

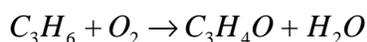
## Separations and Reactors

### Acrylic Acid Production via the Catalytic Partial Oxidation of Propylene

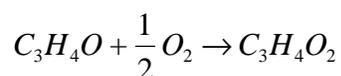
#### Process Information

#### Background

Acrylic acid (AA) is used as a precursor for a wide variety of chemicals in the polymers and textile industries. There are several chemical pathways to produce AA, but the most common one is via the partial oxidation of propylene. The usual mechanism for producing AA utilizes a two step process in which propylene is first oxidized to acrolein and then further oxidized to AA. Each reaction step usually takes place over a separate catalyst and at different operating conditions. The reaction stoichiometry is given below:

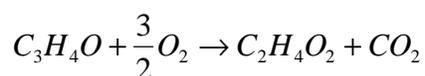
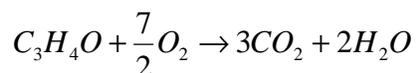


Acrolein

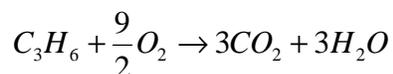


Acrylic Acid

Several side reactions may occur, most resulting in the oxidation of reactants and products. Some typical side reactions are given below:



Acetic Acid



Therefore, the typical process set-up consists of a two-reactor system with each reactor containing a separate catalyst and operating at conditions so as to maximize the production of AA. The first reactor typically operates at a higher temperature than the second unit.

#### Process Description

A base case process is shown in Figure 1. This process produces 50,000 metric tons per year of 99.9 mole % of acrylic acid (AA) product. The number of operating hours should be taken as 8000/yr. The reactor in the process shown in Figure 1 uses a proprietary catalyst that eliminates the

C-301 A/B	E-301	P-301 A/B	R-301	V-301	T-301	P-302 A/B	X-301	T-302	E-303	P-303 A/B	V-301	E-304	P-304 A/B	E-305
Inlet Air Blower	Molten Salt Cooler	Molten Salt Circulation Pumps	Reactor	Phase Separator	Off-Gas Absorber	Quench Pumps	Extraction Unit	Acid Tower	Acid Reboiler	Acid Reflux Pumps	Acid Reflux Drum	Acid Condenser	Product Pumps	Product Cooler

