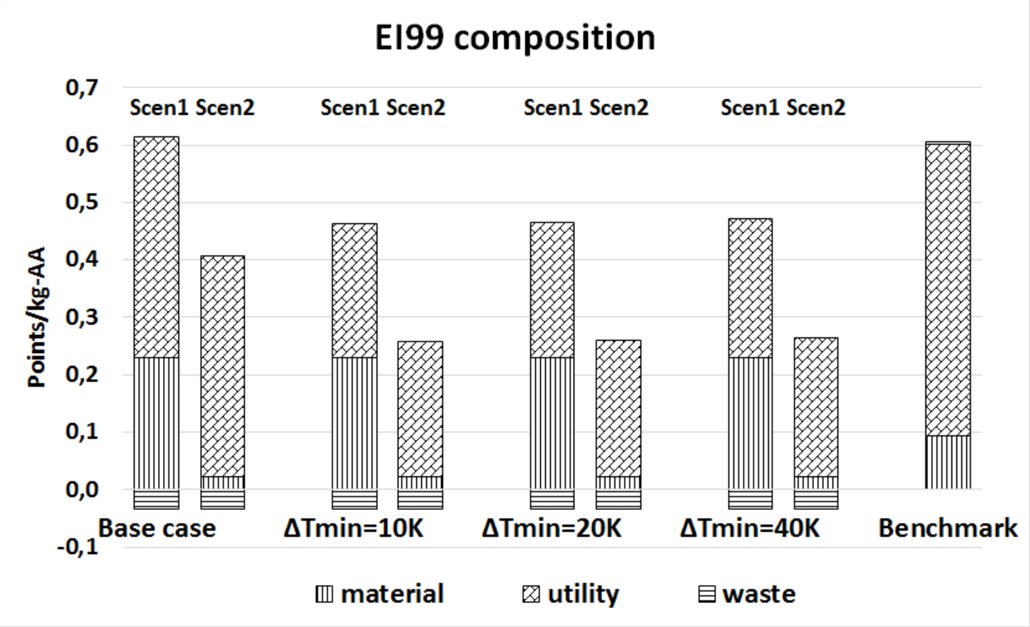

Figure 4.15: EI99 decomposition to material, utilities and waste impacts.

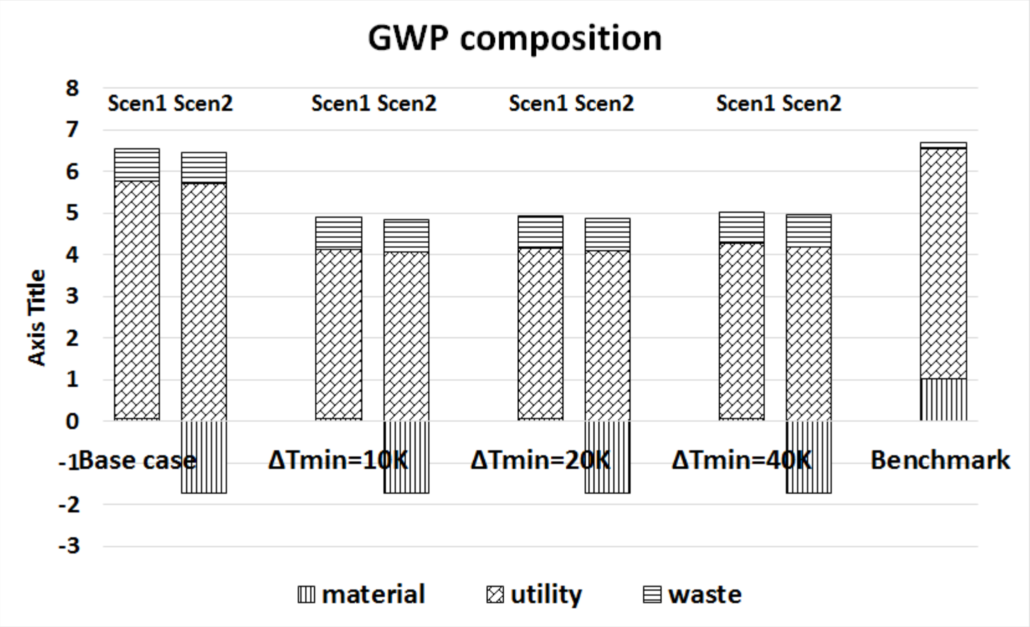

Figure 4.16: GWP decomposition to material, utilities and waste impacts.

Figure 4.15 and Figure 4.16 respectively illustrate stacked composition of EI99 and GWP indicator of benchmark model and glycerol based models with/without heat recovery.

Utility use is the biggest part of the environmental impact for almost all the cases. Similar to CED, for EI99 indicator gly-Scenario 1 becomes less environmentally friendly since other forms of heat resources shall be involved for compensation of thermal energy loss from glycerol, while gly-Scenario 2 can save material and energy for waste treatment and produce acrylic acid instead by posing less harm to the environment. However, there is a difference when utilizing glycerol to produce acrylic acid with respect to GWP indicator for the both scenarios. This is owing to emission of CO_2 from burning glycerol as an alternative scenario of glycerol utilization. Still, the emission prevention from incineration for thermal energy is smaller than from waste treatment, which explains why negative parts in gly-Scenario 2 is larger than gly-Scenario 1 and total numbers of gly-Scenario 2 lower than gly-Scenario 1 as shown in Figure 4.14. This is also shown in the material decomposition in Figure 4.17 and Figure 4.18.

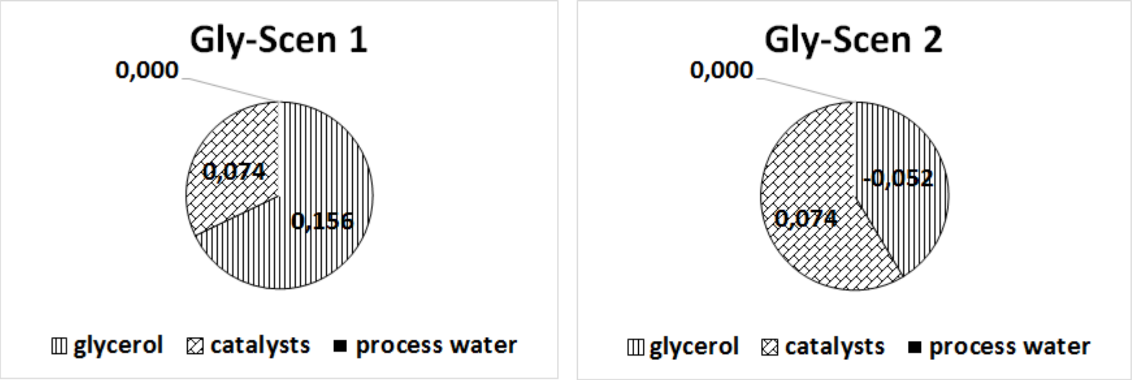

Figure 4.17: EI99: Material decomposition from glycerol to produce acrylic acid of two glycerol based scenarios (Unit: Points/kg-AA)

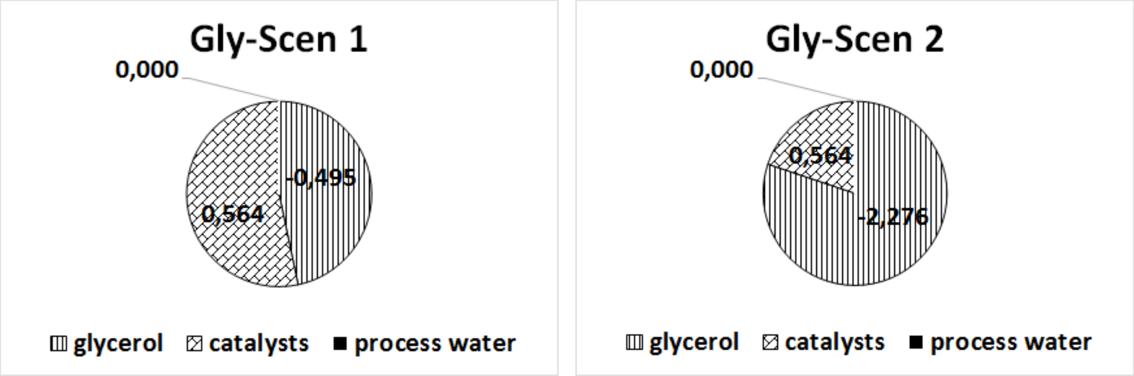

Figure 4.18: GWP: Material decomposition from glycerol to produce acrylic acid of two glycerol based scenarios (Unit: $kgCO_{2\text{-eq}}/kg\text{-}AA$)

Figure 4.19 and Figure 4.20 present the utility decomposition of EI99 indicator and GWP indicator, respectively. Similar to the CED indicator, heat and nitrogen are the two main drivers, accounting for most of the impact on environment. Heat demand and natural gas use can be lowered by approximately one third with heat recovery.

