

Article

# Coproduction of Acrylic Acid with a Biodiesel Plant Using CO<sub>2</sub> as Reaction Medium: Process Modeling and Production Cost Estimation

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**Abstract:** Producing value-added chemicals from glycerol is imperative for the sustainable future of biodiesel. Despite worldwide efforts, the commercial production of acrylic acid from glycerol faces challenges, both technologically and economically. Based on our new technology using CO<sub>2</sub> as a reaction medium in a two-step process to catalytically convert glycerol to acrylic acid, we established computer simulation models to analyze the energy efficiency and estimate production costs at different scenarios. The analysis was conducted in conjunction with published data of a typical, intermediate-sized biodiesel facility, aiming at the feasibility of producing acrylic acid on-site in the context of a circular economy. Variable analysis in response to the market value of glycerol, the source and cost of carbon dioxide recycling, and the changes in process scale and conditions are also presented. Results indicates that a cost-effective supply of CO<sub>2</sub> to the acrylic acid plant is key to the further research and development.

**Keywords:** glycerol; catalytic dehydration; acrolein; partial oxidation; value-added chemicals; circular economy

## 1. Introduction

Current biodiesel production, although utilizing renewable resources, fits into a linear economy, which is a take–make–dispose model. For a sustainable future of biofuels, it is imperative to move away from a linear economy toward a circular economy with key elements of prioritizing regenerative resources, using waste as a resource, designing for the future, preserving and extending what is already made, and collaborating to create joint value [1]. The common biodiesel production through transesterification of oils produces ~10% by weight of crude glycerol as coproducts. Because of the massive volume of biodiesel production, a worldwide effort to valorize glycerol was initiated [2,3]. Among the value-added chemicals that can be derived from glycerol, acrylic acid produced via the intermediate of glycerol dehydration to acrolein received much attention because this appears to be one of the most promising ways to valorize glycerol [4,5]. There have been extensive efforts in recent years to improve glycerol dehydration to acrolein, including glycerol conversion in sub- and supercritical water [6–8], as well as selective gas-phase conversions [9–13]. Although these different processes gave adequate glycerol conversion rates and selectivity to acrolein, a continuous process catalyzed by solid acids is desirable for industrial application.

However, despite their positive initial performance, few solid acid catalysts are known to maintain their catalytic activity long enough for practical application without the need for regeneration, as the high functionality of glycerol leads to severe coking on the catalysts. This fast catalyst deactivation remains a major technical problem for the commercial production of acrolein and acrylic acid from glycerol [5,14].

We recently developed a novel technology in which supercritical carbon dioxide (SC-CO<sub>2</sub>) was used for the first time as a reaction medium for the dehydration of glycerol to acrolein catalyzed by a solid acid, showing potential for its industrial application by achieving unprecedented catalyst stability over 528 h of time-on-stream [15]. Further development enabled an integrated process of glycerol dehydration to acrolein, followed by partial oxidation of acrolein to continuously generate acrylic acid wherein crude glycerol with minimum pretreatment can be used as feedstock [16].

Although the process optimization for our new technology is still needed, technical and economic feasibility of the technology needs to be fully understood. At the early stage of a new biobased technology, process modeling and production cost estimation can help to assess potential economic feasibilities, bottlenecks, operation targets for process improvement and identify further research and development effort requirements. Haas et al. [17] reported a process model to estimate the capital and operating costs of a moderate-sized industrial biodiesel production facility using crude, degummed soybean oil as the feedstock; the major process operations in the plant were modeled as continuous-process vegetable oil transesterification, and ester and glycerol recovery. The flexible model could be modified to calculate the effects on capital and production costs of changes in feedstock cost, changes in the type of feedstock employed, changes in the value of the glycerol coproduct, and changes in process chemistry and technology.

Although economies of scale usually indicate the cost per unit of output decreasing with increasing production scale, value-added chemical production from glycerol in the context of a circular economy should be considered in conjunction with a typical biodiesel plant. This would enable integrated and cascading processing, better energy efficiency, and minimized cost associated with glycerol handling and shipment. Therefore, the aim of this study was to establish a process simulation model to analyze the technical and economic feasibility of producing acrylic acid from glycerol in conjunction with a typical intermediate-sized biodiesel facility, based on our new technology of using carbon dioxide as a reaction medium in a two-step process to catalytically convert glycerol to acrylic acid. Variable analysis in response to the market value of glycerol, the source and cost of carbon dioxide recycling, and the changes in process scale and conditions are also presented, demonstrating the usefulness of process modeling at the early stages of a new technology.

## 2. Materials and Methods

The intermediate-sized biodiesel facility is based on the one reported by Haas et al.; results of the modeling analysis are available [17]. Table 1 summarizes the key scale data and modeling analysis results. The glycerol output of this biodiesel facility is used as a benchmark to design a cascading chemical plant producing acrylic acid from glycerol.

**Table 1.** Summary of relevant data modeling an intermediate-sized biodiesel facility (based on [17]).

<b>Key scale data</b>
Annual consumption of 33,635 metric tons degummed soybean oil as feedstock
Modeled as continuous process of vegetable oil transesterification, biodiesel refining, and ester and glycerol recovery
Annual revenues are from 38 million liters (10 million gallons) biodiesel plus 3810 metric tons crude glycerol (80 wt.%)
<b>Key modeling analysis results (based on 2003 price)</b>
Capital costs \$11.3 million to build the biodiesel facility
Annual operating cost \$21 million
Soybean oil feedstock accounts for 88% of total production cost, which is linearly dependent on feedstock cost
Unit biodiesel production cost = \$0.53/L (\$2.00/gal) vs. selling price of biodiesel = \$0.61/L (\$2.32/gal)
Crude glycerol revenue = \$0.33/kg, which reduces production costs by ~6%.
\$0.022/kg (\$0.01/lb) reduction in glycerol value results in \$0.0022/L (\$0.0085/gal) increase of production cost

### 2.1. Main Steps of Converting Glycerol to Acrylic Acid

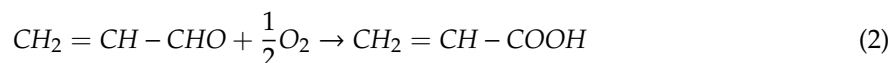
Technical data input to our modeling is based on our experimental laboratory results [15,16]. First, glycerol diluted with water goes through dehydration in the medium of supercritical carbon dioxide catalyzed by a solid acid (ZSM-5 is used in the modeling) to generate acrolein, according to the following equation.



Generation of side products of acetol, acetaldehyde, and propionaldehyde is also considered in this first step.

Carbon dioxide at supercritical conditions, having liquid-like density and gas-like diffusivity, possesses special solvent and transport properties [18]. The major reaction product of acrolein, which is also considered as a coke precursor [5], is soluble in the highly diffusive SC-CO<sub>2</sub> [19] to be quickly moved out of the catalyst bed, preventing it from further secondary reactions that lead to decomposition and coking. Other coke precursors can be dissolved through the combination of water polarity and SC-CO<sub>2</sub> non-polarity, washing out both the hydrophilic and hydrophobic coke precursors and thus enabling long catalyst life [15].

