American
Institute of Chemical Engineers

STUDENT CONTEST PROBLEM

1985

345 East 47 Street • New York, New York 10017

CONTEST PROBLEM

1985

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS STUDENT CHAPTERS

Open Only to Undergraduates or Those
Without a Degree in Chemical Engineering

DEADLINE FOR MAILING

Solution must be postmarked not later than midnight, June 1, 1985

RULES OF THE CONTEST

Solutions will be graded on (a) substantial correctness of results and soundness of conclusions, (b) ingenuity and logic employed, (c) accuracy of computations, and (d) form of presentation. Accuracy of computations is intended to mean primarily freedom from mistakes; extreme precision is not necessary.

It is to be assumed that the statement of the problem contains all the pertinent data except for those readily available in handbooks and similar reference works. The use of textbooks, handbooks, journal articles, and lecture notes is permitted. In cases where there is disagreement in the data reported in the literature, the values given in the statement of the problem have been chosen as being most nearly applicable.

The problem is not to be discussed with any person whatever until June 1, 1985. This is particularly important in cases where neighboring institutions may not begin the problem until after its completion by another chapter. Submission of a solution for the competition implies adherence to the foregoing condition.

A period of not more than thirty consecutive days is allowed for completion of the solution. This period may be selected at the discretion of the individual counselor, but in order to be eligible for an award a solution must be postmarked not later than midnight, June 1, 1985.

The finished report should be submitted to the chapter counselor within the thirty-day period. There should not be any variation in form or content between the solution submitted to the chapter counselor and that sent to the AIChE office. The report should be neat and legible, but no part need be typewritten.

The solution should be accompanied by a letter of transmittal giving only the contestant's name, school address, home address, and student chapter, lightly attached to the report. This letter will be retained for identification by the Secretary of the Institute. The solution itself must bear no reference to the student's name or institution by which it might be identified. In this connection, graph paper bearing the name of the institution should be avoided.

Each counselor should select the best solution or solutions, not to exceed two, from his chapter and send these by registered mail to:

J.C. Forman, Executive Director
American Institute of Chemical Engineers
345 East 47 Street
New York, New York 10017