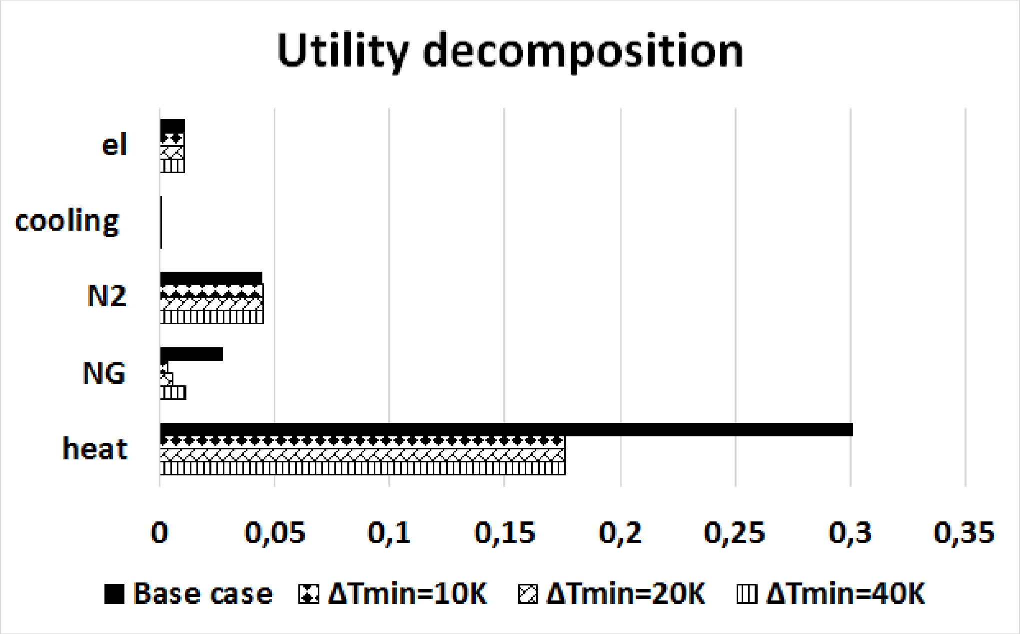

Figure 4.19: EI99: Utility decomposition from glycerol to produce acrylic acid of two glycerol based scenarios (Unit: Points/kg-AA)

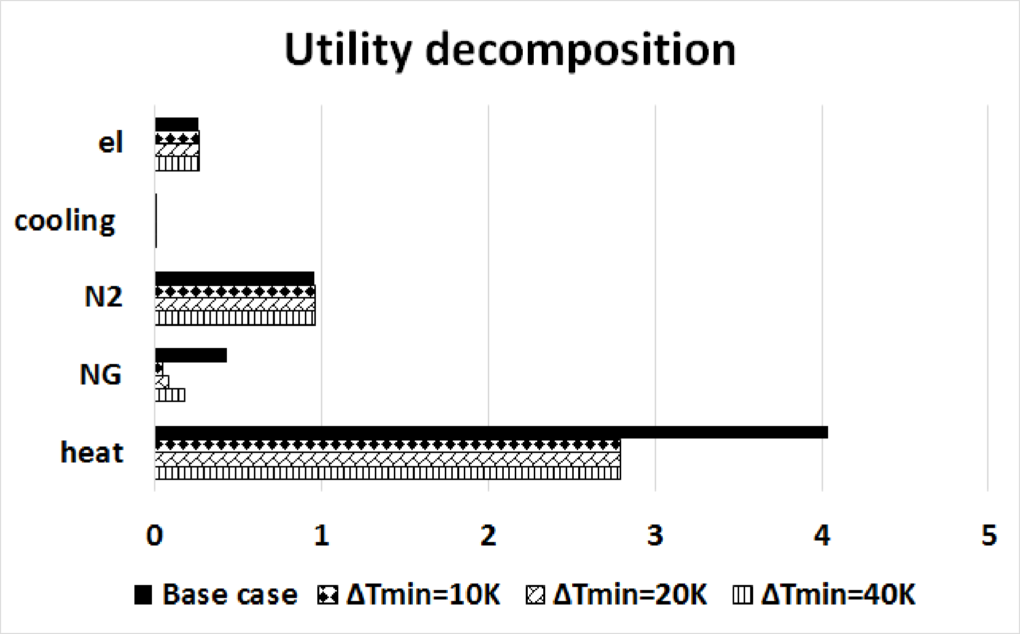

Figure 4.20: GWP: Utility decomposition from glycerol to produce acrylic acid of two glycerol based scenarios (Unit: $kgCO_{2\text{-eq}}$/kg-AA)

In the waste decomposition, the situation for the two indicators is different. In EI99 indicator, the thermal energy released from burning methanol removal of crude glycerol still overcomes the impact posed by waste water, catalyst disposal, ash disposal and CO_2 emission; however, the contribution from waste gas incineration is much smaller when coming to GWP indicator. Moreover, the CO_2 emission from burning the waste vapor also contributes to the global warming potential owing to involvement of organics in the waste emission.

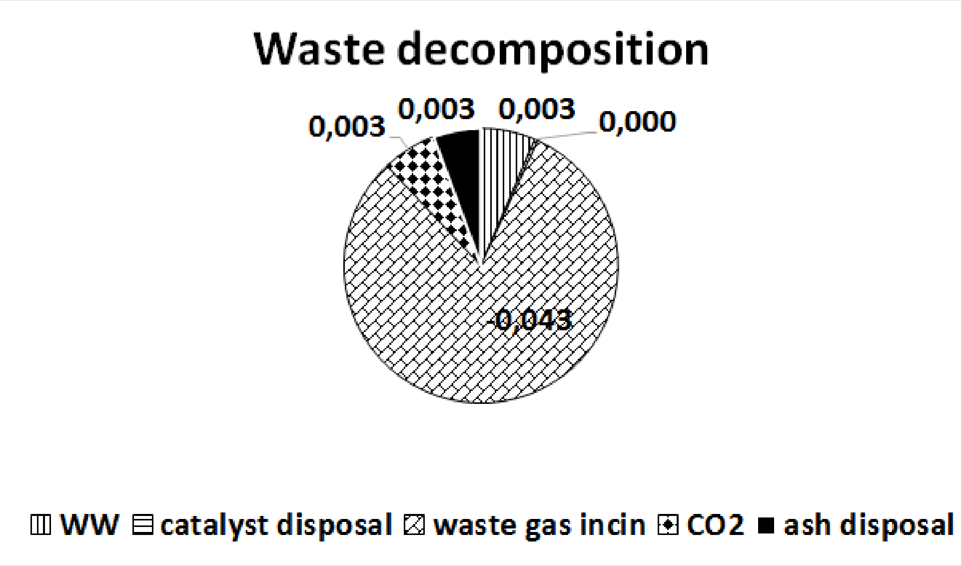

Figure 4.21: EI99: Waste decomposition from glycerol to produce acrylic acid of two glycerol based scenarios (Unit: Points/kg-AA)

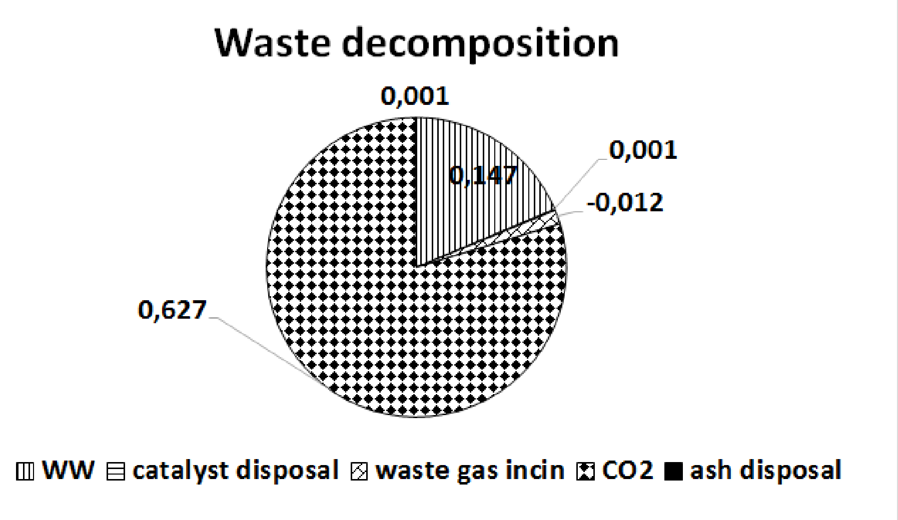

Figure 4.22: GWP: Waste decomposition from glycerol to produce acrylic acid of two glycerol based scenarios (Unit: $kgCO_{2\text{-eq}}$/kg-AA)

