CHE654 – Plant Design Project #1
Semester 1, 2022

DESIGN OF AN MTBE PRODUCTION PROCESS

(Courtesy of the Department of Chemical Engineering at West Virginia University)

Introduction

Methyl Tertiary-Butyl Ether (MTBE) is a gasoline additive used to increase octane number that is produced from methanol and isobutylene. The purpose of this project is to continue a preliminary analysis to determine the feasibility of constructing a chemical plant to manufacture 60,000 tonne/year MTBE.

Methanol is purchased, and the isobutylene is obtained from a refinery stream. The stream contains 23% isobutene, 20% 1-butene, and 57% 2-butene, which is modeled as trans-2-butene. Only isobutene reacts with methanol; 1-butene and 2-butene are inert for this reaction.

A suggested process flow diagram (PFD) is shown in Figure 1. You should use this as a starting point only. Your job is to analyze a simplified MTBE production process, to suggest profitable operating conditions, and to write a final report summarizing your findings.

In reporting your best case, clearly indicate the modified process and state not only the operating conditions for the (modified) process but also the corresponding values for the single-pass conversion of methanol, the overall conversion of methanol, and EAOC (to be defined later in this document). Also, state any recommendations you have for additional process improvements that you were not able to incorporate into the process calculations. Note that although you are to look for a "best" solution in your design, optimization is NOT required in this design project.

Chemical Reaction

The reaction is facilitated by a sulfonated ion-exchange resin catalyst. The reactions and reaction kinetics are as follows:

$$CH_3OH + (CH_3)_2C = CH_2 \underset{\leftarrow}{\longrightarrow} (CH_3)_3C - O - CH_3 \qquad (1)$$

$$-r = \Psi \cdot k_f \frac{C_{IB}^2 \cdot C_{MeOH}^2 - \dfrac{C_{MTBE}^2}{K^2}}{\left(C_{MeOH}^2 + K' \cdot C_{MTBE}^2\right)^3} \qquad (2)$$

where

$$k_f = 1.3 \times 10^{-6} \exp\left(-\frac{84{,}300}{RT}\right) \tag{3}$$

$$K = 4.742 \times 10^{-9} \exp\left(\frac{65000}{RT}\right) \tag{4}$$

$$K' = 0.778 \tag{5}$$

The units of reaction rate, r_i, are mol/kg catalyst h, forward rate constant, k_f, are mol^3/(m^6 site hr), and the activation energy is in J/mol. The kinetics were determined at temperatures ranging from 45 to 90 ˚C. The concentrations of methanol and isobutene and temperature are known to modify the solubility of the catalyst. As a result, these characteristics of the reaction medium influence the reactivity of the catalyst. The ratio of isobutene to methanol concentrations studied experimentally ranged from 0.5 to 2.

The sulfonated ion-exchange resin catalyst initially has a site density of 3x10^{24} sites per kg of catalyst and becomes deactivated at higher temperatures. The deactivation kinetics are represented by the following reaction kinetics:

$$\frac{d\Psi}{dt} = -k_D \cdot \Psi \tag{6}$$

$$k_D = 200 \exp\left(-\frac{70{,}000}{RT}\right), \tag{7}$$

where Ψ is the catalytic site density in units of sites/kg catalyst and the deactivation rate constant, k_D, has units of sec^{-1}.

Process Description

The PFD for the (starting) process is given in Figure 1.

Process Details

Feed Stream and Effluent Streams

Stream 1: Methanol – stored as a liquid at the desired pressure of the reaction.

Stream 2: Mixed butene stream – 23% isobutene, 20% 1-butene, 57% 2-butene.

Stream 8: MTBE product – must be 95 wt% pure.

Stream 11: Process water – see utility list for more information

Stream 12: Waste butenes – returned to refinery – contains 1-butene and 2-butene with less than 1 wt% other impurities.