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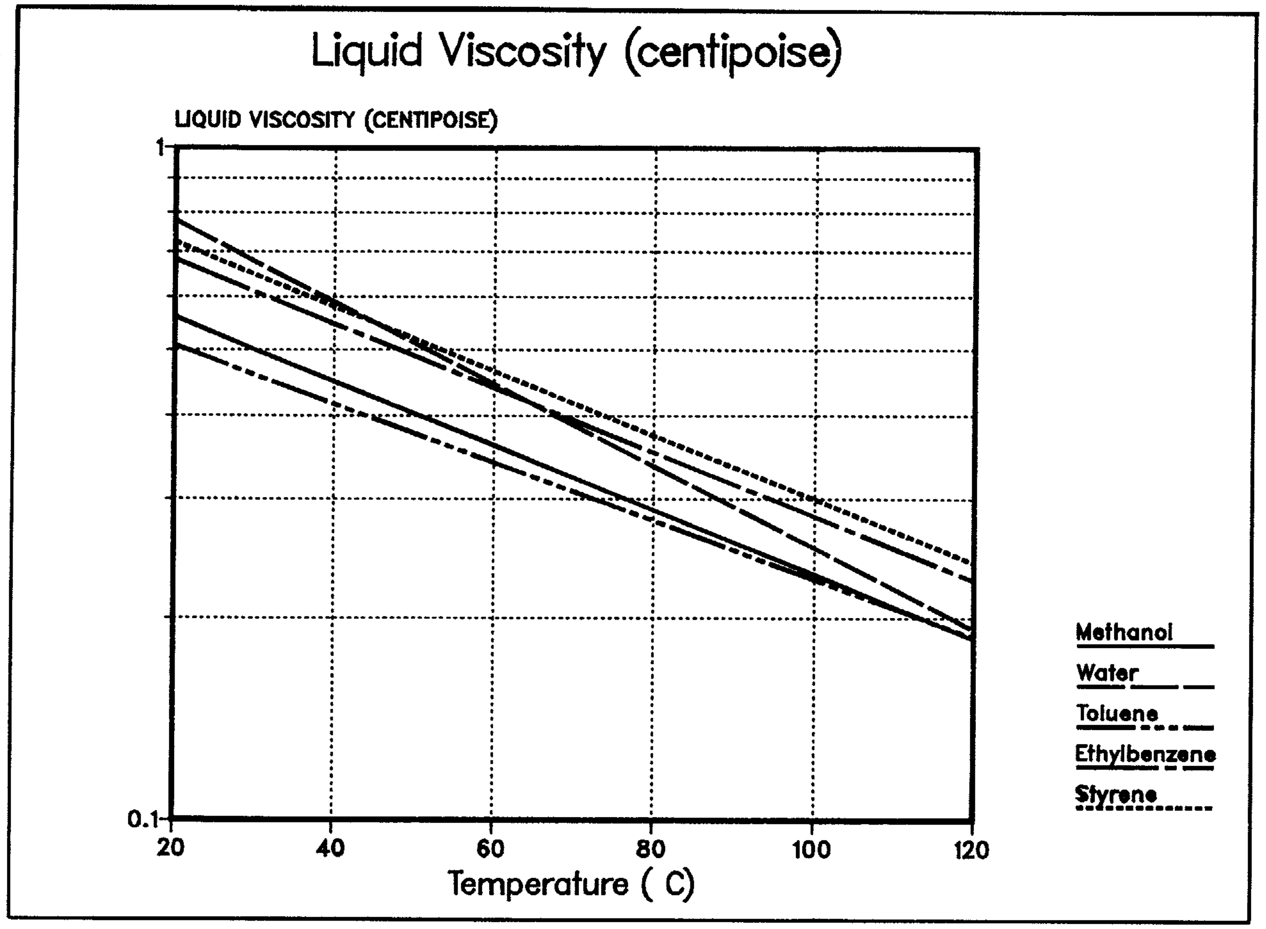
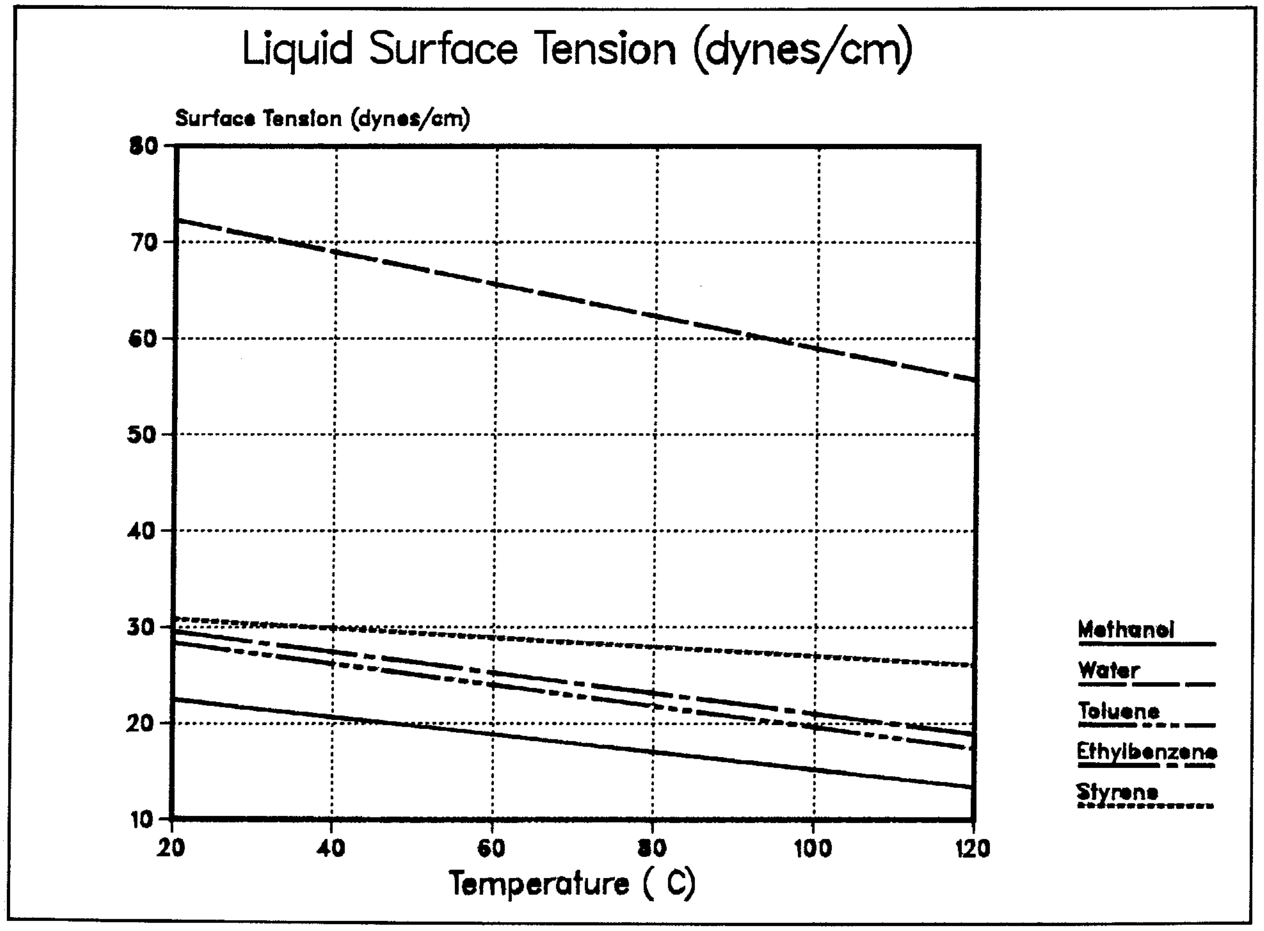