Down the stream, the process is similar to that in the industrial production of acrylic acid via oxidation of propylene to acrolein. The use of CO<sub>2</sub> here also provides a safe reaction medium for performing oxidation reactions within. After pressure release and a condensation step where all unconverted glycerol and acetol (both have a relatively high boiling point) are separated for further refining, the remaining gaseous stream containing acrolein, acetaldehyde, propionaldehyde, and CO<sub>2</sub> is passed through the second reaction of partial oxidation with air catalyzed by a Mo-V based catalyst. Here, acrolein is converted to acrylic acid according to Equation (2).



Acetic acid and a small amount of propionic acid are generated as side products from the oxidation of acetaldehyde and propionaldehyde, respectively.

Acrylic acid is the main revenue product, and acetol and acetic acid are also considered as revenue products. The yield of acrylic acid, acetol, and acetic acid from glycerol is 65 mol%, 12 mol%, and 16 mol%, respectively.

### 2.2. Process Modeling

Unlike the biodiesel model [17] that was based on well-established processes with years of commercial operations, modeling in this work was based on our experimental data at lab scale that was then projected to larger scales of contemporary engineering practices. SuperPro Designer software (Version 8.5, Intelligen Inc., Scotch Plains, NJ, USA) was used to conduct the modeling work, providing modeling of manufacturing and end-of-pipe treatment processes under a single umbrella, as well as project economic evaluation.

Because this process modeling was motivated to help assess the potential economic feasibilities, bottlenecks, operation targets for process improvement and identify further research and development effort requirements at the early stage of new biobased technology, the model is intended to capture key unit operations for the conversion of glycerol to acrylic acid and the product refining, representative of contemporary industry practices. However, this modeling is not meant to represent the actual design offered by any single technology provider. Although the model is in its relatively preliminary stages in terms of the level of its detail, it is not intended to replace the thorough engineering analysis that is required in the final design and construction of such a plant; we designed a plant that can recycle most of its process water and carbon dioxide in light of a future circular economy, possibly adding extra cost to the establishment.

The plant is designed to continuously operate three shifts per day, 350 days per year, converting 3810 metric tons of glycerol (80 wt.%) from an intermediate-sized biodiesel facility to acrylic acid (1700 metric tons) with acetol (314 metric tons) and acetic acid (350 metric tons) as coproducts. It is noteworthy that this is rather small scale comparing to 80–160 metric tons annually for a commercial acrylic acid plant using propylene as feedstock. The SuperPro Designer flowchart is presented in Figure 1, with four color-coded process sections modeling glycerol dehydration to acrolein, acrolein oxidation to acrylic acid, product refining, and CO<sub>2</sub>/energy recycling.

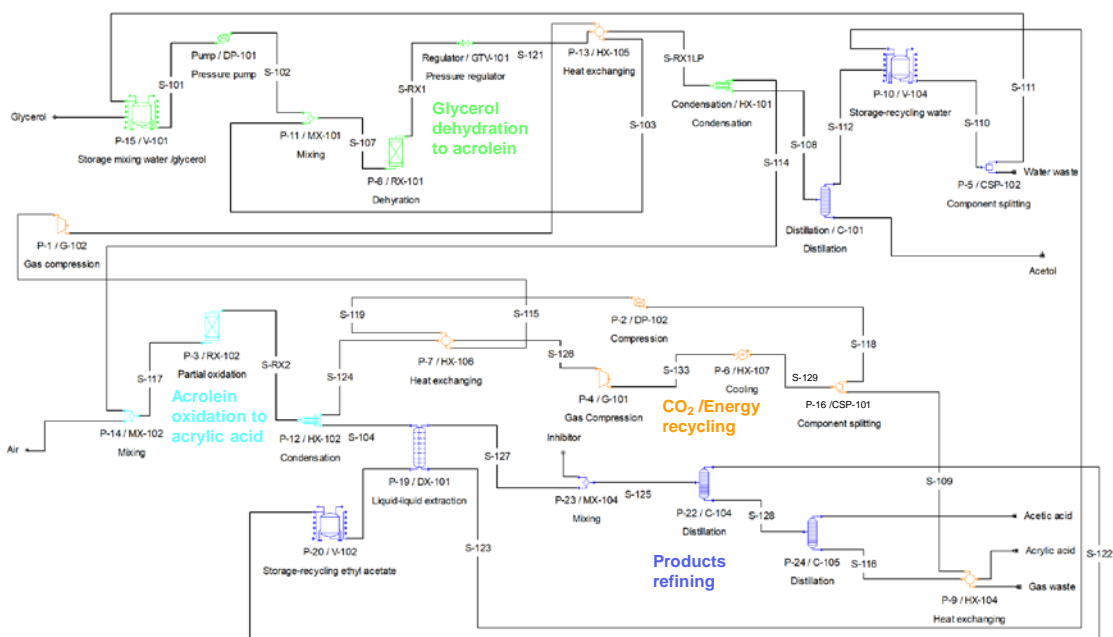


Figure 1. Flowchart for modeling acrylic acid production from glycerol.

Glycerol feed is first diluted with recycled water to 30 wt.% (V-101), and pressurized to 7.8 MPa (DP-101). This feedstock of 30 wt.% glycerol is merged with recycled CO<sub>2</sub> at the same pressure (MX-101) and flows into the dehydration reactor (RX-101) operated at 320 °C and 7.8 MPa with ZSM-5 as a solid acid catalyst, where the glycerol is converted to acrolein with acetol, acetaldehyde, and propionaldehyde as byproducts. After being depressurized (GTV-10) and cooled with a line of recycled CO<sub>2</sub> (HX-105), the reaction effluent passes through a condensation step (HX-101), where part of water and all the acetol and unconverted glycerol are condensed. The condensates go through a distillation (C-101) medium to generate 99.8% acetol as a revenue product. The uncondensed stream (S-114) is mixed with air (MX-102) and flows into the partial oxidation reactor (RX-102), which is operated at 300 °C at near-atmospheric pressure, where the acrolein is converted to acrylic acid with acetic acid and propionic acid as side products; a Mo-V based catalyst is used in this reactor [16].

A condensation step (HX-102) separates the second reaction effluent into two streams. The gaseous stream (S-124) contains CO<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub>, and the CO<sub>2</sub> is recycled. The condensate stream (S-104), consisting of acrylic acid, acetic acid, propionic acid, and water, passes through a liquid-liquid extraction (DX-101) with ethyl acetate as the extractant, which can be recycled (via stream S-122 and unit V-102). The bottom partition of the extractor mainly consists of water (S-123), which is recycled. The top partition, comprised of extracted acrylic acid, acetic acid, and propionic acid in ethyl acetate, is first added with hydroquinone as the inhibitor (MX-104) to prevent polymerization of acrylic acid, before passing through two stages of distillation. The first stage of distillation (C-104) recovers ethyl acetate (via stream S-122); the second distillation generates acetic acid (99.5%) at the top and acrylic acid (99.1% plus 0.23% hydroquinone as anti-polymerization additive) at the bottom.