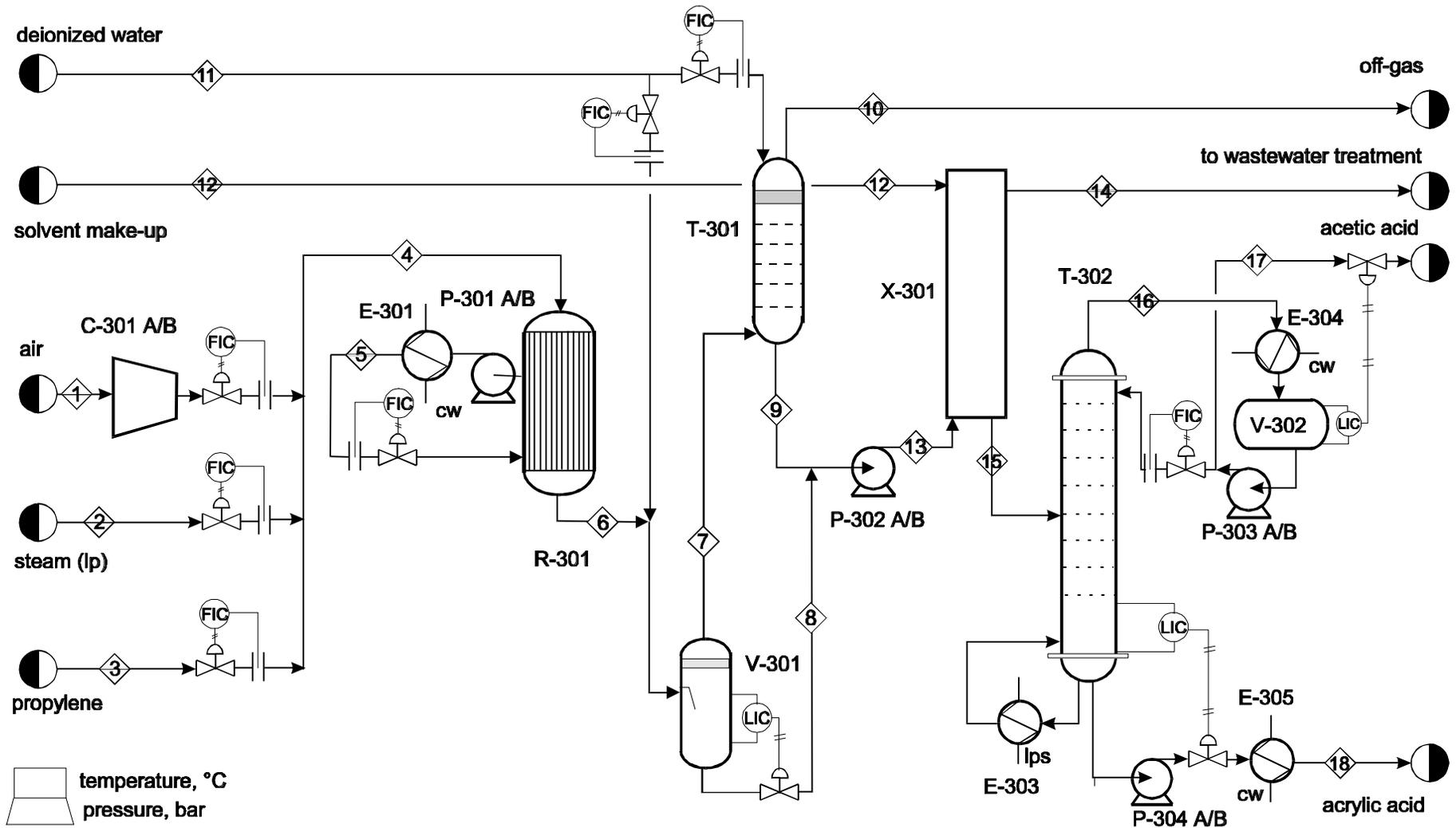


Figure 1: PFD for Unit 300 - Acrylic Acid from Propylene

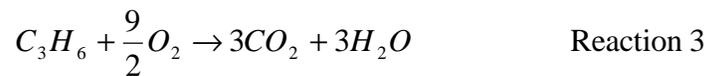
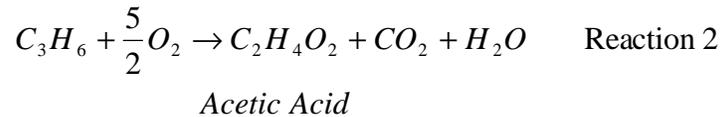
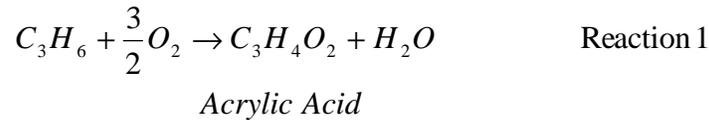
production of the intermediate, acrolein. Therefore, this process requires only a single reactor. After reaction, it is essential to cool the products (reactor effluent) quickly to avoid further homogeneous oxidation reactions. This is achieved by rapidly quenching the reactor effluent, Stream 6, by injecting deionized water into it. The homogeneous combustion reactions will not take place so long as the reactor effluent is cooled to below 100°C immediately after the reactor. Additional recovery of AA and acetic acid (a by-product) from the gas, Stream 7, leaving the phase separator (V-301) is achieved in the absorber, T-301.

The liquid stream, Stream 9, leaving the absorption section is a dilute aqueous acid. It is combined with the liquid from the phase separator, V-301, to form the feed to the extractor section, Stream 13. This stream is sent to the liquid-liquid extraction section, X-301, to remove preferentially the acid fraction from the water prior to purification. There are several columns, exchangers, pumps, vessels, and other miscellaneous equipment in X-301. **Do not to attempt** to design this section of the plant. This part of the design will be contracted out to another company. The organic phase leaving X-301, Stream 15, contains 99.5 % of the AA and acetic acid in Stream 13 and essentially no water or other components. This is sent to the acid purification column, T-302, where 95% by mole acetic acid by-product is produced overhead and 99.9 % by mole AA is produced as a bottom product and cooled prior to being sent to storage.

The aqueous phase from the extractor, Stream 14, is sent to a wastewater treatment plant, where it is decontaminated prior to being returned to the environment.