AIChE STUDENT CONTEST PROBLEM

1985

Styrene From Toluene and Methanol

INTRODUCTION

Styrene monomer (SM) is currently produced in a two-step process from benzene and ethylene. First, benzene is alkylated with ethylene to form ethylbenzene (EB). After purification, the ethylbenzene is catalytically dehydrogenated to produce styrene. The dehydrogenation step is endothermic and requires a large quantity of steam mixed with the ethylbenzene to maintain the desired reaction temperature, to depress coking of the catalyst and to dilute the reaction concentration to enhance the reaction equilibrium.

Our research department has discovered a catalyst which will produce styrene from toluene and methanol in one step. Steam addition is not required. Some byproduct ethylbenzene is also produced which can be sold to conventional styrene producers. This catalyst discovery might give us the opportunity to develop a new, low-cost route to styrene.

The need, therefore, is to synthesize a flowsheet and prepare a preliminary design and economic evaluation for a new process which would produce styrene from toluene and methanol.

STATEMENT OF THE PROBLEM

Your assignment is to:

1. Synthesize the optimum flowsheet and material balance for the new styrene process. (Final purification of crude styrene is beyond the scope of your assignment.)
2. Size and estimate the costs of the major pieces of equipment.
3. Estimate the installed equipment capital cost.
4. Estimate the manufacturing cost.
5. Using net present value (NPV) as the economic indicator, estimate the after-tax profitability of the optimum process. Base the estimate on the following assumptions: 10 year life, 48% income tax, 7% inflation rate, 12% interest rate, and working capital as 20% of the manufacturing capital. Also assume the following sales values and product charges:

Product Values	
Crude Styrene product	\$0.91/kilogram
Ethylbenzene byproduct	\$0.57/kilogram
Administration, Distribution, Marketing and R&D Costs	\$0.09/kilogram of crude styrene product

DESCRIPTION OF THE NEW STYRENE PROCESS

The overall process is shown in Figure 1, with the proposed reaction step already synthesized by our R&D personnel. The optimum design may require additional heat exchangers. The separation steps, however, have not been designed.

The saturated vapor (at 570 kPa) feed streams of toluene and methanol are mixed, superheated in an interchanger and fired heater, and then fed to a catalytic reactor where the following reactions take place:

$$\text{Toluene + Methanol} \rightleftharpoons \text{Styrene + Water + Hydrogen}$$

$$\text{Toluene + Methanol} \rightleftharpoons \text{Ethylbenzene + Water}$$

For this preliminary evaluation, we can assume that byproduct formation and polymerization of styrene monomer are negligible and that the catalyst does not coke or deactivate with time.

Heat is recovered from the reactor effluent in an interchanger before the effluent is condensed with cooling tower water (CTW) and cooled to 38°C.

TECHNICAL DATA

A. Reactor Performance

Research has taken the following data for determining the adiabatic reactor performance. Use linear interpolation between temperatures for intermediate values.

Inlet Temperature, °C	480	495	510	525
Inlet pressure, kPa abs.	400	400	400	400
Conversion	0.68	0.71	0.76	0.82
Yield	0.87	0.83	0.78	0.72
Rate	36	73	130	190

Conversion = moles toluene reacted/moles toluene fed
Yield = moles styrene formed/moles toluene reacted
Rate = gmoles toluene reacted/m³ catalyst/min

In collecting these reactor performance data, research used only stoichiometric feed to the reactor. Therefore, your design should be based only on stoichiometric feed (i.e., equal moles of toluene and methanol).

B. Physical Properties

Some physical properties are given in Table 1 and Figure 2. These values have been rounded off and the plots have been simplified for ease of application. All pressures are absolute. Use these values in your design, in preference to data from other references.

C. Vapor-Liquid Equilibrium

For this preliminary design, distillation calculations may be based on the assumption of binary separation using light key and heavy key for the separation split. For this system, the average relative volatilities of the binaries ($\alpha = K_{LK}/K_{HK}$)

may be approximated as follows:

	RELATIVE VOLATILITY
Methanol/Toluene, below the azeotrope. Methanol and toluene form an azeotrope at 87 mole % methanol in the liquid phase.	3.58
Toluene/Ethylbenzene, if the methanol has not been removed from the feed in a prior distillation step.	2.28
Toluene/Ethylbenzene, if the methanol has already been removed from the feed.	1.86
Ethylbenzene/Styrene	1.31

Ignore the effect of temperature on these relative volatilities.