To efficiently utilize process heat and CO<sub>2</sub>, the gaseous stream after the condensation of the second reaction effluent (S-124) is first cooled with a recycled line of CO<sub>2</sub> (HX-106), followed by compression

to 2.2 MPa (G-101) and chilling to  $-20\text{ }^{\circ}\text{C}$  (HX-107), so the  $\text{CO}_2$  in the liquid phase is separated from gaseous  $\text{N}_2$  and  $\text{O}_2$  (CSP-101) and recycled. The recycled  $\text{CO}_2$  line (S-118), going through two stages of compression (DP-102 and G-102) to reach 7.8 MPa, is heated with the effluent line of the dehydration reaction (S-121), before flowing back to the dehydration reactor (RX-101) via the mixer (MX-101).

### 2.3. Estimation of Production Costs

A depreciable life of 10 years was assumed for the project. Estimation of production costs was based on the flowchart above (Figure 1) that forms the “Base Model” of this study. The following categories that could be specified in SuperPro Designer were considered in the estimation of production costs.

1. Material-related information. This includes the different unit costs (e.g., purchase price, selling price, waste treatment/disposal cost) of pure components, and stock mixtures.
2. Stream-related information. This includes the classification of input and output streams into different categories (e.g., raw materials, revenues, wastes, etc.).
3. Operation-related information. This includes the costs of labor and utilities (heat transfer agents and power) for each operation.
4. Equipment-related information. This includes the capital and operating costs for each equipment (e.g., purchase cost, installation, maintenance, consumables, etc.).

We used the built-in cost model and database in SuperPro Designer that estimated each equipment purchase cost based on size, the material of construction, and other characteristics, and the cost was brought up to the year of 2017 with an inflation rate of 2% per year. All the process vessels were specified to meet The American Society of Mechanical Engineers (ASME) standards of vessel construction that would increase the cost. Concerning construction materials, all the unit operation vessels or reactors are specified to be constructed of stainless steel with the exceptions of the two large  $\text{CO}_2$  compressors (G-101 and G-102), having carbon steel as the specified construction material.

We followed the methodology of parametric input of Haas et al. [17] to the SuperPro Designer for capital investment adjustment. Direct fixed capital was estimated based on the total equipment purchase cost plus the installation cost. Unlisted equipment purchase cost was estimated as 20% of the listed equipment purchase cost, and unlisted equipment installation cost is two times the unlisted equipment purchase cost. Working capital was estimated to cover 30 days of utilities, labor, and raw materials, and the startup and validation cost account for 5% of the direct fixed capital. In the same way, operating cost was adjusted considering the facility-dependent cost that included depreciation, maintenance, and miscellaneous costs of insurance, local taxes, and factory expenses. A lumped estimate of 16,800 labor-hours per year was assigned to labor cost. Because environmental pollution regulations vary from location to location, no precise calculation of waste stream treatment costs was attempted. However, in the annual operating budget, \$50,000 was allocated for waste stream disposal charges.

Because this study focused on process modeling and production cost estimation at the early stage of a developing technology, economic factors of economic life, internal rate of return, corporate tax rate, salvage value, debt fraction, construction interest rate, long term interest rate, and marketing and distribution expenses, were not accounted for. The existence of governmental credits or subsidies was not considered.

Based on the input of material throughputs and operation conditions, SuperPro Designer would first solve the mass and energy balances, and then perform economic calculations. Importantly, the establishment of the Base Model allowed adjustment of input parameters for variable analysis in response to the market value of glycerol, the source and cost of carbon dioxide recycling, and the changes in process scale and conditions. All the following tables and figures are based on our modeling and economic calculations using SuperPro Designer.

### 3. Results and Discussion

#### 3.1. Overview of Base Model

A summary of the production cost estimation is presented in Table 2. Detailed information on the data and terminology is provided in the annotated economic evaluation report generated by SuperPro Designer (Supplemental Information). Approximately \$7.5 million total capital investment is needed to establish the designed facility converting glycerol to acrylic acid. Also listed in Table 2 are major operating costs and revenue values of our input into the modeling. The purchasing price of crude glycerol is taken from the selling price reported in Haas et al. [17]. This price and those for revenue products represent a medium value of their fluctuating prices in the past ten years. The total labor cost is estimated as \$462,000 annually, slightly less than that (\$490,600) of an intermediate-sized biodiesel facility reported in Haas et al. [17], since this project has fewer number of unit operations.

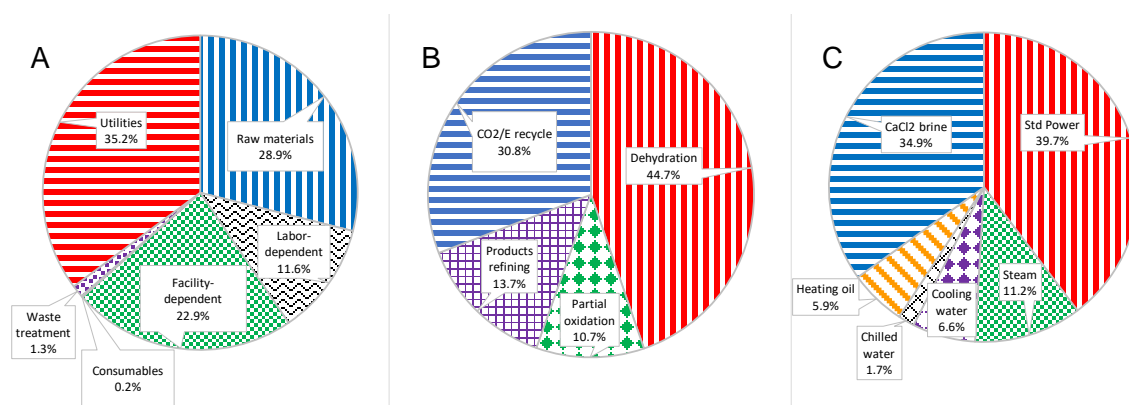
**Table 2.** Results of production cost estimation for Base Model (2017 price).