Stream 16: Waste water – must be treated – must contain 99 wt% water – See the utility list for more information.

Equipment

Pump (P-901 A/B, includes spare pump)

The pump increases the pressure of the mixed feed to the reaction conditions. The liquid density may be estimated using a linear average of the pure component densities, weighted by their mass fractions in the mixture. The cost of electricity to run the pump is a utility cost based on the required power for the pump. The required power is the work multiplied by the mass flowrate of Stream 4.

Heat Exchanger (E-901)

This heat exchanger heats the feed to the reactor feed temperature. Each component must remain in the liquid phase at the chosen pressure. The cost of the heat source is a utility cost.

Reactor (R-901)

This is where the reaction occurs. The reactor is adiabatic, and the reaction is exothermic. Therefore, the heat generated by the reaction raises the temperature of the exit stream. The exit temperature is a function of the conversion. The reaction must be run at a pressure and temperature to ensure that all components remain in the liquid phase in the reactor.

Methanol must be present in the reactor feed at a minimum 200% excess to suppress undesired side reactions that produce undesired products.

The reactor operating conditions (feed and exit temperatures, pressure) are to be optimized. An operating pressure must be chosen. An optimum temperature and conversion must be determined.

Distillation Column (T-901)

This column runs at 19 atm. (The pressure is controlled by a valve, that is not shown on the PFD, in the product stream from R-901.) Separation of methanol and MTBE occurs in this column. Of the methanol in Stream 7, 98% enters Stream 9. Similarly, 99% of MTBE in Stream 7 enters Stream 8.

Heat Exchanger (E-902)

In this heat exchanger, the some of the contents of the stream leaving the bottom of T-901 going to E-902 are vaporized and returned to the column. The amount returned to the column is equal to the amount in Stream 8. The temperature of these streams is the boiling point of MTBE at the column pressure. There is a cost for the amount of steam needed to provide energy to vaporize the stream; this is a utility cost. The steam temperature must always be higher than the temperature of the stream being vaporized.

Heat Exchanger (E-903)

In this heat exchanger, the contents of the top of T-901 are partially condensed from saturated vapor to saturated liquid at the column pressure. 99% of the MTBE and water condense and 99% of all other components remain in the vapor phase. The remaining 1% of all other components condense with the MTBE. It may be assumed that this stream condenses at the boiling point of methanol at the column pressure. There is a cost for the amount of cooling water needed; this is a utility cost. The cooling water leaving E-903 must always be at a lower temperature than that of the stream being condensed.

Absorber (T-902)

The absorber runs at 5 atm and 90°C (outlet streams and Stream 11). In the absorber, 99% of the methanol in Stream 9 is absorbed into the water. All other components enter Stream 12. The cost of Stream 9 is a raw material cost. Process water sent to scrubber is controlled so that 5.0 kmol of water are used for every 1.0 kmol of methanol.

Distillation Column (T-903)

This column runs at 5 atm. (The pressure is controlled by a valve in the product stream from T-903, which is not shown on the PFD.) Separation of methanol and water occurs in this column. Of the methanol in Stream 14, 99% enters Stream 15. Similarly, 99% of water in Stream 14 enters Stream 16.

Heat Exchanger (E-902)

In this heat exchanger, the some of the contents of the stream leaving the bottom of T-903 going to E-904 are vaporized and returned to the column. The amount returned to the column is equal to the amount in Stream 16. The temperature of these streams is the boiling point of water at the column pressure. There is a cost for the amount of steam needed to provide energy to vaporize the stream; this is a utility cost. The steam temperature must always be higher than the temperature of the stream being vaporized.

Heat Exchanger (E-905)

In this heat exchanger, the contents of the top of T-903 are completely condensed from saturated vapor to saturated liquid at the column pressure. It may be assumed that this stream condenses at the boiling point of methanol at the column pressure. The flowrate of the stream from T-902 to E-905 is three times the flowrate of Stream 15. There is a cost for the amount of cooling water needed; this is a utility cost. The cooling water leaving E-905 must always be at a lower temperature than that of the stream being condensed.