DESIGN DATA
(Including Simplifying Assumptions)

A. Material Balance

The proposed plant capacity is 300,000 metric tons per year of crude styrene monomer, which includes 300 ppm of contained ethylbenzene. The onstream time is 95% (8,320 hours per year). Yield losses due to trace byproducts have been ignored.

1. Impurities in purchased methanol and toluene are negligible.
2. Water, EB and SM recycled to the reactor feed are at small enough concentrations to pass through as inerts.

B. Three-Phase Separator

The reactor effluent condensed with cooling tower water forms three phases: organic, aqueous and vapor phases. (Phase phenomena are given below.) The vapor phase will not be processed in this preliminary design but will be given a fuel-value credit. Also, the aqueous phase will not be processed in this preliminary design. The organic phase will be processed to recover unreacted toluene and methanol for recycle and to purify the styrene and ethylbenzene streams to meet specifications.

For sizing the Decanter, use 30 minutes liquid holdup time and 60% liquid-full.

The lowest acceptable process outlet temperature for *all* water-cooled heat exchangers is 38°C and is limited by the cooling tower water supply temperature.

1. VAPOR PHASE

- Activity coefficients for all condensables in the organic phase of the three-phase separator are approximately 1.0 for purposes of calculating the vapor-phase composition.

- The activity coefficient for water in the aqueous phase is 1.0.

- Solubility of hydrogen is negligible in both liquid phases.

- The off-gas will be given a credit as fuel at its lower heating value. This value is the calories evolved from complete combustion of all of the components in the stream at 25°C, when the final state of all of the water formed and originally present in the fuel is vapor.

2. AQUEOUS PHASE

- Except for methanol, negligible organics will partition into the aqueous phase.

- The partition coefficient for methanol is 1.40 (ratio of mole fraction in the organic phase to mole fraction in the aqueous phase).

- Design of a column to separate methanol and water is not required for this evaluation, since this separation can be achieved elsewhere in the existing plant. However, the overall plant material balance must include the methanol/water separation in order to define recycle streams. Neglect water in the recycle methanol and neglect methanol losses. Ignore the cost of the methanol/water separation for this evaluation. Methanol recycle is saturated vapor at 570 kPa.

3. ORGANIC PHASE

Negligible water will partition into the organic phase. (Thus, only methanol partitions into both organic and aqueous phases.)