<b>Summary</b>	
Total capital investment	\$7,468,000
Annual operating cost	\$3,987,000
Main product revenue	\$3,882,797
Co-products revenue	\$573,117
Total revenue	\$4,455,914
Unit production cost	\$2.33/kg acrylic acid
Unit production revenue	\$2.60/kg acrylic acid
Gross profit margin	10.53%
<b>Capital investment itemized</b>	
Equipment purchase cost	\$2,782,000
Direct fixed capital	\$6,866,000
Working capital	\$258,605
Startup & validation	\$343,318
<b>Material throughputs</b>	
Annual consumption of glycerol (80%)	3,810,000 kg
Annual production of acrylic acid	1,712,437 kg
Annual production of acetic acid	351,194 kg
Annual production of acetol	314,778 kg
<b>Major operating costs and revenue values</b>	
Glycerol (feedstock)	\$0.33/kg
Acrylic acid (main revenue)	\$2.27/kg
Acetic acid (revenue)	\$0.74/kg
Acetol (revenue)	\$1.00/kg
Total labor cost	\$462,000/year

Generally, this “Base Model” acrylic acid plant is profitable, although the profit margin is smaller, comparing to the intermediate-sized biodiesel facility [17]. Because the model is relatively preliminary in the level of its detail, and it is not meant to replace the thorough engineering analysis that is required in the final design and construction of such a plant, we will focus on the difference between the unit production cost and unit production revenue (profit margin) relative to the Base Model in the ensuing analysis and discussion. This will help to assess the potential economic feasibilities, bottlenecks, operation targets for process improvement and identify further research and development effort requirements at the early stage of a new biobased technology.

Breaking down annual operating costs reveals more information (Figure 2). Unlike the intermediate-sized biodiesel facility where the soybean oil feedstock accounts for 88% of total operating cost, the largest portion of annual operating cost is the utilities, followed in order by raw materials, facility-dependent costs, and labor (Figure 2A). Dividing the operating cost by the four designed

process sections shows that the dehydration section occupies the highest percentage, followed by the CO<sub>2</sub>/Energy recycle section (Figure 2B). After analysis of the utilities category (Figure 2C), we found that the top contributors to utility costs are standard power and CaCl<sub>2</sub> brine used for deep cooling. It is noteworthy to point out that the most expensive piece of equipment (~\$1 million) is the CO<sub>2</sub> compressor (G-101) that initially pressurizes a large volume of CO<sub>2</sub> from near atmospheric pressure to 2.2 MPa before deep cooling to separate and recycle the CO<sub>2</sub>. The standard power consumption of this CO<sub>2</sub> compressor ranks third-highest among all unit operations, after the dehydration reactor (RX-101) and the partial oxidation reactor (RX-102) that handle reactions at high temperatures of ~300 °C. This analysis indicates that the use of SC-CO<sub>2</sub> as a reaction medium and its recycling entails a high operating cost, especially in terms of utilities.



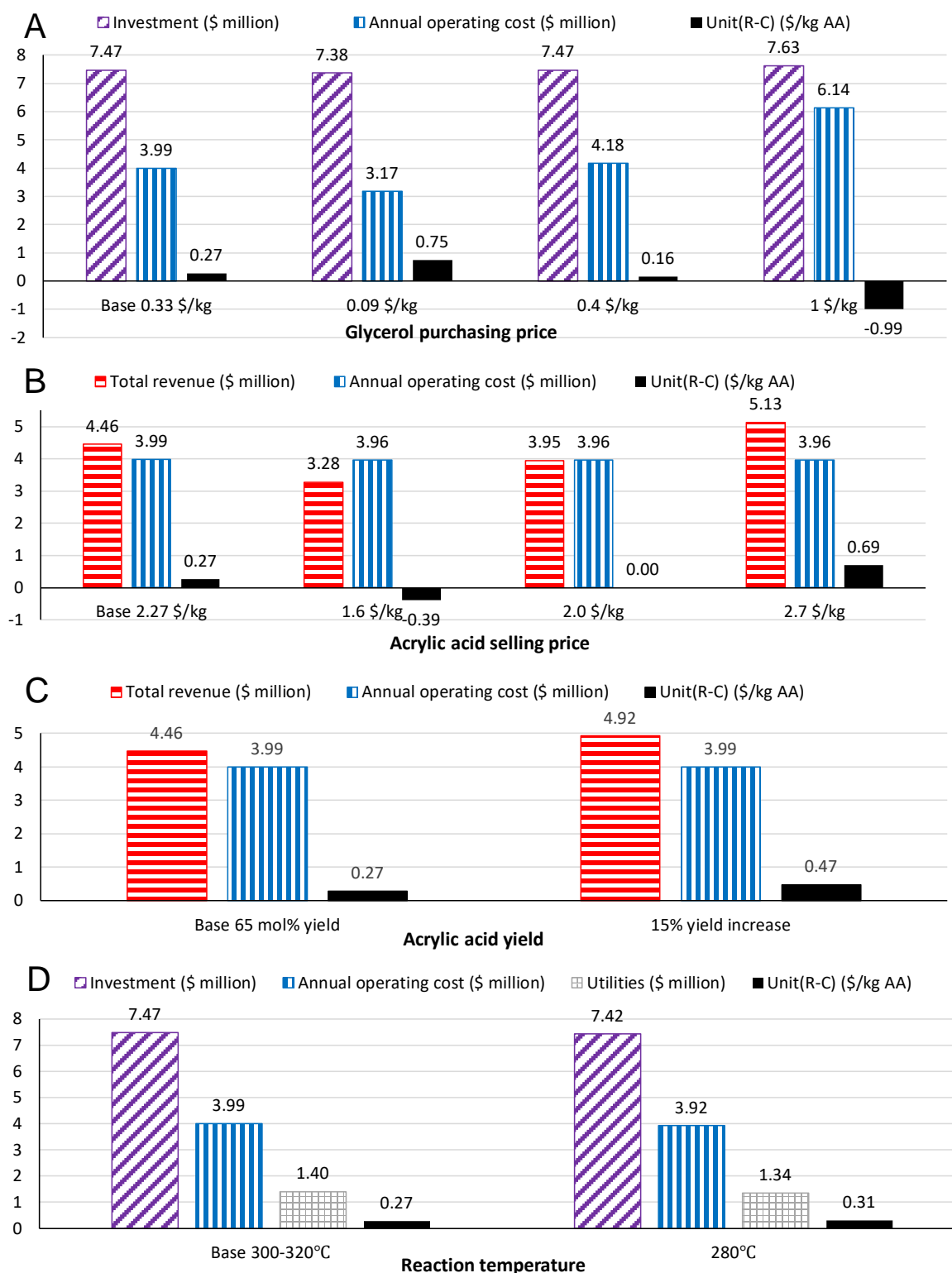
**Figure 2.** Breakdown of annual operating cost for the Base Model, (A) by categories, (B) by process sections, and (C) further breakdown of the utility category.

### 3.2. Factor Effects on Base Model

Factors and their effects on the Base Model are presented in Figure 3. Here we define the unit production revenue minus unit production cost for acrylic acid (AA) as “Unit(R-C)”; when this value becomes negative, the plant will not be profitable. The glycerol purchasing price slightly affects the total investment for the facility but has a more pronounced impact on the annual operating cost. This Base Model plant can be marginally profitable if the feedstock price rises to \$0.40/kg (Figure 3A).