4.3.3 Results of operating cost assessment

Price of crude glycerol is same in gly-Scenario 1 and gly-Scenarios 2, hence, results of total operating cost are exactly the same in the two scenarios. Figure 4.23 shows that the glycerol based production of acrylic acid can be competitive to the conventional fossil based one and outperforms the glucose based production. The operating cost of the base case is at the price level of the RER case, and can be further reduced by around 13% with heat recovery. On the contrary, benchmark model requires around 14% more than the price of the acrylic acid prices in the RER case. Unlike glycerol based model, material use account for more than half of the total operating cost in benchmark case, which is mainly owing to the expensive glucose feedstock and nutrient use for fermentation. Only a tiny piece of cost share needs to be paid for waste both in glycerol and benchmark models.

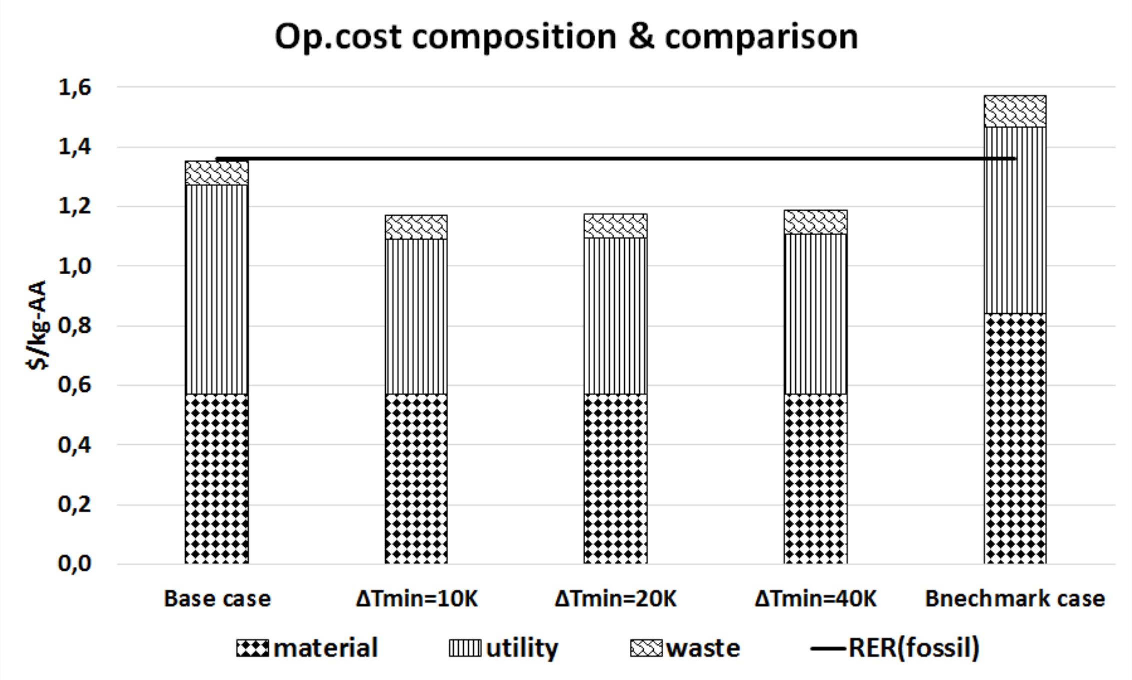

Figure 4.23: Operating cost of producing AA based on glycerol and glucose compared to EU standard production (RER)

Figure 4.24 presents the material decomposition in operating cost. It can be seen that catalysts account for 20% of the total operating costs, slightly higher than crude glycerol. With respect to utilities decomposition in Figure 4.25, heat demand is still the biggest contributor, however, closely followed by the expensive pure nitrogen. Cost of natural gas has been substantially reduced to nearly zero with heat integration (ΔT_{min}=10K). Electricity use and cooling utility account together for less than \$0.1 per kg of acrylic acid. As shown in Figure 4.26, the total cost of waste treatment is less than \$0.1 per kg of acrylic acid.

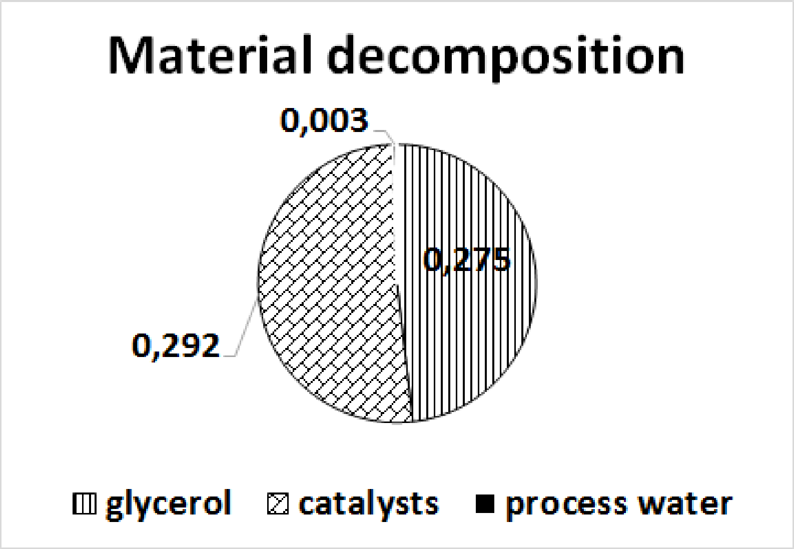

Figure 4.24: Op. cost: Material decomposition from glycerol to produce acrylic acid of two glycerol based scenarios (Unit: USD/kg-AA)

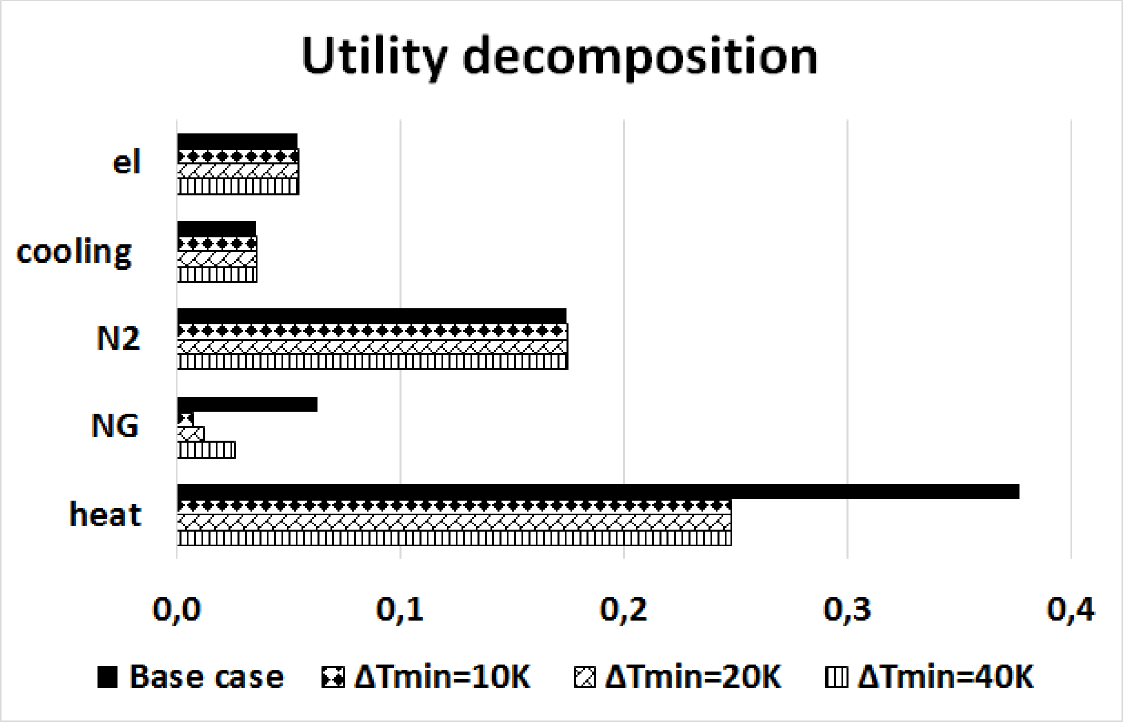

Figure 4.25: Op. cost: Utility decomposition from glycerol to produce acrylic acid of two glycerol based scenarios (Unit: USD/kg-AA)