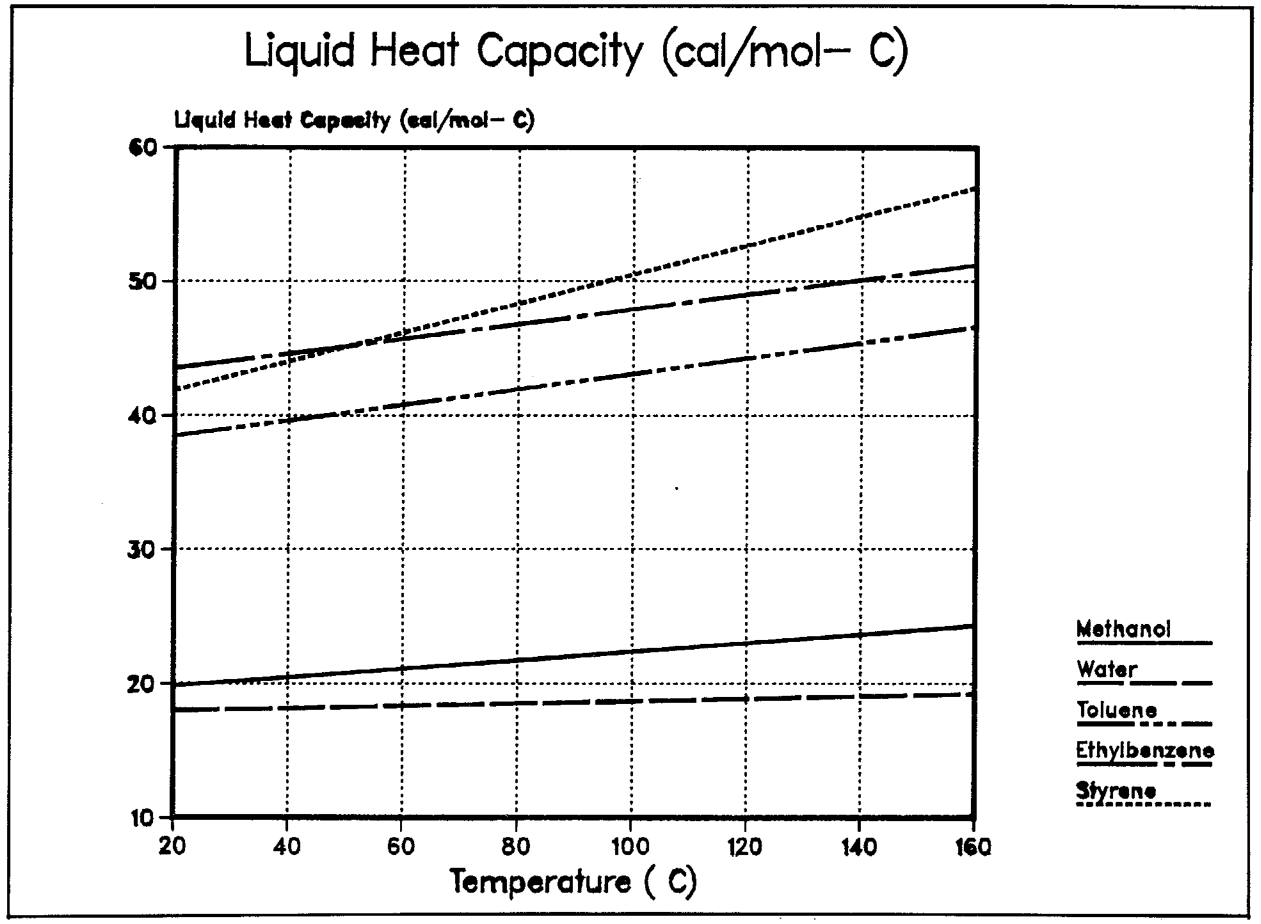
C. Distillation

1. Nominal atmospheric distillations will operate at 136 kPa (k = kilo, Pa = Pascals) top tray pressure and 123 kPa condenser outlet pressure. Avoid column operating pressures above nominal atmospheric. Allow 5 kPa pressure drop between the top of the column and the condenser outlet for vacuum columns.
2. Do not exceed 145°C in any column with more than 50 wt% SM in the bottoms, in order to minimize SM polymerization.
3. Use only the two key components, with their relative volatilities given earlier, to calculate each separation. Normalize composition as a pseudo-binary (i.e., the mole fractions of the key components sum to 1.0) to calculate the number of stages, reflux ratio, bubble point of the feed and q of the feed. (q indicates liquid mole fraction in feed: q = 0.0 for dewpoint, q = 1.0 for bubble point, and q > 1.0 for subcooled feed.) Ignore non-key components. That is, you must use the shortcut binary method of Fenske for minimum stages and Underwood for minimum reflux. (Ref.: *Perry's Handbook*, 5th ed.) Instead of using the Erbar-Maddox correlation plotted in *Perry's Handbook*, use Eduljee's equation (*Hydro. Proc.*, Sept. 1975, p. 120) for Gilliland's correlation for operating reflux, given the theoretical number of stages:

$$\frac{N - N_m}{N + 1} = 0.75 - 0.75\left(\frac{R - R_m}{R + 1}\right)^{0.5668}$$

(Units are defined in *Perry's*.)

4. For the number of theoretical stages, an initial guess of two times minimum stages may be used. Do not assume this is the economic optimum.
5. Sieve tray columns will be assumed for all distillations. Tray spacing is 60 cm (24 inches).
6. Column diameters may be estimated by the method of Fair, given in Peters and Timmerhaus, *Plant Design and Economics for Chemical Engineers*, 3rd ed., 1980. Overall column efficiencies may be estimated by the method of O'Connell, also given in Peters and Timmerhaus.
7. Use 10 minutes holdup time and 60% liquid-full for sizing the reflux drums.
8. Use all of the feed components in the heat balance for sizing the condenser and reboiler and for determining top