Historically, the acrylic acid price greatly fluctuated, heavily dependent on the petroleum market and the supply of propylene. Nonetheless, the global acrylic acid market is expected to reach USD \$22.6 billion by 2022, with demand in superabsorbent polymer production as a key driving factor for market growth, according to a study by Grand View Research, Inc., San Francisco, CA, USA [20]. It appears that acrylic acid priced at \$2/kg is the break-even point for the Base Model (Figure 3B).

With further research and development in reaction catalysis, it is reasonable to achieve higher acrylic acid yield and lower reaction temperatures. The profit margin can be increased by 74% if the acrylic acid yield can be increased by 15% to reach 80 mol% (Figure 3C). If the reaction temperature for both dehydration and partial oxidation can be lowered to 280 °C, the total capital investment and annual operating cost will be reduced by 0.7% and 1.8%, respectively; utility costs will be reduced by 4.3%, while the Unit(R-C) will be increased by 14.8% (Figure 3D).



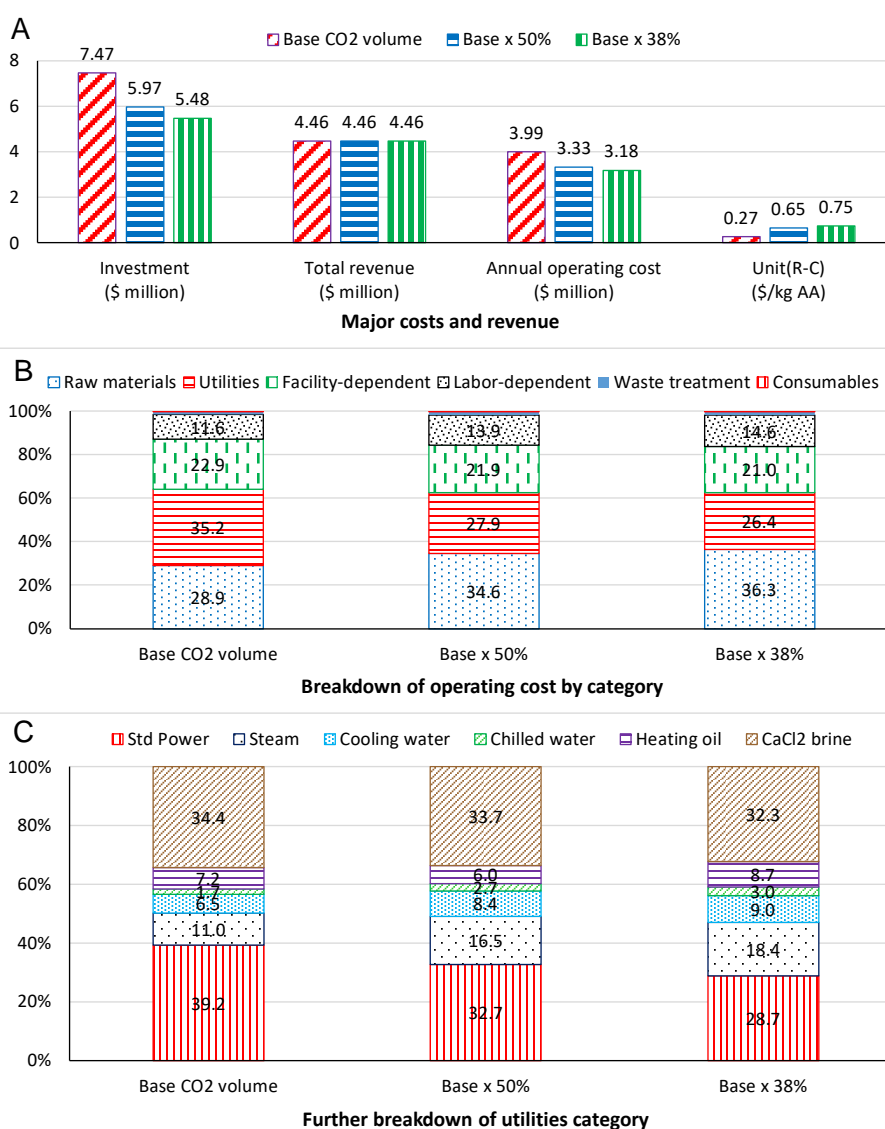
**Figure 3.** Factor effects on Base Model, (A) effect of glycerol purchasing price, (B) effect of acrylic acid selling price, (C) effect of increasing acrylic acid yield, and (D) effect of lowering reaction temperature.

### 3.3. Effect of CO<sub>2</sub> Input on Base Model

In our research and development of the SC-CO<sub>2</sub> technology to extend the service life of solid acid catalysts, the amount of CO<sub>2</sub> input has not been optimized. The Base Model requires cycling



9270 kg per hour of CO<sub>2</sub>, 50 times the molar input of glycerol. Our simulation results shown in Figure 4 demonstrate the critical need to reduce the CO<sub>2</sub> input for the improvement of this new technology.