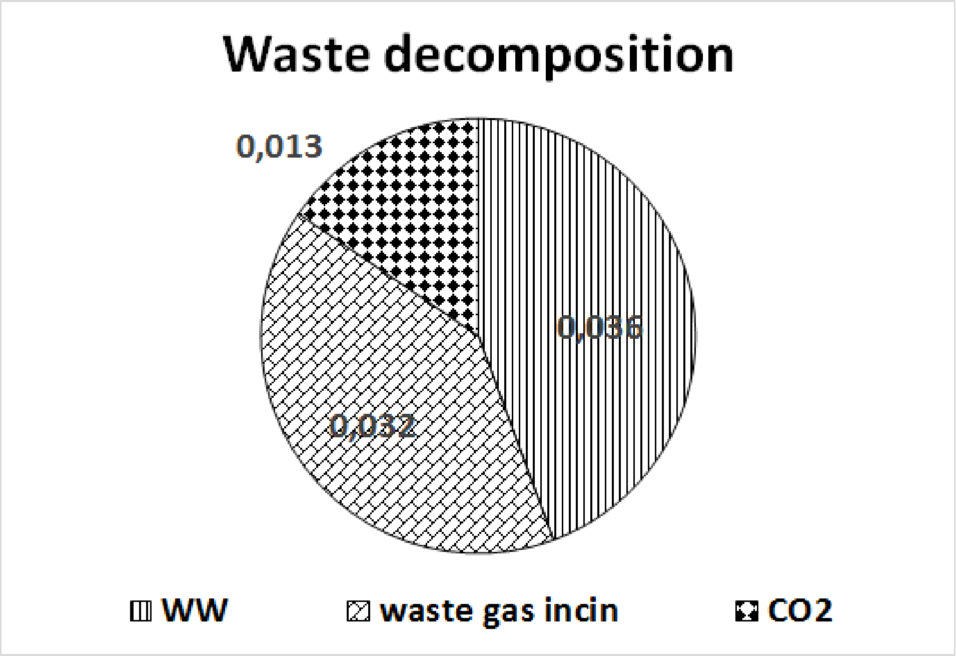

Figure 4.26: Op. cost: Waste decomposition from glycerol to produce acrylic acid of two glycerol based scenarios (Unit: USD/kg-AA)

4.4 A brief summary of results

This conceptual glycerol based model can be technologically and economically feasible by achieving high purity of acrylic acid (99.94 wt% of AA) through high conversion from crude glycerol (2.48 kg crude glycerol converted into 1 kg of AA) without requiring harsh process conditions, such as too high or too low (vacuum) pressure or temperature. The two-reactor system (each followed by purification) facilitates the recovery of unreacted glycerol, the flow of less by-products to the next steps and the final purification of acrylic acid. The whole performance of glycerol based model is better than that of the glucose based model and competitive at some points with the conventional production method measured by life cycle indicators and operating cost.

Heat recovery does help lowering the running cost and becoming more environmentally friendly. Since the total process is not very complicated, 70% of maximum energy recovery target can be reached by simply adding seven heat-exchange units. In the base model, oxidation process happens to be an exothermal reaction, therefore, it is wise to recover the high-level heat. The improvement getting from "ΔT_{min}=10K" model is of course highest together with the most expensive capital investment, whereas, the advantages are not quite outstanding. Nevertheless, distillation columns can not be covered by background streams of adjacent temperature, thus 78% of new heat demand (lower than 200 °C) after heat recovery is required by columns.

Nitrogen is used as the carrier gas only during dehydration, and it has been proved that involvement of oxygen has poor performance on the selectivity in acrolein from glycerol [3]. However, the results of this study have shown that the impact on economy and environment when using pure N_2 is quite large. For the required kinetic concern, it is better not to change the flow ratio, neither. Whereas, as for impacts from catalysts, due to missing information of reusability and background data of catalyst $FePO_4$, the relative high impact posed by this catalyst shall be worried, and more analysis of catalyst shall be performed.

The electricity use, cooling, process water, ash disposal and catalyst disposal do not account for much energy demand, operating costs and environmental impacts.

In the three LCA indicators, the alternative scenario of utilizing crude glycerol plays a crucial role. If the crude glycerol used for producing acrylic acid was supposed to be burnt as a fuel, mixture of other thermal energy (natural gas, biomass, etc.) shall be used for compensating the heat loss of glycerol. On the contrary, if the crude glycerol cannot be used as fuel and has to be treated in conventional waste treatment plants, to utilize glycerol for chemical product saves the energy and material required in the waste treatment plant.

The assessment scores of the benchmark model fed by glucose exceed the RER fossil based production a lot for all the four indicators, and are also higher than the glycerol based model (only lower in CED for the base case of gly-Scenario 1). This is mostly because of the feedstock and nutrients for fermentation. No matter from corn or sugarcane, glucose is a kind of primary energy with high cost.

5

Conclusion

As the by-product of biodiesel production, availability of glycerol has been benefited from the increasing biodiesel generation; at the same time, value added processes of glycerol have caught lots of attention to consume the glycerol. This thesis project aims at using crude glycerol as the raw material to produce acrylic acid on industrial scale via acrolein as the intermediate product. Demand of acrylic acid is predicted to grow steady and reach to nearly 8.2 million tonnes by the end of 2020.

It has been confirmed that two chemical reactions are involved in this production route, namely dehydration and oxidation. According to the previous literature outcomes, two-bed system are selected for achieving high conversion with two kinds of catalysts based on the reported performances, such as selectivity, yield, regeneration. Catalyst $FePO_4$ synthesized by hydrothermal method is used in dehydration reaction, while V-Mo in oxidation reaction. Most of the research work mainly focuses on the synthesis and testing of performances of (new) catalysts, little work concerns about purification of product flow and process design.

In this project, software Aspen Plus ® helps the flowsheet simulation, from prelimenary treatment of crude glycerol to purifying the final product flow. Input data (feedstocks and yield of products) is mainly gathered from literature data with linear scale-up, and reaction condition is set at the optimum temperature and pressure from the results. Although diverse by-products have been discovered from their experiment and large amount of water and inert gases has been introduced into the system, the proposed process design has successfully purified the product flow and purity of acrylic acid reaches nearly 100%. To this end, 2.48 kg of crude glycerol are converted to 1 kg of acrylic acid of 99.94%wt purity.

Pinch analysis and heat integration lowers the heat demand by 100MW in average, 70% of maximum energy recovery target of background streams can be easily achieved. Overally, approximate 34 MJ of heat is needed for 1 kg of acrylic acid with requirement of 25 MJ from the duties of three reboilers.

Alternative process of using crude glycerol plays a significant role in life cycle assessment. The results prove that use of crude glycerol to produce acrylic acid via acrolein route can be regarded as a very promising way in places where glycerol incineration is not an option. Valorization of glycerol can prevent the environmental impact of waste treatment or landfill (landfill has been restricted within EU [42]). $1.35 is required to pay for 1 kg of acrylic acid with around $1.18 is needed with heat integration. Moreover, capital cost is not included within the conceptual design in this project of economic assessment, and it may have impact on decision making.

A glucose based model, as another renewable production way of producing acrylic acid, is introduced for comparison. The assessment results of this benchmark model exceed the EU standard a lot and are higher than those of glycerol based models in almost every indicator. Hence, it seems an unwise choice to adopt glucose to produce acrylic acid in EU.

Of course, more in-depth research on alternative separation, purification method, catalyst findings and testing, governmental subsidies and other aspects are required and expected to help the development of glycerol based biorefinery in the future.

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A

Appendix

A.1 Conversion and yield of glycerol based model

Table A.1 is the yield of dehydration products. Table A.2 is the fractional conversion of components during oxidation process. The values are calculated based on former experiment results and linear estimation during 70 h duration.