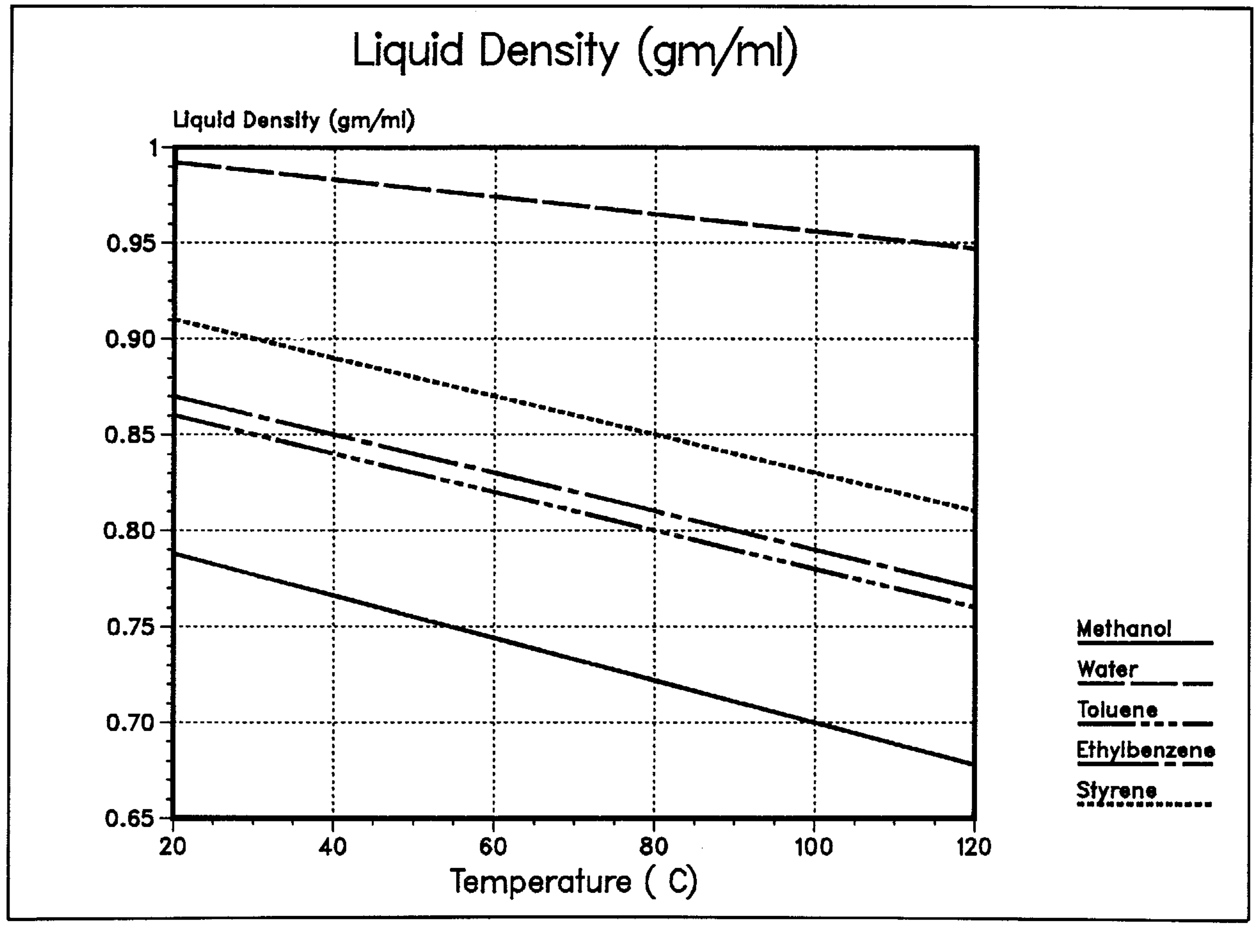
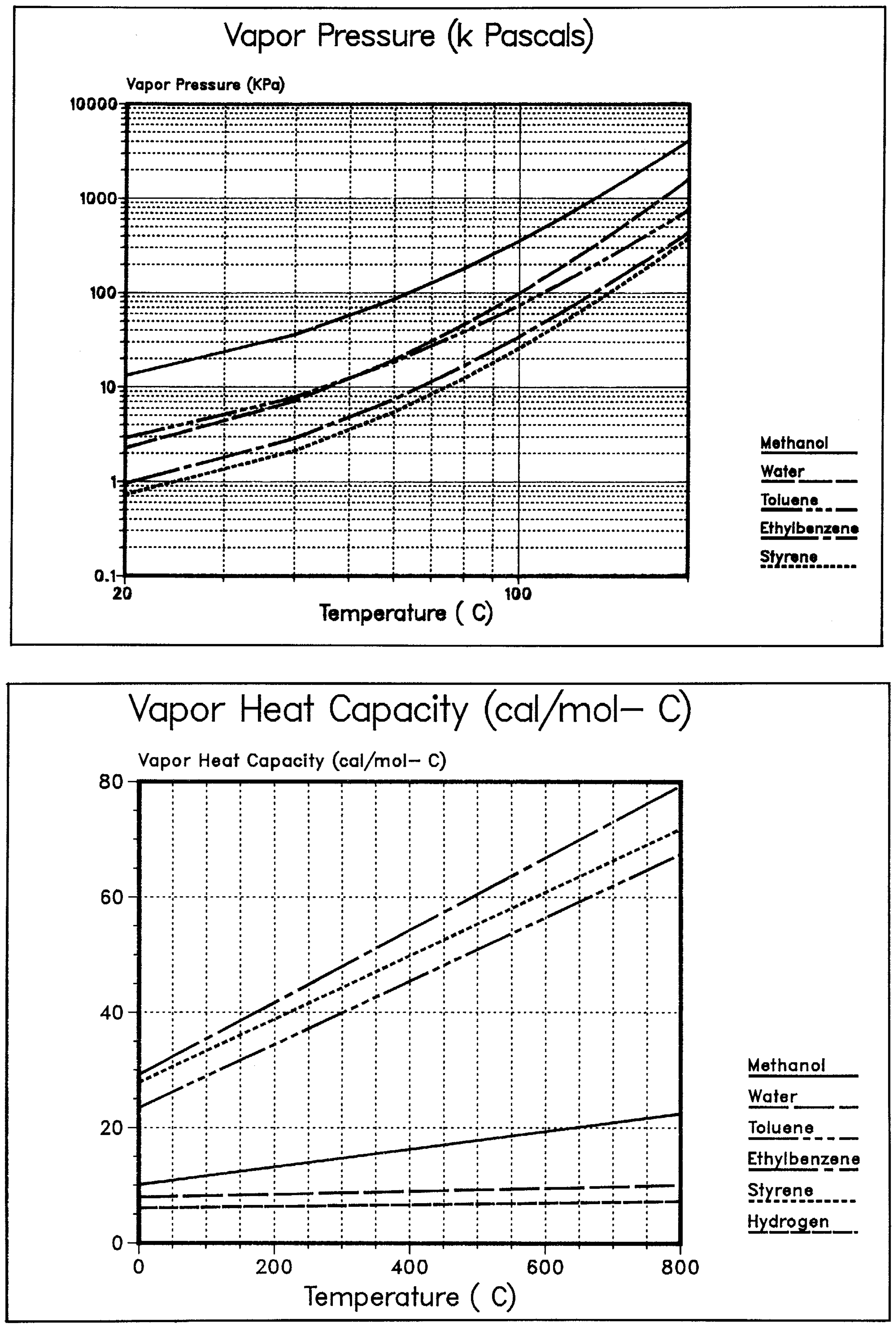