### Reaction Kinetics and Reactor Configuration

The reactions taking place are all irreversible. The reaction kinetics for the catalyst used in this process are given below:



where  $-r_i = k_{o,i} \exp\left[\frac{-E_i}{RT}\right] p_{propylene} p_{oxygen}$

Partial pressures are in kPa and the activation energies and pre-exponential terms for reactions 1-3 are given below:

$i$	$E_i$ kcal/kmol	$k_{o,i}$ kmol/m <sup>3</sup> reactor/h/(kPa) <sup>2</sup>
1	15,000	$1.59 \times 10^5$
2	20,000	$8.83 \times 10^5$
3	25,000	$1.81 \times 10^8$

The kinetics presented above are valid in the temperature range, 250 – 330°C. Above 330°C the catalyst starts to coke-up (carbon deposits on the surface of the catalysts causing it to deactivate), and below 250°C the rate of reaction drops off rapidly. Due to these effects, the catalysts should never be operated outside of these temperature limits.

The reactor configuration used for this process should be a packed bed reactor. Details about the design of the reactor are given in the Appendix of this problem statement.

### Safety Considerations

It is recommended that the steam-to-propylene ratio at the reactor inlet never be set less than 4:1 on a mole basis. This steam is used to inhibit the formation of coke on the catalyst below temperatures of 330°C.

As with any reaction involving the partial oxidation of a fuel-like feed material (propylene) considerable attention must be paid to the composition of hydrocarbons and oxygen in the feed stream. This stream is a potential explosion hazard. Operation outside of the explosion limits (LEL and UEL) is strongly recommended for a packed bed reactor. The explosion limits for propylene in air at 25°C are LEL = 2.0 mol% propylene and UEL = 11.1 mol% propylene. At elevated temperatures and using a 4:1 steam-to-propylene ratio (see above) in the feed, the lower explosion limit (LEL) is changed significantly. In this case it is easier to define a minimum oxygen concentration (MOC) for the stream. Below the MOC, flame propagation and hence explosions are not possible. For the packed bed reactor you can assume an average value of MOC = 5.6 mol % oxygen. The UEL at typical temperatures used for this reaction is 15.3 mol % propylene.

The second safety concern is that associated with the highly exothermic polymerization of AA which occurs in two ways. First, if this material is stored without appropriate additives, then free radical initiation of the polymerization can occur. This potentially disastrous situation is discussed by Kurland and Bryant [1]. Secondly, AA dimerizes when in high concentrations at temperatures greater than 90°C. Therefore, process conditions in the separation section (X-301 and T-302) should never exceed this temperature.

## CHEMCAD Hints

It is recommended that any simulation for this process be performed using the UNIQUAC K-value and the SRK enthalpy options on CHEMCAD™. These should give reasonable results for preliminary process design.

For heat exchangers with multiple zones, it is recommended that you simulate each zone with a separate heat exchanger. Actual equipment may include several zones, so costing should be based on the actual equipment specifications.

For the distillation column and absorber, you should use the shortcut method (SHOR) to get estimates for the rigorous distillation simulation (TOWR or SCDS). The shortcut method may be used for T-302 until an optimum case is near. It is then expected that everyone will obtain a final design using rigorous simulation of this column.

The fixed bed reactor should be modeled in detail, integrating the differential forms of the material balance, mechanical energy balance, and heat transfer equations using POLYMATH. Dr. Miller will give further information on this during ChE 172. The results from CHEMCAD™ for this reactor should be compared to the solutions obtained using POLYMATH.

When simulating a process using “fake” streams and equipment, it is absolutely necessary that the process flow sheet that you present not included any “fake” streams and equipment. It must represent the actual process.

### Project Objective

The objective of this project is to maximize the before-tax profit (*BTF*) defined below:

$$BTF = \sum \text{revenue from products and byproducts} - \sum \text{cost of utilities} - \sum \text{cost of raw materials} \\ - (0.3) \sum \text{Installed cost of equipment}$$

All chemical prices can be obtained from the *Chemical Marketing Reporter* in the Evansdale Library. Use the prices from the last issue for January 1999. A list of available utilities is attached in the Appendix.

## Specific Assignments

### General

Optimize the process using decision variables of your choosing. You should choose as decision variables the design variables most strongly affecting the objective function.

### ChE 112 - Separations

Detailed designs of the absorber, T-301, and the acid purification tower, T-302, are required. For both towers, you should specify the important design parameters, e.g., diameter, height, number of trays/height of packing, % flooding, operating pressures and pressure drop across the packing/trays, % open area on trays, etc. Supporting calculations and CHEMCAD outputs should be provided in the appendix.