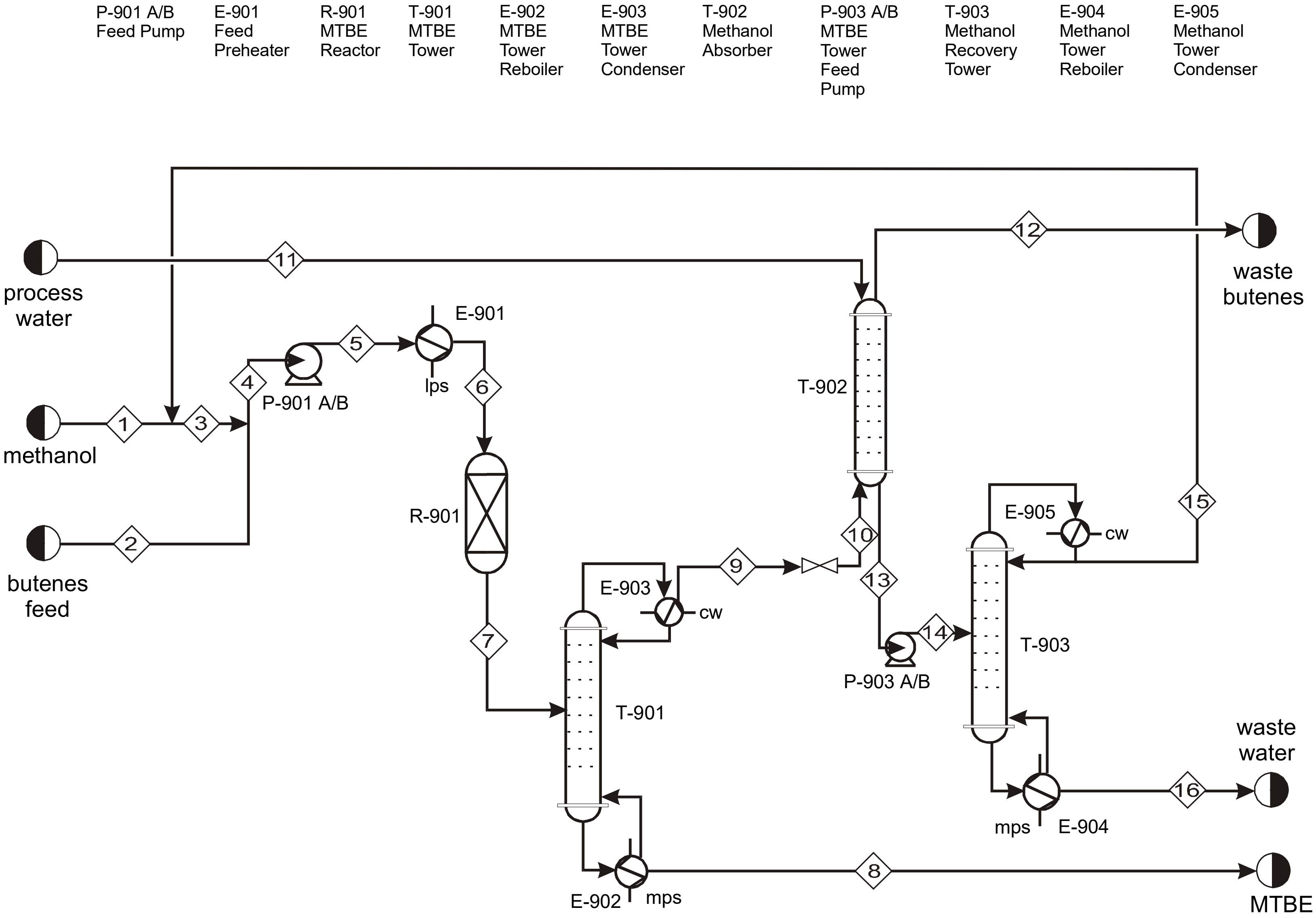

Figure 1: Unit 900 - MTBE Production Facility

Design of Heat Exchanger E-901

A detailed design of E-901 is required for base-case conditions. It should be assumed that cooling water and other utilities are available at the conditions specified in the Appendix of this problem statement. For this heat exchanger design, the following information should be provided:

- Diameter of shell
- Number of tube and shell passes
- Number of tubes per pass
- Tube pitch and arrangement (triangular/square/..)
- Number of shell-side baffles, if any, and their arrangement (spacing, pitch, type)
- Diameter, tube-wall thickness, shell-wall thickness, and length of tubes
- Calculation of both shell- and tube-side film heat transfer coefficients
- Calculation of overall heat transfer coefficient (you may assume that there is no fouling on either side of the exchanger)
- Heat transfer area of the exchanger
- Shell-side and tube-side pressure drops (calculated, not estimated)
- Materials of construction
- Approximate cost of the exchanger

A detailed sketch of the exchanger should be included along with a set of comprehensive calculations in an appendix for the design of the heat exchangers. You should use ASPEN Exchanger Design & Rating (EDR) in the ASPEN Plus simulator to carry out the detailed design.

Utility Costs

Low-Pressure Steam (618 kPa, saturated, cost or credit)	\$7.78/1000 kg
Medium-Pressure Steam (1135 kPa, saturated, cost or credit)	\$8.22/1000 kg
High-Pressure Steam (4237 kPa, saturated, cost or credit)	\$9.83/1000 kg
Natural Gas or Fuel Gas (446 kPa, 25°C)	
cost	\$6.00/GJ
credit	\$5.00/GJ
Electricity	\$0.06/kWh
Boiler Feed Water (at 549 kPa, 90°C)	\$2.45/1000 kg

(There is a cost for boiler feed water only if the steam produced enters process streams. If, on the other hand, the steam produced is subsequently condensed, it can be made into steam again. In that case, there would be no net cost for boiler feed water.)

Cooling Water	\$0.354/GJ
available at 516 kPa and 30°C	
return pressure ≥ 308 kPa	

return temperature should be no more than 15°C above the inlet temperature

Refrigerated Water	\$4.43/GJ
available at 516 kPa and 5°C	
return pressure ≥ 308 kPa	
return temperature should be no higher than 15°C	
Process Water	\$0.067/1000 kg
available at desired pressure and 30°C	
Waste Water Treatment	\$56/1000 m^3
based on total volume treated	

Data

Data for methanol and H_2O are available in your textbook.[1] The following data are provided for the other components.

Heat of Formation at 25°C, [kJ/kg] – all in gas phase

MTBE	isobutene	1-butene	2-butene
-3216.1	-301.3	-9.62	-199.1

Heat of Vaporization [kJ/kmol] at normal boiling point, T_b [°C]

	MTBE	isobutene	1-butene	2-butene
ΔH_v	2.81×10^4	2.22×10^4	2.24×10^4	2.29×10^4
T_b	55.2	-6.9	-6.25	0.88

Liquid-Phase Heat Capacity – use the following equation

$C_p = A + BT + CT^2 + DT^3 + ET^4$, **where T is in [K] and C_p is in [J/kmol K]**

	MTBE	isobutene	1-butene	2-butene
A	140,120	179,340	140,200	112,760
B	-9	-1467	-554.87	-104.7
C	0.563	10.323	2.6242	0.521
D		-0.03	-0.003	
E		3.395×10^{-5}		

Vapor-Phase Heat Capacity – use data from the CD accompanying the text[1]

Vapor Pressure Equation Constants – use the following equation

$\ln [P^*] = A - (B/T) + C\ln T + DT^E$, **where P^* is in [Pa] and T is in [K]**

	MTBE	isobutene	1-butene	2-butene
A	55.875	95.222	67.78	77.551
B	5132	4867	4429	4848
C	-4.96	-12.567	-7.2064	-8.7864
D	1.91×10^{-17}	0.0178	8.4×10^{-6}	1.172×10^{-5}
E	6	1	2	2

Additional Information

The equipment costs for the MTBE plant as follows. Each cost is for an individual piece of equipment, including installation.