FIGURE 2—PHYSICAL PROPERTIES—Pages 8-10



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and bottom temperatures. Assume ideal behavior to predict column temperatures.

9. Aromatic Phase Specifications:

Recycle methanol	No specified limit on toluene.
Recycle toluene	No specified limit on methanol. 4 wt % EB maximum. 5 wt % maximum for sum of EB and SM.
EB byproduct	0.8 wt % toluene maximum. 3 wt % SM maximum.
Crude SM product	300 ppm EB maximum. (ppm = parts per million by weight)

D. Equipment Pressure Drop

For preliminary design, the following pressure drops may be assumed:

Fired heater	66 kPa
Reactor	70 kPa
Heat exchangers* (shell and tube sides)	13 kPa
Condensers under vacuum	5 kPa
Other major equipment	13 kPa
Distillation Trays:	
1.0 kPa per theoret. stage for pressure columns.	
0.6 kPa per theoret. stage for vacuum columns.	

* Includes condensers, vaporizers, interchangers and all other exchangers except condensers operated under vacuum.

Negligible pressure drop through piping may be assumed.

E. Heat Transfer Coefficients

The following overall heat transfer coefficients may be assumed, kcal/hr/m²/°C:

SYSTEM	OVERALL COEFFICIENT
Gas/Gas	50
Gas/Liquid	100
Gas/Boiling Liquid	200
Gas/Condensing Vapor	200
Liquid/Liquid	500
Liquid/Boiling Liquid	700
Liquid/Condensing Vapor	700
Boiling Liquid/Condensing Vapor	1000

F. Compression Efficiency

The isentropic compression efficiency can be assumed to be 80%. The combined mechanical and electrical efficiency is approximately 90%.

ECONOMIC DATA

It has been difficult in recent years to forecast costs over the lifetime of new projects. The cost data given here are tentative, therefore, and appropriate only for preliminary economic evaluations. All costs are for the Houston Gulf Coast, where the plant will be located.

A. Capital Costs

For this preliminary design, only the major pieces of equipment need to be designed and cost-estimated. (Pumps are not included as major equipment. Storage tanks are not included in this evaluation.) The installed equipment cost (i.e., manufacturing capital) can be estimated by multiplying the sum of the major equipment costs by the Lang factor (= 5). Assume that no spare items are required.

You can estimate the equipment costs using the factors given in the table below, with costs adjusted for size by the following equation:

$$\text{Equipment Cost} = (\text{Referenced Cost}) \times \left(\frac{\text{Required Size}}{\text{Referenced Size}}\right)^{\text{Exponent}}$$

EQUIPMENT COST (1986 DOLLARS)

Equipment Item	Type	Referenced Cost ($K)	Referenced Size	Exponent
Distillation Column, with Trays	Sieve Tray	6.9/tray	2.54 meter diameter	1.24
Fired Heater	Box-type, Gas fired	362	21×10^9 joules/hr	0.63
Gas Compressor, with driver	Centrifugal, Electric drive	430	2.69×10^9 joules/hr	0.74
Heat Exchanger	Fixed tubesheet, 19 mm ID tube, 6 m length	21.7	93 meter²	0.69
Reactor	Pressure Vessel	51	3.8 meter³ catalyst	0.30
Catalyst	Pellets	1	100 liter	1.0
Vaporizer	Horizontal tube	140	93 meter²	0.56
Tank	Separator	6.7	3.8 meter³	0.56

Other equipment may be estimated from the literature. Use 1986 as the base year to purchase the equipment and to build the plant. Depreciation begins in 1987.