### ChE 172 - Reactors

A detailed design of a packed bed reactor with countercurrent cooling should be provided in your final report. Therefore, optimize the process for this reactor. You must choose and discuss your choice of decision variables. At no place along the length of the process side of the reactor should the temperature exceed 350°C. Also, the reactor process-side inlet temperature must be at least 250°C so the reaction can commence. A filler material is available which has the same density, diameter, void fraction, heat capacity, price, etc., of the catalyst. It is inert and may be installed within the reactor without catalyzing the reaction. Since CHEMCAD has no allowance for the Ergun equation, hand estimate the pressure drop on the process side of the reactor and plug it into CHEMCAD for each simulation. Your design team must provide a copy of the design equations that include the Ergun equation, and plots of coolant and reactor temperature, pressure, and concentrations of the chemical species versus reactor length for the optimal reactor design. Solve these equations using Polymath or another ordinary differential equation solver. Discuss and compare both the analytical and CHEMCAD design at your optimum operating conditions. Include a disc copy of your Polymath and CHEMCAD programs with your final report.

### **References**

1. Kurland, J.J. and D.B. Bryant, "Shipboard Polymerization of Acrylic Acid," Plant Operations Progress, **6**, 4, 203-207 (1987).

# Appendix

## Cost Data

### Equipment Costs (Purchased)

Pumps	$\$630 (\text{power, kW})^{0.4}$
Heat Exchangers	$\$1030 (\text{area, m}^2)^{0.6}$
Compressors	$\$770 (\text{power, kW})^{0.96} + 400 (\text{power, kW})^{0.6}$
Turbine	$\$2.18 \times 10^5 (\text{power output, MW})^{0.6}$ assume 65% efficiency
Fired Heater	$\$635 (\text{duty, kW})^{0.8}$ assume 80% thermal efficiency assume can be designed to use any organic compound as a fuel
Vessels	$\$[1.67(0.959 + 0.041P - 8.3 \times 10^{-6}P^2)] \times 10^z$ $z = (3.17 + 0.2D + 0.5 \log_{10}L + 0.21 \log_{10}L^2)$ $D = \text{diameter, m } 0.3 \text{ m} < D < 4.0 \text{ m}$ $L = \text{height, m } L/D < 20$ $P = \text{absolute pressure, bar}$
Catalyst	$\$2.25/\text{kg}$
Packed Tower	Cost as vessel plus cost of packing
Packing	$\$(-110 + 675D + 338D^2)H^{0.97}$ $D = \text{vessel diameter, m; } H = \text{vessel height, m}$
Tray Tower	Cost as vessel plus cost of trays
Trays	$\$(187 + 20D + 61.5D^2)$ $D = \text{vessel diameter, m}$

It may be assumed that pipes and valves are included in the equipment cost factors. Location of key valves should be specified on the PFD.

## Equipment Cost Factors

Pressure (absolute)	< 10 atm, 0.0 10 - 20 atm, 0.6 20 - 40 atm, 3.0 40 - 50 atm, 5.0 50 - 100 atm, 10	does not apply to turbines, compressors, vessels, packing, trays, or catalyst, since their cost equations include pressure effects
Carbon Steel	0.0	
Stainless Steel	4.0	

Total Installed Cost = Purchased Cost (4 + material factor + pressure factor)

## Raw Materials Costs

Propylene (polymer grade) (available as a sat'd vapor at 25°C)	see <i>Chemical Marketing Reporter</i>
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## Product Prices

Acrylic Acid (99.9 mol%) (1.0 bar, 40°C)	see <i>Chemical Marketing Reporter</i>
Acetic Acid (95 mole% required) (1.0 bar, 40°C)	see <i>Chemical Marketing Reporter</i>

## Utility Costs

Low Pressure Steam (600 kPa saturated)	\$6.62/1000 kg
Medium Pressure Steam (1135 kPa saturated)	\$7.31/1000 kg
High Pressure Steam (4237 kPa saturated)	\$8.65/1000 kg
Natural Gas (446 kPa, 25°C)	\$3.00/GJ
Fuel Gas (446 kPa, 25°C)	\$2.75/GJ
Electricity	\$0.06/kW h
Boiler Feed Water (at 549 kPa, 90°C)	\$2.54/1000 kg
Distilled Deionized Water	\$1.00/1000 kg