Equipment	Installed Cost in millions of $
Reactor, R-901	0.5
Tower, T-901	2.0
Absorber, T-902	0.3
Tower, T-903	0.5
Any heat exchanger	0.15

Fired heater installed cost in dollars:

$$11 \times 10^{x}$$

where

$$x = 2.5 + 0.8 \log_{10} Q$$

where Q is the heat duty in kW

Additionally, the following raw material and product costs should be used:

Raw Material or Product	$/kg
methanol	0.50
i-butene	0.45
MTBE	0.50

Other Information

You should assume that a year equals 8,000 hours. This is about 330 days, which allows for periodic shutdown and maintenance.

Economic Analysis

When evaluating alternative cases, you should carry out an economic evaluation and profitability analysis based on a number of economic criteria such as payback period, internal rate of return, and cash flow analysis. In addition, the following objective function should be used. It is the equivalent annual operating cost (EAOC), and is defined as

EAOC = – (product value – feed cost – other operating costs – capital cost annuity)

A negative EAOC means there is a profit. It is desirable to minimize the EAOC; i.e., a large negative EAOC is very desirable, although you are **not** being asked to carry out optimization.

Other operating costs are utilities, such as steam, cooling water, natural gas, and electricity.

The capital cost annuity is an ***annual*** cost (like a car payment) associated with the ***one-time***, fixed cost of plant construction. The capital cost annuity is defined as follows:

$$capital\ cost\ annuity = FCI\,\frac{i(1+i)^n}{(1+i)^n - 1}$$

where *FCI* is the installed cost of all equipment; *i* is the interest rate, $i = 0.15$; and *n* is the plant life for accounting purposes, $n = 10$.

For detailed sizing, costing, and economic evaluation including profitability analysis, you may use the Aspen Process Economic Analyzer (formerly Aspen Icarus Process Evaluator) in Aspen Plus Version 8. However, it is also a good idea to independently verify the final numbers based on other sources such as cost data given below.

Final Comments

As with any open-ended problem; i.e., a problem with no single correct answer, the problem statement above is deliberately vague. You may need to fill in some missing data by doing a literature search, Internets search, or making assumptions. 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.

Moreover, in some areas (e.g. sizing/costing) you are given more data and information than what is needed. You must exercise engineering judgment and decide what data to use. Also you should also seek additional data from the literature or Internet to verify some of the data, e.g. the prices of products and raw materials.

Reference

1. Himmelblau, D. M. and J. B. Riggs, *Basic Principles and Calculations in Chemical Engineering (7th ed.)*, Prentice Hall, Englewood Cliffs, NJ, 2004.

Appendix 1
Economic Data

Feed and Product Prices

Mixed-butenes feed	\$ 0.160/lb
Methanol feed	\$ 0.87/US gallon
MTBE	\$ 1.43/US gallon
Butene waste stream	\$ 0.155/lb
Methanol in MTBE	\$ 0.60/US gallon

Equipment Costs (Purchased)

Note: The numbers following the attribute are the minimum and maximum values for that attribute. For a piece of equipment with a lower attribute value, use the minimum attribute value to compute the cost. For a piece of equipment with a larger attribute value, extrapolation is possible, but inaccurate.