Table A.1: Product yield from glycerol during dehydration

	Component	Carbon (%)	Yield from Gly (%)	Equation no.
Resource	Glycerol	16.5		/
Main product	Acrolein	71.4	71.4	2.1
Main by-products	Acetaldehyde	2.06	5.7	2.5
		2.2		2.9
		0.75		2.10
		0.79		2.8
	Hydroxyacetone	0.2	0.2	2.12
	Propanal	0.2	0.2	2.2
Other by-products	Formaldehyde	1.03	3.3	2.5
	Acetone	0.945		2.3
	Allyl alcohol	0.8		2.4
	Formic acid	0.375		2.10
	Propanoic acid	0.1		2.6
	Acrylic acid	0.05		2.7
Missing carbon	CO2	0.395	2.7	2.8
	CO	1.1		2.9
	Coke	1.205		2.11

Table A.2: Conversion of each component during oxidation

Equation no.	Fractional conversion
2.13	95 % of Acrolein
2.14	60 % of Acetaldehyde
2.15	60 % of Acetone
2.16	50 % of Formic acid
2.17	100 % of CO
2.18	60 % of Hydroxyacetone

A.2 Background data for the environmental and economic assessment

Table A.3 is the background data of resources used in the glycerol and glucose based model. LCA assessment and operating cost calculation is performed from these data, which is mainly acquired from Ecoinvent database [39].

Table A.3: Background data for the environmental and economic assessment with respect to resources consumption

Substance	CED ($MJ_{\text{-eq}}$/kg)	EI99 (Points/kg)	GWP ($kgCO_{2\text{-eq}}$/kg)	Price (USD/t)
Process water	2.8×10^{-4}	1.8×10^{-6}	2.4×10^{-5}	1
Quartz sand	0.33	0.001	0.02	39.6 (31.2 €/2005)
Pure Glycerol	23.9	0.73	1.99	270
Crude Gly - Incin	-19.7	-0.063	0.20	111
Crude Gly - WWTP	9.97	0.021	0.92	111
Heat (MP)	1.57	0.01	0.10	20
Heat (LP)	1.2	0.004	0.08	14
Electricity	9.87	0.02	0.49	0.10
Cooling water from river	0.00	0.00	0.00	0.15
V-Mo (only Mo)	118.00	39.66	7.67	79375 (62500 €/2005)
Silicon carbide (SiC)	160.42	0.49	7.18	870 (685 €/2005)
N_2	8.73	0.02	0.43	78.1 (61.5 €/2005)
Cooling medium	1.82	0.02	0.15	281.9 (222 €/2005)
Natural gas	1.24	0.004	0.012	0.01
Media	18.60	0.08	1.04	1000
CO_2	10.5	0.04	0.82	139.7 (110 €/2005)
CO_2 emission	—	5.46×10^{-3}	1	20
Phosphoric acid	20.0	0.23	1.42	1100 (900 €/2005)
Glucose from sugar beet	6.49	0.05	0.51	390
Zeolites (used for $FePO_4$)	73.7	0.39	4.20	400
Catalyst (zeolite) disposal	0.16	7.6×10^{-4}	5.0×10^{-3}	—

Table A.4 is the environmental impact and cost of per hour of the total amount of waste steams of glycerol and benchmark models. The calculation method follows Rerat et al. [40]. These values shall be divided by acrylic acid production of per hour.

Table A.4: Background data for the environmental and economic assessment with respect to waste treatment

Waste stream	CED ($MJ_{\text{-eq}}$/hr)	EI99 (Points/hr)	GWP ($kgCO_{2\text{-eq}}$/hr)	Price (USD/hr)
WW (Gly based model)	34605.8	74.2	3187.2	521.3
Waste Incin (Gly based model)	-293694.8	-938.9	-250.8	-1254.3
WW (Benchamrk model)	39207.6	92.5	3476.2	1326.7

As for the operating cost of waste water treatment and waste incineration, besides the values above in Table A.4, it shall also include second cost, which is as follow:
For waste water: $The\ amount\ of\ waste\ water \times 0.003(USD/kg)$.
For waste incineration: $The\ amount\ of\ waste\ vapor/\ gas \times 0.2(USD/kg)$.
The detailed results of waste streams are shown in Table A.5.

Table A.5: Results of the environmental and economic assessment with respect to waste treatment

Model	Component of waste stream	CED ($MJ_{\text{-eq}}$/kg-AA)	EI99 (Points/kg-AA)	GWP ($kgCO_{2\text{-eq}}$/kg-AA)	Price (USD/kg-AA)
Gly based model	catalyst disposal	0.043	0.000	0.001	/
	waste incin	-13.522	-0.043	-0.012	0.032
	waste water	1.593	0.003	0.147	0.036
	ash disposal	0.04	0.003	0.001	/
Benchmark model	waste water	1.798	0.004	0.159	0.103

A.3 Overview units

Table A.6: Overview units of producing acrylic acid from glucose

Process Unit	t (°C)	p (bar)	Further Information
Multi-evaporation			
PE-101	37	5	Pump
FE-101	154	5	Flash vessel
FE-102	146	4	Flash vessel
FE-103	138	3	Flash vessel
FE-104	134	2	Flash vessel
FE-105	133	1	Flash vessel
HX108	132	4	Cooler
HX107	132	3	Cooler
HX106	128	2	Cooler
HXFE101	146	5	Cooler
HXFE102	138	4	Cooler
HXFE103	132	3	Cooler
HXFE104	121	2	Cooler
HXFE105	95	1	Cooler
PE-103	133	5	Pump
Dehydration+Purification			
R-101	140	5	Reactor
D-101	tc=105 tr=156	1,2 1,6	Distillation column
D-102	tc=144 tr=155	1,1 1,5	Distillation column
D-103	tc=144 tr=195	1,1 1,1	Distillation column
PD-101	156	2	Pump
PD-103	145	5	Pump
PD-104	155	2	Pump
PD-107	196	5	Pump
PR-101	26	5	Pump
PR-102	140	5	Pump
HX-109	144	5	Heater
HX-WW	20	1	Cooler

Table A.7: Overview units of producing acrylic acid from glycerol

Process Unit	t (°C)	p (bar)	Further Information
Pre-treatment			
FILTASH	20	1	Split
HXCRU-01	190	1	Heater
EVAPMETH	190	1	Flash vessel
REMONG	190	1	Seperator. Remove fat acid
WCOOL	25	1	Cooler
WTANK	25	1	Mixture
P-WS	20	1	Pump
Dehydration+Purification			
HX-GLY	200	1	Heater
HX-GLY1	280	1	Heater
COMP-N2	52	1.3	Compressor
HX-N2	200	1.3	Heater
HX1-N2	280	1.3	Heater
REACTOR1	280	1	Dehydration reactor. Reaction see
REM-C	280	1	Seperator. Remove carbon solid
HX-PR-11	15	1	Cooler
F-01	15	1	Flash vessel
COMP-PR1	266	9	Compressor
P-PR1	13	9	Pump
HX-PR-14	53	9	Cooler
F-02	15	9	Flash vessel
D-01	t_c=96 t_r=101	1	Distillation column
F-03	105	1	Flash vessel
P-REC	105	1.3	Pump
HX-REC	200	1.3	Heater
HX1-REC	280	1.3	Heater
Oxidation+Purification			
HX-P-21	200	1	Heater
HX-P-22	300	1	Heater
COMP-AIR	52	1.3	Compressor
HX-AIR	200	1.3	Heater
HX1-AIR	300	1.3	Heater
REACTOR2	300	1	Oxidation reactor. Reaction see
HX-PR30	15	1	Cooler
HX-PR31	0	1	Cooler.Need cooling medium for 0
F-04	0	1	Flash vessel
D-02	t_c=99 t_r=100	1	Distillation column
D-03	t_c=100 t_r=141	1	Distillation column
Waste water			
HX-WW	15	1	Cooler
Vapor emission			
COMB-EM	/	1	Reactor. Combustion of vapor emission

A.4 Overview flows

Table A.8: Overview flows of producing acrylic acid from glucose (1)