Cooling Water available at 516 kPa and 30°C return pressure $\geq$ 308 kPa return temperature is no higher than 45°C	\$0.16/GJ
Refrigerated Water available at 516 kPa and 10°C return pressure $\geq$ 308 kPa return temperature is no higher than 20°C	\$1.60/GJ
Refrigeration	\$60/GJ

## Design Information

### **Reactor Information**

#### Packed Bed Reactor

Assume the catalyst for the packed bed reactor to have the following physical properties

Catalyst particle diameter,  $d_p = 5$  mm

Catalyst particle density,  $\rho_{cat} = 2100$  kg/m<sup>3</sup>

Packing void fraction,  $\epsilon = 0.45$

Heat transfer coefficient from packed bed to tube wall,  $h = 50$  W/m<sup>2</sup>°C

Use standard tube sheet layouts as for heat exchangers.

It is suggested that either a molten salt or Dowtherm™ A heat transfer fluid is used in the reactor shell to cool the catalyst filled tubes (just like a 1-shell – 1-tube pass heat exchanger with the catalyst filling the tubes)

Properties of Dowtherm™ A and molten salt are given in Perry's Handbook.

Due to the highly exothermic nature of the reaction the maximum tube diameter should be set at 1 inch. You may wish to dilute the catalyst with inert packing – just assume that this packing has the same physical properties as the catalyst but does not promote any reactions.

Purchased cost of packed bed reactor = \$ 10,000/m<sup>2</sup> of heat transfer surface

#### Solvent Extraction Unit, X-301

The design of the solvent extraction unit is very complicated and beyond the scope of the present project. However, the following economic information is available for estimating the profitability of the process:

Installed Cost of X-301 =  $1.0 \times 10^6$  [flowrate of water in Stream 13 (kmol/h)]<sup>0.3</sup>

Operating cost of X-301 =  $0.7 \times 10^6$  [flowrate of water in Stream 13 (kmol/h)]<sup>0.7</sup>

The above operating cost includes the cost of all utilities used by the unit, plus the cost of treating the wastewater, Stream 14, and the cost of make-up solvent, Stream 12.

#### Heat Exchangers

For heat exchangers, use the following approximations for heat transfer coefficients to allow you to determine the heat transfer area:

<b>situation</b>	<b><math>h</math> (W/m<sup>2</sup>°C)</b>
Condensing steam	6000
Condensing organic	1000
boiling water	7500
boiling organic	1000
flowing liquid	600
flowing gas	60

## **Other Information**

You should assume that a year equals 8000 hours. This is about 330 days, which allows for periodic shutdown and maintenance.

Unless specifically stated in class, the information in this document is that which is valid for this project only. Any information in the sophomore projects not specifically stated in this document is invalid for this project.

### **Deliverables**

Each group must deliver a report (two identical copies, one for each professor) written using a word processor. The report should be clear and concise. The format is explained in the document *Written Design Reports*. Any report not containing a labeled PFD and a stream table, each in the appropriate format, will be considered unacceptable. PFDs from CHEMCAD are generally unsuitable unless you modify them significantly. When presenting results for different cases, graphs are superior to tables. For the optimal case, the report appendix should contain details of calculations that are easy to follow. There should be separate appendices for each class, ChE 112 and ChE 172, each containing calculations appropriate for the respective class. These may be handwritten if done so neatly. Calculations that cannot be easily followed will lose credit. A copy of the CHEMCAD output for the final optimized case should also be included in the Appendix.

Each group will give an oral report in which the results of this project will be presented in a concise manner. The oral report should be between 15-20 minutes, and each group member must speak. A 5-10 minute question-and-answer session will follow. Instructions for presentation of oral reports are provided in a separate document entitled *Oral Reports*. The oral presentations will be Wednesday, April 21, 1999 starting at 11:00 a.m. and running until approximately 3:00 p.m. It is possible that some presentations will be on Thursday, April 22, 1999, beginning at 11:00 am. Attendance is required of all students during their classmates' presentations (this means in the room, not in the hall or the computer room). Failure to attend any of the above required sessions will result in a decrease of one-letter grade (per occurrence) from your project grade in ChE 112 and ChE 172.

The written project report is due by 11:00 a.m. Wednesday, April 21, 1999. Late projects will receive a minimum of a one letter grade deduction.

### **Revisions**

As with any open-ended problem (i.e., a problem with no single correct answer), the problem statement above is deliberately vague. The possibility exists that, as you work on this problem, your questions will require revisions and/or clarifications of the problem statement. You should be aware that these revisions/clarifications may be forthcoming.