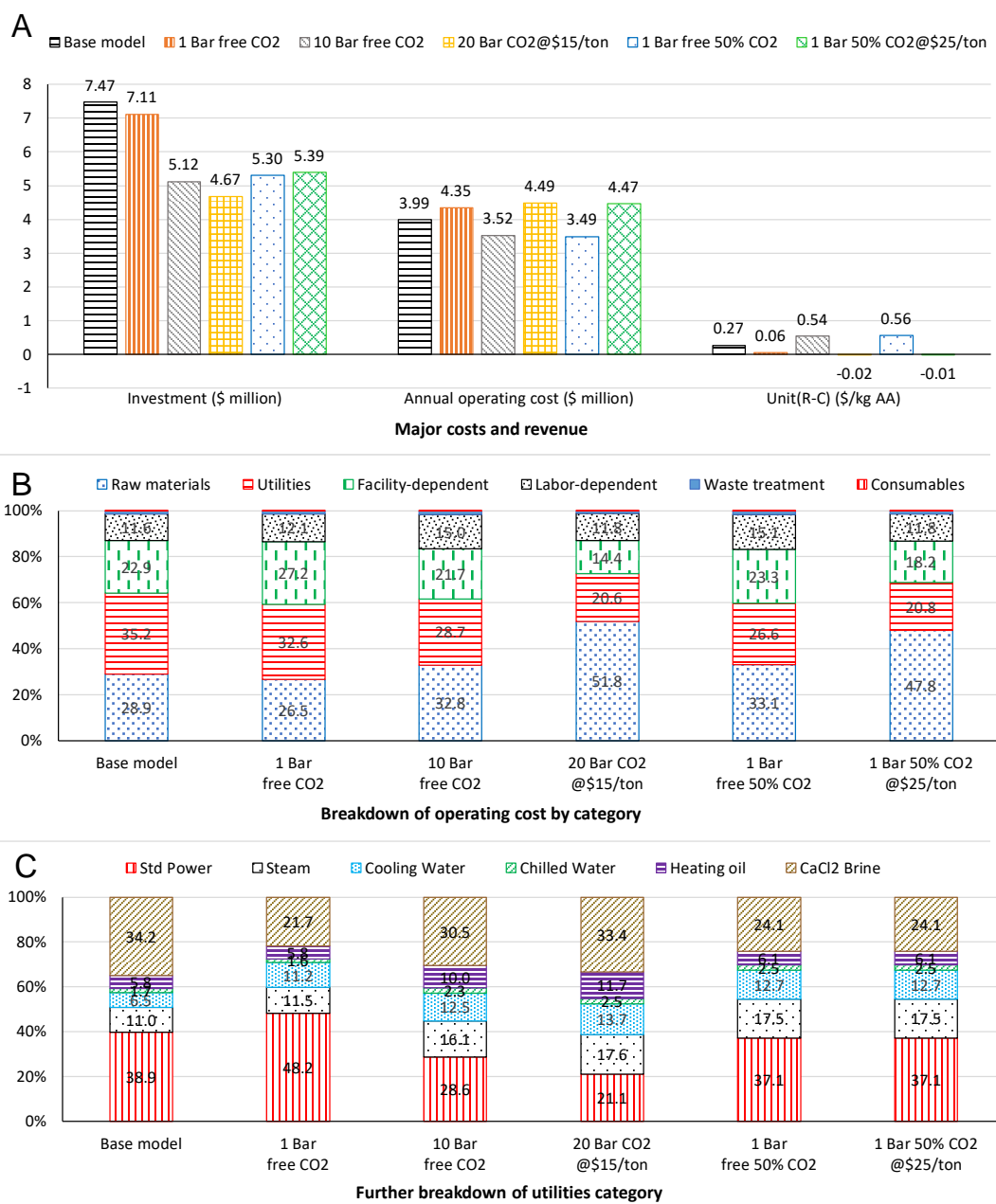
**Figure 4.** Effects of reducing CO<sub>2</sub> input on Base Model, (A) on major costs and revenue, (B) on operating cost by category, (C) on itemized utility costs.

If the CO<sub>2</sub> input can be cut down by 50%, the total capital investment will be reduced by 20% from \$7.47 million to \$5.97 million; the annual operating cost will be decreased by 17% from \$3.99 million to \$3.33 million, and the Unit(R-C) will be increased by 140% from 0.27 to \$0.65/kg AA. Further cutting down CO<sub>2</sub> input to 38% of that of the Base Model will further reduce capital investment and operating cost, elevating the profit margin (Figure 4A).

Breaking down the operating cost by category reveals that the utility costs exhibit a significant reduction with the decreasing CO<sub>2</sub> input, and raw materials rise to the top cost category (Figure 4B). Among the utilities used, the reduction of standard power consumption is pronounced (Figure 4C). Future research should prioritize the reduction of CO<sub>2</sub> input without sacrificing its function of extending catalyst service life.

### 3.4. Effect of No CO<sub>2</sub>/Energy Recycling

Changes are made to the Base Model by removing the process section of CO<sub>2</sub>/Energy recycling shown in Figure 1, while keeping other process conditions the same. In this NR-Model, there is a source of CO<sub>2</sub> as input to the plant, requiring two gas compressors and an extra heater to bring the input CO<sub>2</sub> to the required pressure and temperature before entering the dehydration reactor. Five scenarios are considered for the NR-Model in contrast to the Base Model (Figure 5): (1) the input CO<sub>2</sub> has a pressure of 1 Bar with no cost; (2) the input CO<sub>2</sub> has a pressure of 10 Bar with no cost; (3) the input CO<sub>2</sub> has a pressure of 20 Bar and costs \$15 per metric ton; (4) the input CO<sub>2</sub> at 1 Bar has no cost and the volume can be cut down by 50%; and (5) the input CO<sub>2</sub> at 1 Bar can be cut down by 50% in volume and costs \$25 per metric ton.



**Figure 5.** Effects of five scenarios of no CO<sub>2</sub>/Energy recycling on NR-Model in contrast to Base Model, (A) on major costs and revenue, (B) on operating cost by category, (C) on itemized utility costs.

Although the total capital investment can be lowered by ~5% if we do not recycle CO<sub>2</sub>/Energy in the first scenario, the annual operating cost would be increased by 10%, resulting in a 78% lower profit margin (Figure 5A) compared to the Base Model. This proves the advantage of including CO<sub>2</sub>/Energy recycling in the design of our Base Model. If the input CO<sub>2</sub> is at 10 Bar (scenario 2), significant reductions of capital investment (by 31%) and operating cost (by 12%) can be achieved with an increase of profit margin by 100%, comparing to the Base Model. This analysis indicates that the initial compression of a large volume of CO<sub>2</sub> input at near atmospheric pressure is an energy-intensive process, also requiring costly large equipment. Further rise of the input CO<sub>2</sub> pressure to 20 Bar (scenario 3) would render a plant close to the break-even point even if the CO<sub>2</sub> costs \$15 per metric ton. As we have shown in the analysis for the Base Model in Section 3.3, the reduction of CO<sub>2</sub> input volume has a pronounced impact on lowering investment and operating costs. The same is true for the NR-Model if the CO<sub>2</sub> input is cut down by 50% (scenario 4), and the plant would be close to the break-even point even if the CO<sub>2</sub> costs \$25 per metric ton (scenario 5).

Figure 5B shows the relative percentage changes of each operating cost category for all the five scenarios in comparison with the Base Model, reinforcing that (1) initial compression of a large volume of CO<sub>2</sub> is costly in terms of both utilities and facility; (2) the top two utilities cost items are the standard power and CaCl<sub>2</sub> brine which are mainly used for CO<sub>2</sub> compression and cooling (Figure 5C); and (3) the reduction of CO<sub>2</sub> input would significantly increase profit margin. It is noteworthy to point out that the future development of this bio-based technology should consider cascading processing in conjunction with emerging Carbon Capture and Utilization or Recycling (CCU or CCR) technologies that can efficiently provide CO<sub>2</sub>.