Stream number		SE-101	SE-102	SE-103	SE-104	SE-105	SE-106	SE-107	SE-108	SE-109	SE-110	SE-111	SE-112	SE-113
Temperature	°C	37	37,1	153,6	153,6	146,0	146,0	146,0	132,3	138,4	138,4	138,4	132,3	133,8
Pressure	Bar	1,01	5,17	5,07	5,07	4,05	4,05	4,96	3,86	3,04	3,86	3,04	2,94	2,03
Vapor Fraction		0	0	0	1	1	0	0	0	1	0	0	0	1
Liquid Fraction		1	1	1	0	0	1	1	1	0	1	1	1	0
Mass Flow	kg/hr	330299	330299	229245	101054	85815,16	143430	101054	143430	69452,11	85815,16	73977,38	73977,38	32739,14
Mole Flow	kmol/hr	16977,55	16977,55	11374,96	5602,593	4754,734	6620,227	5602,593	6620,227	3839,732	4754,734	2780,496	2780,496	1793,42
Enthalpy Flow	kW	-1380000	-1380000	-905870	-369700	-314170	-543300	-429740	-545620	-254200	-365690	-249060	-249510	-119220
Phase		Liquid	Liquid	Liquid	Vapor	Vapor	Liquid	Liquid	Liquid	Vapor	Liquid	Liquid	Liquid	Vapor
Mass component														
WATER	kg/hr	299745	299745	198843	100902	85618,54	113224	100902	113224	69104,28	85618,54	44120,12	44120,12	32201,41
CO2	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0
Acrylic acid	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0
3-HP	kg/hr	30554,42	30554,42	30401,71	152,703	196,623	30205,09	152,703	30205,09	347,828	196,623	29857,26	29857,26	537,7248
Phosphoric acid	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0

Table A.9: Overview flows of producing acrylic acid from glucose (2)

Stream number		SE-114	SE-115	SE-116	SE-117	SE-118	SE-119	SE-120	SE-127	WW-01	WW-02
Temperature	°C	132,2	133,8	127,8	132,9	121,1	132,9	95,0	100,1	100,1	21,1
Pressure	Bar	2,94	2,03	1,98	1,01	1,98	1,01	1,01	1,01	1,01	1,01
Vapor Fraction		0	0	0	1	0,914	0	0	0,173	0,197	0
Liquid Fraction		1	1	1	0	0,086	1	1	0,827	0,803	1
Mass Flow	kg/hr	69452,11	41238,24	41238,24	9532,392	32739,14	31705,85	9532,392	298593	308499	308499
Mole Flow	kmol/hr	3839,732	987,0759	987,0759	503,4087	1793,42	483,6672	503,4087	16493,89	16994,07	16994,07
Enthalpy Flow	kW	-296120	-110710	-110880	-33935,01	-121180	-71289,1	-39897,02	-1252600	-1286300	-1353000
Phase		Liquid	Liquid	Liquid	Vapor	Mixed	Liquid	Liquid	Mixed	Mixed	Liquid
Mass component											
WATER	kg/hr	69104,28	11918,7	11918,7	8953,217	32201,41	2965,483	8953,217	296779	305493	305493
CO2	kg/hr	0	0	0	0	0	0	0	0	0,998	0,998
Acrylic acid	kg/hr	0	0	0	0	0	0	0	0	1181,554	1181,554
3-HP	kg/hr	347,828	29319,54	29319,54	579,175	537,7248	28740,36	579,175	1814,054	1814,078	1814,078
Phosphoric acid	kg/hr	0	0	0	0	0	0	0	0	9,919	9,919

Table A.10: Overview flows of producing acrylic acid from glucose (3)

Stream number		SR-101	SR-102	SR-103	SR-105	SR-106	SR-107	SR-108	SR-109	SR-110	SR-111	SR-115	SR-119
Temperature	°C	133,2	25	26,4	194,5	144,8	140	140	140	143,8	100	105,3	155,9
Pressure	Bar	5,10	1,01	5,10	5,10	5,10	5,00	5,00	5,17	5,10	10,00	1,21	1,57
Vapor Fraction		0	0	0	0	0	0	0	0	0	1	1	0
Liquid Fraction		1	1	1	1	1	1	1	1	1	0	0	1
Mass Flow	kg/hr	31705,85	10,02	10,02	1242,92	186326,00	219276,00	21686,58	21686,58	21686,58	1,00	9893,44	209383,00
Mole Flow	kmol/hr	483,67	0,10	0,10	13,60	2585,58	3185,01	315,00	315,00	315,00	0,02	500,05	2901,89
Enthalpy Flow	kW	-71284,58	-36,10	-36,09	-3817,19	-254870	-329500	-32588,17	-32587,95	-32554,25	-2,46	-33627,52	-287630
Phase		Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Vapor	Vapor	Liquid
Mass component													
WATER	kg/hr	2965,483	0	0	0	TRACES	4805,798	475,2987	475,2987	475,2987	0	8713,395	TRACES
CO2	kg/hr	0	0	0	0	0,0018355	0,002	TRACES	TRACES	TRACES	0,998	0,998	0,002
Acrylic acid	kg/hr	0	0	0	250,895	186326	193939	19180,8	19180,8	19180,8	0	1179,02	208391
3-HP	kg/hr	28740,36	0	0	TRACES	TRACES	19538,54	1932,383	1932,383	1932,383	0	0,024	TRACES
Phosphoric acid	kg/hr	0	10,024	10,024	992,0259	TRACES	991,921	98,102	98,102	98,102	0	TRACES	991,921

Table A.11: Overview flows of producing acrylic acid from glucose (4)

Stream number		SD-101	SD-104	SD-108	SD-109	SD-110	SD-111	SD-118	SD-120	SD-121	SD-122	SD-123	PROD2
Temperature	°C	155,9	144,4	154,8	154,8	144,4	144,4	194,7	144,4	194,7	194,7	195,7	139,9
Pressure	Bar	1,67	1,12	1,47	1,57	1,12	1,12	1,12	1,12	1,12	1,12	5,10	1,12
Vapor Fraction		0	0	0	0	0	0	0	0	0	0	0	0
Liquid Fraction		1	1	1	1	1	1	1	1	1	1	1	1
Mass Flow	kg/hr	209383	188209	21174,54	21174,54	186326	1882,085	1245,35	19929,19	1232,896	12,4535	1232,896	19929,19
Mole Flow	kmol/hr	2901,89	2611,701	290,189	290,189	2585,584	26,117	13,639	276,550	13,503	0,136	13,503	276,550
Enthalpy Flow	kW	-287630	-257470	-31030,87	-31030,76	-254900	-2574,707	-3820,032	-27263,28	-3781,831	-38,2	-3781,097	-27296,98
Phase		Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid
Mass component													
WATER	kg/hr	TRACES	TRACES	TRACES	TRACES	TRACES	TRACES	0	0	0	0	0	0
CO2	kg/hr	0,002	0,002	TRACES	TRACES	0,002	TRACES	0	0	0	0	0	0
Acrylic acid	kg/hr	208391	188209	20182,62	20182,62	186326	1882,085	253,429	19929,19	250,895	2,534	250,895	19929,19
3-HP	kg/hr	TRACES	TRACES	TRACES	TRACES	TRACES	TRACES	TRACES	TRACES	TRACES	TRACES	TRACES	TRACES
Phosphoric acid	kg/hr	991,921	TRACES	991,921	991,921	TRACES	TRACES	991,921	TRACES	982,002	9,919	982,002	TRACES

Table A.12: Overview flows of producing acrylic acid from glycerol (1)