Pumps $\log_{10}(\text{purchased cost}) = 3.4 + 0.05\log_{10} W + 0.15[\log_{10} W]^2$
W = power (kW, 1, 300)
assume 80% efficiency

Heat Exchangers $\log_{10}(\text{purchased cost}) = 4.6 - 0.8\log_{10} A + 0.3[\log_{10} A]^2$
A = heat exchange area (m^2, 20, 1000)

Compressors $\log_{10}(\text{purchased cost}) = 2.3 + 1.4\log_{10} W - 0.1[\log_{10} W]^2$
W = power (kW, 450, 3000)
assume 70% efficiency

Compressor Drive $\log_{10}(\text{purchased cost}) = 2.5 + 1.4\log_{10} W - 0.18[\log_{10} W]^2$
W = power (kW, 75, 2600)

Turbine $\log_{10}(\text{purchased cost}) = 2.5 + 1.45\log_{10} W - 0.17[\log_{10} W]^2$
W = power (kW, 100, 4000)
assume 65% efficiency

Fired Heater $\log_{10}(\text{purchased cost}) = 3.0 + 0.66\log_{10} Q + 0.02[\log_{10} Q]^2$
Q = duty (kW, 3000, 100,000)
assume 80% thermal efficiency
assume can be designed to use any organic compound as a fuel

Vertical Vessel $\log_{10}(\text{purchased cost}) = 3.5 + 0.45\log_{10} V + 0.11[\log_{10} V]^2$
V = volume of vessel (m^3, 0.3, 520)

Horizontal Vessel $\log_{10}(\text{purchased cost}) = 3.5 + 0.38\log_{10} V + 0.09[\log_{10} V]^2$
V = volume of vessel (m^3, 0.1, 628)

Catalyst	\$2.25/kg
Packed Tower	Cost as vessel plus cost of packing
Packing	$\log_{10}(\text{purchased cost}) = 3 + 0.97\log_{10} V + 0.0055[\log_{10} V]^2$ V = packing volume (m^3, 0.03, 628)
Tray Tower	Cost as vessel plus cost of trays
Trays	$\log_{10}(\text{purchased cost}) = 3.3 + 0.46\log_{10} A + 0.37[\log_{10} A]^2$ A = tray area (m^2, 0.07, 12.3)
Storage Tank	$\log_{10}(\text{purchased cost}) = 5.0 - 0.5\log_{10} V + 0.16[\log_{10} V]^2$ V = volume (m^3, 90, 30,000)
Reactors	For this project, the reactor is considered to be a vessel.

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

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

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

Utility Costs

Low Pressure Steam (618 kPa saturated)	\$7.78/1000 kg
Medium Pressure Steam (1135 kPa saturated)	\$8.22/1000 kg
High Pressure Steam (4237 kPa saturated)	\$9.83/1000 kg
Natural Gas (446 kPa, 25°C)	\$6.00/GJ
Fuel Gas Credit	\$5.00/GJ
Electricity	\$0.06/kWh
Boiler Feed Water (at 549 kPa, 90°C)	\$2.45/1000 kg
Cooling Water available at 516 kPa and 30°C return pressure ≥ 308 kPa return temperature is no more than 15°C above the inlet temperature	\$0.354/GJ
Refrigerated Water available at 516 kPa and 10°C return pressure ≥ 308 kPa return temperature is no higher than 20°C	\$4.43/GJ
Deionized Water available at 5 bar and 30°C	\$1.00/1000 kg
Waste Treatment of Off-Gas	incinerated - take fuel credit
Refrigeration	\$7.89/GJ
Wastewater Treatment	\$56/1000 m^3

Any fuel gas purge may be assumed to be burned elsewhere in the plant at a credit of \$2.50/GJ. Steam produced cannot be returned to the steam supply system for the appropriate credit. Steam produced in excess of that required in this process is purged with no credit.

Appendix 2
Other Design Data

Heat Exchangers

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

situation	***h* (W/m²°C)**
condensing steam	6000
condensing organic	1000
boiling water	7500
boiling organic	1000
flowing liquid	600
flowing gas	60