### 3.5. Effect of Threefold Scale-Up

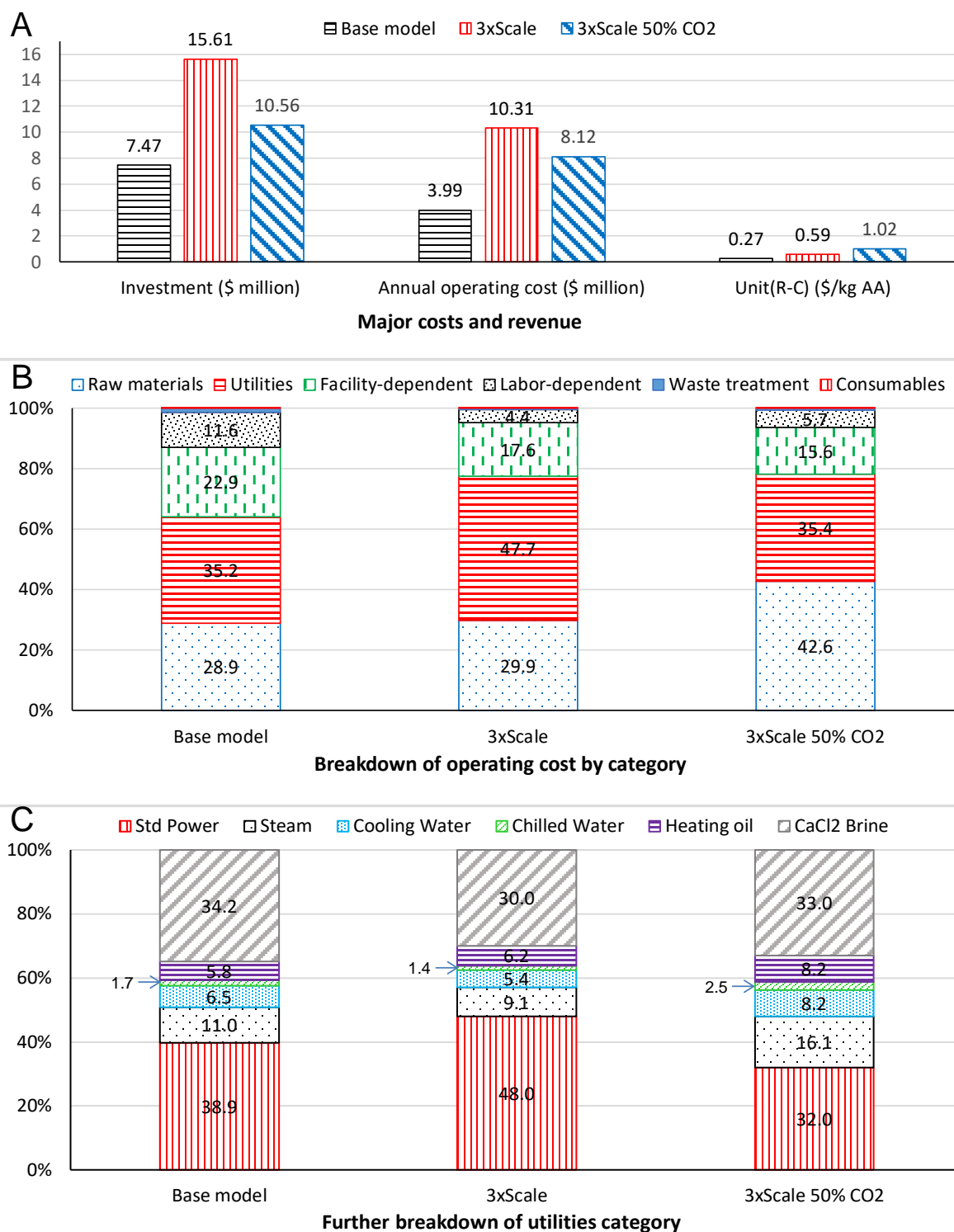
Although we intended to conduct the process modeling and production cost estimation of a cascading acrylic plant based on a typical intermediate-sized biodiesel facility, larger scales of biodiesel facilities exist. Therefore, we scale up the Base Model to evaluate the scaling impact. Two scenarios are considered here as shown in Figure 6 in contrast to the Base Model: (1) a threefold scale-up in term of glycerol input volume (and proportionally other inputs of materials) keeping all process conditions the same as those of the Base Model, and (2) a threefold scale-up in term of glycerol input volume keeping all process conditions the same as those of the Base Model, except that the CO<sub>2</sub> input is reduced by 50%.

The threefold scale-up (3 × scale) plant requires approximately a doubled capital investment and 2.6 times the annual operating cost, comparing to the Base Model, and the profit margin is doubled as indicated by the Unit(R-C). Reducing CO<sub>2</sub> input by 50% significantly lowers the capital investment and operating cost, leading to a more than tripled profit margin (Figure 6A).

With the threefold scale-up, the relative percentage of utilities cost jumps to nearly a half of the total operating cost, while that of the facility-dependent cost shrinks (Figure 6B), although now the most expensive piece of equipment for initial CO<sub>2</sub> compression (G-101) costs nearly \$2.9 million, indicating an energy-intensive plant. Reducing CO<sub>2</sub> input by 50% brings the percentage of the cost of utilities down to the same level as that for the Base Model (Figure 6B). Looking further into the itemized utility costs (Figure 6C) reveals that the scale-up increases the percentage of standard power cost to 48% of the total utilities cost, again mainly due to the large power consumption for compressing the CO<sub>2</sub>. It is clear that even for a threefold scale-up, the reduction of CO<sub>2</sub> input should be prioritized in further research and development.

Although continuous development of better catalysts remains as one way to extend catalyst life [21], the potential of “green” process engineering should be explored. We would like to point out that Carbon Capture and Utilization or Recycling (CCU or CCR) technologies are advancing quickly. In the North American market, ammonia producers in the United States are used to a price range of around US\$3–15 per metric ton for bulk gaseous/supercritical CO<sub>2</sub>, which varies significantly depending on the location; the price for pipelined CO<sub>2</sub> has historically been in the range of US\$9–26 per metric ton, which includes the cost of the pipeline infrastructure (capital and operational costs) [22].

Ethanol is already a part of the bioeconomy. A typical ethanol plant producing 50 million gallons of ethanol per year also produces ~150,000 metric tons of high-purity CO<sub>2</sub> annually [23]. These are potential sources that could provide CO<sub>2</sub> to an acrylic acid plant in a cost-effective manner.



**Figure 6.** Effects of two scenarios of scale-up in contrast to Base Model, (A) on major costs and revenue, (B) on operating cost by category, (C) on itemized utilities costs.

#### 4. Conclusions and Future Perspective

This study establishes simulation models in the context of a circular economy to analyze the technical and economic feasibility of producing acrylic acid from glycerol in conjunction with a typical intermediate-sized biodiesel facility, based on our new technology of using carbon dioxide as reaction medium in a two-step process to catalytically convert glycerol to acrylic acid. The results of our process modeling and production cost estimation indicate that coproduction of acrylic acid with an intermediate-sized biodiesel plant can be economically feasible, contributing to the bioeconomy and circular economy, and the profit margin can be doubled with a threefold scale-up.