Stream number		CRUDGLY	CRUDGLY0	CRUDGLY1	CRUDGLY2	GLY	METHANOL	FILT1OUT	WTOINC	WTOTANK	MONG	WAT-SUP	WAT-SUP1	GLYSOLUT
Temperature	°C	20	20	190	190	190	190	20	25	25	190	20	20	64,5
Pressure	Bar	1	1	1	1	1	1	1	1,01	1,01	1	1	1,3	1
Vapor Fraction		0	0	0,248	0	0,001	1	0	0	0	0	0	0	0
Liquid Fraction		1	1	0,752	1	0,999	0	1	1	1	1	1	1	1
Solid Fraction		0	0	0	0	0	0	0	0	0	0	0	0	0
Mass Flow	kg/hr	56289,72	53228,31	53228,31	48798,23	43408,52	4430,08	3061,41	9819,786	9819,786	5389,71	65652,15	65652,15	109061
Mole Flow	kmol/hr	732,30	724,98	724,98	545,39	527,42	179,59	7,32	197,56	197,56	17,97	3644,25	3644,25	4171,67
Enthalpy Flow	kW	-109770	-108660	-100670	-89039,55	-85376,63	-11631,29	-1102,114	-18362,06	-18362,06	-3654,947	-289690	-289690	-375060
Phase		Liquid	Liquid	Mixed	Liquid	Mixed	Vapor	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid	Liquid
Mass component														
Glycerol	kg/hr	43046,670	42616,200	42616,200	42095,440	42095,440	520,763	430,467	520,763	520,763	0	0	0	42095,440
Acrolein	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0
Acrylic acid	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0
Water	kg/hr	3394,232	3360,290	3360,290	1207,856	1207,856	2152,434	33,942	2152,434	2152,434	0	65652,15	65652,15	66860,010
O2	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0
H2	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0
Acetaldehyde	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0
Acetone	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0
CO2	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0
Allyl alcohol	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0
Formic acid	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0
Propanoic acid	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0
Formaldehyde	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0
Propanal	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0
N2	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0
CO	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0
C	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0
Hydroxyacetone	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0
Acetic acid	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0
Argon	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0
Methanol	kg/hr	1867,399	1848,725	1848,725	105,228	105,228	1743,497	18,674	1743,497	1743,497	0	0	0	105,228
Ash	kg/hr	2549,500	25,495	25,495	25,495	0	0	2524,005	25,495	25,495	25,495	0	0	0
Fat acid	kg/hr	5431,917	5377,598	5377,598	5364,216	0	13,382	54,319	5377,598	5377,598	5364,216	0	0	0

Table A.13: Overview flows of producing acrylic acid from glycerol (2)

Stream number		GLYGAS0	GLYGAS1	N2-AM	N2-P	N2-P-H	N2-P-H1	GLY+N2	O2	PR-10	PR-11	PR-12	PR-13-L	PR-13-L1
Temperature	°C	200	280	20	51,7	200	280	280	279,9	280	280	15	15	12,8
Pressure	Bar	1	1	1	1,3	1,3	1,3	1	1	1	1	1	1	9
Vapor Fraction		0,925	1	1	1	1	1	1	1	0,997	1	0,284	0	0
Liquid Fraction		0,075	0	0	0	0	0	0	0	0	0	0,716	1	1
Solid Fraction		0	0	0	0	0	0	0	0	0,003	0	0	0	0
Mass Flow	kg/hr	109061	109061	48519,35	48519,35	48519,35	48519,35	157580	216,31	175163	174927	174927	107937	107937
Mole Flow	kmol/hr	4171,67	4171,67	1732	1732	1732	1732	5903,67	6,76	7443,42	7423,74	7423,74	5314,93	5314,93
Enthalpy Flow	kW	-319660	-309050	-70,06	373,65	2462,63	3603,68	-305440	14,54	-350400	-350410	-437280	-426560	-426530
Phase		Mixed	Vapor	Vapor	Vapor	Vapor	Vapor	Vapor	Vapor	All	Vapor	Mixed	Liquid	Liquid
Mass component														
Glycerol	kg/hr	42095,440	42095,440	0	0	0	0	42095,440	0	8257,187	8257,187	8257,187	8257,182	8257,182
Acrolein	kg/hr	0	0	0	0	0	0	0	0	21884,520	21884,520	21884,520	7013,383	7013,383
Acrylic acid	kg/hr	0	0	0	0	0	0	0	0	22,712	22,712	22,712	22,159	22,159
Water	kg/hr	66860,010	66860,010	0	0	0	0	66860,010	0	91478,750	91478,750	91478,750	91457,210	91457,210
O2	kg/hr	0	0	0	0	0	0	0	216,312	1,137	1,137	1,137	TRACES	TRACES
H2	kg/hr	0	0	0	0	0	0	0	0	40,061	40,061	40,061	TRACES	TRACES
Acetaldehyde	kg/hr	0	0	0	0	0	0	0	0	2095,318	2095,318	2095,318	268,778	268,778
Acetone	kg/hr	0	0	0	0	0	0	0	0	301,651	301,651	301,651	61,901	61,901
CO2	kg/hr	0	0	0	0	0	0	0	0	285,116	285,116	285,116	0,652	0,652
Allyl alcohol	kg/hr	0	0	0	0	0	0	0	0	254,022	254,022	254,022	221,317	221,317
Formic acid	kg/hr	0	0	0	0	0	0	0	0	312,157	312,157	312,157	241,053	241,053
Propanoic acid	kg/hr	0	0	0	0	0	0	0	0	93,340	93,340	93,340	91,386	91,386
Formaldehyde	kg/hr	0	0	0	0	0	0	0	0	507,240	507,240	507,240	21,818	21,818
Propanal	kg/hr	0	0	0	0	0	0	0	0	63,505	63,505	63,505	19,220	19,220
N2	kg/hr	0	0	48519,350	48519,350	48519,350	48519,350	48519,350	0	48519,350	48519,350	48519,350	6,251	6,251
CO	kg/hr	0	0	0	0	0	0	0	0	505,344	505,344	505,344	0,071	0,071
C	kg/hr	0	0	0	0	0	0	0	0	236,393	0	0	0	0
Hydroxyacetone	kg/hr	0	0	0	0	0	0	0	0	199,948	199,948	199,948	195,904	195,904
Acetic acid	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0
Argon	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0
Methanol	kg/hr	105,228	105,228	0	0	0	0	105,228	0	105,228	105,228	105,228	58,611	58,611
Ash	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0
Fat acid	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0	0

Table A.14: Overview flows of producing acrylic acid from glycerol (3)

Stream number		PR-13-V	PR-13-V1	PR-14	PR-15	PR-20	PR-21	CARBON	REC-01	REC-02	REC-03	REC-04	REC-05
Temperature	°C	15	265,7	59,9	53	15	95,6	280	101,035	105	105,0165	200	280
Pressure	Bar	1	9	9	9	9	1	1	1	1	1,3	1,3	1,3
Vapor Fraction		1	1	0,272	0,266	0	1	0	TRACES	0	0	0,851	1
Liquid Fraction		0	0	0,728	0,734	1	0	0	1	1	1	0,149	0
Solid Fraction		0	0	0	0	0	0	1	0	0	0	0	0
Mass Flow	kg/hr	66989,68	66989,68	174929	174929	126005	83175,15	236,39	42829,7	17366,64	17366,64	17366,64	17366,64
Mole Flow	kmol/hr	2108,81	2108,81	7423,85	7423,85	5691,64	3699,56	19,68	1992,07	587,16	587,16	587,16	587,16
Enthalpy Flow	kW	-10724,16	-5156,734	-431690	-433040	-437270	-223180	17,67	-164300	-54876,3	-54876,1	-48134,2	-45774,4
Phase		Vapor	Vapor	Mixed	Mixed	Liquid	Vapor	Solid	Mixed	Liquid	Liquid	Mixed	Vapor
Mass component													
Glycerol	kg/hr	0,004	0,004	8257,186	8257,186	8257,186	TRACES	0	8257,186	8253,263	8253,263	8253,263	8253,263
Acrolein	kg/hr	14871,140	14871,140	21884,520	21884,520	20224,780	20224,780	0	TRACES	0	0	0	0
Acrylic acid	kg/hr	0,552	0,552	22,712	22,712	22,707	13,757	0	8,950	3,013	3,013	3,013	3,013
Water	kg/hr	21,534	21,534	91480,770	91480,770	91425,820	57272,890	0	34152,930	8909,497	8909,497	8909,497	8909,497
O2	kg/hr	1,136	1,136	1,137	1,137	0,064	0,064	0	TRACES	0	0	0	0
H2	kg/hr	40,061	40,061	40,061	40,061	0,117	0,117	0	TRACES	0	0	0	0
Acetaldehyde	kg/hr	1826,540	1826,540	2095,318	2095,318	1965,806	1965,806	0	TRACES	0	0	0	0
Acetone	kg/hr	239,750	239,750	301,651	301,651	296,396	296,396	0	TRACES	0	0	0	0
CO2	kg/hr	284,463	284,463	285,116	285,116	129,645	129,645	0	TRACES	0	0	0	0
Allyl alcohol	kg/hr	32,705	32,705	254,022	254,022	253,478	253,478	0	TRACES	0	0	0	0
Formic acid	kg/hr	71,104	71,104	312,159	312,159	311,906	194,036	0	117,870	29,079	29,079	29,079	29,079
Propanoic acid	kg/hr	1,954	1,954	93,340	93,340	93,335	0,441	0	92,894	52,840	52,840	52,840	52,840
Formaldehyde	kg/hr	485,422	485,422	507,240	507,240	467,445	467,445	0	TRACES	0	0	0	0
Propanal	kg/hr	44,286	44,286	63,505	63,505	55,574	55,574	0	TRACES	0	0	0	0
N2	kg/hr	48513,100	48513,100	48519,350	48519,350	2171,315	2171,315	0	TRACES	0	0	0	0
CO	kg/hr	505,273	505,273	505,344	505,344	24,425	24,425	0	TRACES	0	0	0	0
C	kg/hr	0	0	0	0	0	0	236,393	0	0	0	0	0
Hydroxyacetone	kg/hr	4,044	4,044	199,950	199,950	199,939	0,072	0	118,949	118,949	118,949	118,949	118,949
Acetic acid	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0
Argon	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0
Methanol	kg/hr	46,618	46,618	105,228	105,228	104,907	104,907	0	TRACES	0	0	0	0
Ash	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0
Fat acid	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0

Table A.15: Overview flows of producing acrylic acid from glycerol (4)

Stream number		AIR	AIR-P	AIR-P-H	AIR-P-H1	PR-22	PR-23	PR-30	PR-31	PR-32	PR-40	PR-41	PR-FINAL
Temperature	°C	20	51,6908	200	300	200	300	300	15	0	0	100,4	140,8
Pressure	Bar	1	1,3	1,3	1,3	1	1	1	1	1	1	1	1
Vapor Fraction		1	1	1	1	1	1	1	0,865	0,866	0	0	TRACES
Liquid Fraction		0	0	0	0	0	0	0	0,135	0,134	1	1	1
Solid Fraction		0	0	0	0	0	0	0	0	0	0	0	0
Mass Flow	kg/hr	641609	641609	641609	641609	83175,15	83175,15	724784	724784	724784	82237,33	64817,5	21731,81
Mole Flow	kmol/hr	22178,06	22178,06	22178,06	22178,06	3699,56	3699,56	25701,45	25701,45	25701,45	3534,23	2622,40	301,58
Enthalpy Flow	kW	-895,854	4786,068	31601,95	50041,42	-218840	-214430	-192010	-297160	-300000	-290260	-211540	-29765,8
Phase		Vapor	Vapor	Vapor	Vapor	Vapor	Vapor	Vapor	Mixed	Mixed	Liquid	Liquid	Mixed
Mass component													
Glycerol	kg/hr	0	0	0	0	TRACES	TRACES	0	0	0	0	0	0
Acrolein	kg/hr	0	0	0	0	20224,780	20224,780	1011,239	1011,239	1011,239	120,005	TRACES	0
Acrylic acid	kg/hr	0	0	0	0	13,757	13,757	24710,4	24710,400	24710,400	23263,230	22292,99	21719,45
Water	kg/hr	0	0	0	0	57272,890	57272,890	57377,86	57377,860	57377,860	57343,150	41298,86	TRACES
O2	kg/hr	141934	141934	141934	141934	0,064	0,064	135712	135712	135712	3,641	TRACES	0
H2	kg/hr	0	0	0	0	0,117	0,117	20,057	20,057	20,057	TRACES	TRACES	0
Acetaldehyde	kg/hr	0	0	0	0	1965,806	1965,806	982,903	982,903	982,903	37,196	TRACES	0
Acetone	kg/hr	0	0	0	0	296,396	296,396	148,198	148,198	148,198	21,423	TRACES	0
CO2	kg/hr	0	0	0	0	129,645	129,645	787,722	787,722	787,722	0,364	TRACES	0
Allyl alcohol	kg/hr	0	0	0	0	253,478	253,478	253,478	253,478	253,478	183,598	TRACES	TRACES
Formic acid	kg/hr	0	0	0	0	194,036	194,036	97,018	97,018	97,018	50,164	44,707	TRACES
Propanoic acid	kg/hr	0	0	0	0	0,441	0,441	7,529	7,529	7,529	7,172	7,172	7,172
Formaldehyde	kg/hr	0	0	0	0	467,445	467,445	233,722	233,722	233,722	1,810	TRACES	0
Propanal	kg/hr	0	0	0	0	55,574	55,574	50,016	50,016	50,016	5,514	TRACES	0
N2	kg/hr	490815	490815	490815	490815	2171,315	2171,315	492986	492986	492986	10,102	TRACES	0
CO	kg/hr	0	0	0	0	24,425	24,425	0	0	0	0	0	0
C	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0
Hydroxyacetone	kg/hr	0	0	0	0	0,072	0,072	0,036	0,036	0,036	0,034	0,034	0,034
Acetic acid	kg/hr	0	0	0	0	0	0	1493,138	1493,138	1493,138	1173,736	1173,736	5,155
Argon	kg/hr	8859,692	8859,692	8859,692	8859,692	0	0	8859,692	8859,692	8859,692	0,226	TRACES	0
Methanol	kg/hr	0	0	0	0	104,907	104,907	52,453	52,453	52,453	15,957	TRACES	TRACES
Ash	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0
Fat acid	kg/hr	0	0	0	0	0	0	0	0	0	0	0	0

Table A.16: Overview flows of producing acrylic acid from glycerol (5)

Stream number		V-01	V-02	V-03	V-04	WW-01	WW-02	WW-03	WW-04	WW-05
Temperature	°C	15	0	1,1	20	105	99,4	99,8	101,4	15
Pressure	Bar	9	1	1	1	1	1	1	1	1
Vapor Fraction		1	1	1	1	1	1	1	1	0
Liquid Fraction		0	0	0	0	0	0	0	TRACES	1
Solid Fraction		0	0	0	0	0	0	0	0	0
Mass Flow	kg/hr	48923,76	642547	691471	691471	25463,06	17419,82	43085,69	85968,57	85968,57
Mole Flow	kmol/hr	1732,21	22167,22	23899,43	23941,8	1404,91	911,83	2320,83	4637,57	4637,57
Enthalpy Flow	kW	-2139,367	-11159,5	-13298,9	-52716,9	-93460,8	-60694,5	-155520	-309680	-370400
Phase:		Vapor	Vapor	Vapor	Vapor	Vapor	Vapor	Vapor	Mixed	Liquid
Mass component										
Glycerol	kg/hr	TRACES	0	TRACES	0	3,923	0	0	3,923	3,923
Acrolein	kg/hr	1659,737	891,234	2550,971	0	0	120,005	0	120,005	120,005
Acrylic acid	kg/hr	0,005	1447,163	1447,168	0	5,938	970,24	573,546	1549,723	1549,723
Water	kg/hr	54,956	34,710	89,665	4520,218	25243,43	16044,29	41298,86	82586,580	82586,580
O2	kg/hr	1,073	135709	135710	124719	0	3,641	0	3,641	3,641
H2	kg/hr	39,944	20,057	60,001	0	0	TRACES	0	TRACES	TRACES
Acetaldehyde	kg/hr	129,511	945,708	1075,219	0	0	37,196	0	37,196	37,196
Acetone	kg/hr	5,255	126,775	132,029	0	0	21,423	0	21,423	21,423
CO2	kg/hr	155,471	787,357	942,828	14047,71	0	0,364	0	0,364	0,364
Allyl alcohol	kg/hr	0,543	69,881	70,424	0	0	183,598	TRACES	183,598	183,598
Formic acid	kg/hr	0,253	46,854	47,107	0	88,791	5,457	44,707	138,955	138,955
Propanoic acid	kg/hr	0,005	0,357	0,362	0	40,054	TRACES	TRACES	40,054	40,054
FORMALDE	kg/hr	39,795	231,912	271,707	0	0	1,810	0	1,810	1,810
Propanal	kg/hr	7,932	44,502	52,434	0	0	5,514	0	5,514	5,514
N2	kg/hr	46348,030	492976	539324	539324	0	10,102	0	10,102	10,102
CO	kg/hr	480,919	0,000	480,919	0	0	0	0	0	0
C	kg/hr	0	0	0	0	0	0	0	0	0
Hydroxyacetone	kg/hr	0,011	0,002	0,013	0	80,918	TRACES	TRACES	80,918	80,918
Acetic acid	kg/hr	0	319,402	319,402	0	0	TRACES	1168,580	1168,580	1168,580
Argon	kg/hr	0	8859,466	8859,466	8859,466	0	0,226	0	0,226	0,226
Methanol	kg/hr	0,322	36,497	36,818	0	0	15,957	TRACES	15,957	15,957
Ash	kg/hr	0	0	0	0	0	0	0	0	0
Fat acid	kg/hr	0	0	0	0	0	0	0	0	0