Other than market factors such as fluctuating prices of glycerol and acrylic acid, our simulation reveals that from the technical standpoint, the reduction of CO<sub>2</sub> input without sacrificing its function of extending catalyst service life has the highest positive impact on the economic benefit, followed by further increase of acrylic acid yield and reduction to milder reaction conditions. The profit margin can be increased by 74% if the acrylic acid yield can be increased by 15% to reach 80 mol%, whereas the profit margin can be increased by 140% if the CO<sub>2</sub> input can be cut down by 50%. Our results clearly pointed out directions for further research and development of this new technology in the way that should consider cascading processing in conjunction with emerging Carbon Capture and Utilization or Recycling Technologies that can cost-effectively provide CO<sub>2</sub>.

New biobased technologies are emerging as scattered dots, and it is now the time to connect the dots to develop cascading and integrated technologies towards a circular economy.

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**Author Contributions:** X.P.Y. was responsible for conceptualization, methodology, investigation, supervision, writing, reviewing and editing. S.R. conducted the data curation, investigation, draft model preparation. All authors have read and agreed to the published version of the manuscript.

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#### References

1. Carus, M.; Dammer, L. The Circular Bioeconomy—Concepts, Opportunities, and Limitations. *Ind. Biotechnol.* **2018**, *14*, 83–91. [[CrossRef](#)]
2. Ye, X.P.; Ren, S. 3-Value-Added Chemicals from Glycerol. In *Soy-Based Chemicals and Materials*; Brentin, R., Ed.; American Chemical Society: Washington, DC, USA, 2014; pp. 43–80.
3. Johnson, D.T.; Taconi, K.A. The glycerin glut: Options for the value-added conversion of crude glycerol resulting from biodiesel production. *Environ. Prog.* **2007**, *26*, 338–348. [[CrossRef](#)]
4. Katryniok, B.; Paul, S.; Dumeignil, F. Recent Developments in the Field of Catalytic Dehydration of Glycerol to Acrolein. *ACS Catal.* **2013**, *3*, 1819–1834. [[CrossRef](#)]
5. Liu, L.; Ye, X.P.; Bozell, J.J. A Comparative Review of Petroleum-Based and Bio-Based Acrolein Production. *ChemSusChem* **2012**, *5*, 1162–1180. [[CrossRef](#)] [[PubMed](#)]
6. Cheng, L.; Liu, L.; Ye, X.P. Acrolein Production from Crude Glycerol in Sub- and Super-Critical Water. *J. Am. Oil Chem. Soc.* **2013**, *90*, 601–610. [[CrossRef](#)]
7. Ott, L.; Bicker, M.; Vogel, H. Catalytic dehydration of glycerol in sub- and supercritical water: A new chemical process for acrolein production. *Green Chem.* **2006**, *8*, 214–220. [[CrossRef](#)]
8. Akizuki, M.; Oshima, Y. Kinetics of Glycerol Dehydration with WO<sub>3</sub>/TiO<sub>2</sub> in Supercritical Water. *Ind. Eng. Chem. Res.* **2012**, *51*, 12253–12257. [[CrossRef](#)]
9. Cheng, L.; Ye, X.P. A DRIFTS Study of Catalyzed Dehydration of Alcohols by Alumina-supported Heteropoly Acid. *Catal. Lett.* **2009**, *130*, 100–107. [[CrossRef](#)]
10. Liu, L.; Ye, X.P.; Katryniok, B.; Capron, M.; Paul, S.; Dumeignil, F. Extending Catalyst Life in Glycerol-to-Acrolein Conversion Using Non-thermal Plasma. *Front. Chem.* **2019**, *7*, 108. [[CrossRef](#)] [[PubMed](#)]

11. Katryniok, B.; Paul, S.; Belliere-Baca, V.; Rey, P.; Dumeignil, F. Glycerol dehydration to acrolein in the context of new uses of glycerol. *Green Chem.* **2010**, *12*, 2079–2098. [[CrossRef](#)]
12. Tsukuda, E.; Sato, S.; Takahashi, R.; Sodesawa, T. Production of acrolein from glycerol over silica-supported heteropoly acids. *Catal. Commun.* **2007**, *8*, 1349–1353. [[CrossRef](#)]
13. Chai, S.-H.; Wang, H.-P.; Liang, Y.; Xu, B.-Q. Sustainable production of acrolein: Gas-phase dehydration of glycerol over 12-tungstophosphoric acid supported on ZrO<sub>2</sub> and SiO<sub>2</sub>. *Green Chem.* **2008**, *10*, 1087–1093. [[CrossRef](#)]
14. Katryniok, B.; Paul, S.; Capron, M.; Dumeignil, F. Towards the sustainable production of acrolein by glycerol Dehydration. *ChemSusChem* **2009**, *2*, 719–730. [[CrossRef](#)] [[PubMed](#)]
15. Zou, B.; Ren, S.; Ye, X.P. Glycerol Dehydration to Acrolein Catalyzed by ZSM-5 Zeolite in Supercritical Carbon Dioxide Medium. *ChemSusChem* **2016**, *9*, 3268–3271. [[CrossRef](#)] [[PubMed](#)]
16. Ye, X.P. Glycerol Dehydration Methods and Products Thereof. US Patent US9796648B2, 24 October 2017.
17. Haas, M.J.; McAloon, A.; Yee, W.; Foglia, T. A process model to estimate biodiesel production costs. *Bioresour. Technol.* **2006**, *97*, 671–678. [[CrossRef](#)] [[PubMed](#)]
18. Ikushima, Y.; Saito, N.; Arai, M. Supercritical carbon dioxide as reaction medium: Examination of its solvent effects in the near-critical region. *J. Phys. Chem.* **1992**, *96*, 2293–2297. [[CrossRef](#)]
19. Fujita, S.; Tanaka, T.; Akiyama, Y.; Asai, K.; Hao, J.; Zhao, F.; Arai, M. Impact of Carbon Dioxide Pressurization on Liquid Phase Organic Reactions: A Case Study on Heck and Diels–Alder Reactions. *Adv. Synth. Catal.* **2008**, *350*, 1615–1625. [[CrossRef](#)]
20. Grand View Research Inc. Report, Acrylic Acid Market Analysis. 2016. Available online: <https://www.grandviewresearch.com/industry-analysis/acrylic-acid-market> (accessed on 18 August 2020).
21. Yadav, D.G.; Sharma, R.V.; Katole, S.O. Selective Dehydration of Glycerol to Acrolein: Development of Efficient and Robust Solid Acid Catalyst MUICaT-5. *Ind. Eng. Chem. Res.* **2013**, *52*, 10133–10144. [[CrossRef](#)]
22. Varone, A. The CO<sub>2</sub> Economy—The Transformation of Carbon Dioxide from a Liability to an Asset. Institute for Advanced Sustainability Studies. 2016. Available online: <https://www.iass-potsdam.de/en/blog/2016/07/co2-economy-transformation-carbon-dioxide-liability-asset> (accessed on 12 July 2020).
23. Attis Biofuels. Report, Carbon Dioxide. 2020. Available online: <https://www.attisbiofuels.com/by-products/carbon-dioxide> (accessed on 12 July 2020).

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