B. Manufacturing Costs

Since plant startup is targeted for 1987, the manufacturing costs given below are based on that year.
(Basis of units: K = thousands, M = millions, 1987 dollars)

Raw Materials:	
Methanol	$ 0.19/kilogram
Toluene	$ 0.42/kilogram
Credits:	
Off-gas from three-phase separator	$ 3.10/M kilojoules
Utilities:	
Natural gas*	$ 4.40/M kilojoules
Steam	
2865 kPa, sat'd.	$17.30/K kilograms
625 kPa, sat'd.	$12.20/K kilograms
Cooling water	$0.03/K liters
Inlet temp., ave.	31°C
Outlet temp., ave.	41°C maximum

Electricity	$ 0.065/kWH
Condensate and Boiler feed water	$ 2.50/K liters

Direct Manufacturing Expenses:

Operating labor**	$19/hr
Supervision	50% of Labor cost
Payroll charges	30% of (Labor + Supervision)
Repairs	4% of (Mfg. Capital)/yr
Factory supplies	0.3% of (Mfg. Capital)/yr
Lab charges	0.4% of (Mfg. Capital)/yr
Waste disposal	2% of (Mfg. Capital)/yr
Technical service	0.8% of (Mfg. Capital)/yr
Depreciation (st. line)	10% of (Mfg. Capital)/yr
Indirect and Other Expenses	6% of (Mfg. Capital)/yr

* Assume 90% efficiency for the fired heater fuel usage.

** 840 hrs/week total operating labor.

REPORT FORMAT

The final report should include the following:

1. Cover letter
2. Introduction: Give a concise statement of the problem, covering background and objectives.
3. Summary: Give a brief review of the work done and tools used.
4. Conclusions: List the major conclusions, in decreasing order of importance. The conclusions must flow logically from the summary (i.e., new material is not introduced here.)
5. Recommendations: List actions, goals, and other recommendations, in decreasing order of importance. The recommendations must flow logically from the conclusions.
6. Process: Present the process flow diagram for the selected scheme, with the related material balance.
7. Discussion: Present the details of the work done. Include appropriate data, calculations, assumptions, diagrams, references, etc. for complete stand-alone documentation.

TABLE I. PHYSICAL PROPERTIES

	Methanol	Water	Toluene	Ethylbenzene	Styrene	Hydrogen
Molecular Weight	32	18	92	106	104	2
Normal Boiling Point (NBP), °C	65	100	111	136	145	−253
Critical Temperature, °C	239	374	321	344	364	−240
Critical Pressure, kPa	8094	22054	4233	3599	3674	1296
Critical Compress. Factor	0.230	0.232	0.270	0.262	0.252	0.318
C_p/C_v Ratio for Adiabatic Compression Calculations (ref: *Perrys 5th*)						
k	1.2	1.3	1.03	1.03	1.06	1.4
For Ideal Gas at 25°C, kcal/mol:						
Heat of Formation	−48.1	−57.80	11.95	7.12	35.22	0.00
Free Energy of Formation	−38.8	−54.64	29.16	31.21	51.10	0.00
Heat of Vaporization at NBP, cal/mol:	8410	9712	7915	8586	8840	
(Note: The following correlations are plotted in Figure 2.)						
Vapor Heat Capacity = A + BT cal/mol/°C, where T = °C						
A	10.10	7.96	23.46	29.19	27.86	6.88
B	0.0154	0.0026	0.055	0.063	0.055	0.0005
Liquid Heat Capacity = A + BT cal/mol/°C, where T = °C						
A	19.2	17.8	37.3	42.4	39.7	
B	0.032	0.009	0.058	0.055	0.108	
Vapor Pressure: $\log_{10}(p) = A - B/(T + C)$, where T = °C and p = kPa						
A	7.206	7.196	6.076	6.091	6.627	
B	1582	1731	1342	1430	1820	
C	240	233	219	214	249	
Liquid Viscosity: $\ln\mu_L = A - BT$, where μ_L = centipoise, T = °C						
A	−0.36	0.03	−0.478	−0.163	−0.105	
B	0.011	0.014	0.010	0.011	0.011	
Liquid Density: $\rho_L = A - BT$ gm/ml, where T = °C						
A	0.81	1.0	0.88	0.89	0.93	
B	0.0011	0.00044	0.001	0.001	0.001	
Liquid Surface Tension: $\sigma_L = A - BT$ dynes/cm, where T = °C						
A	24.3	75.6	30.6	31.7	31.8	
B	0.091	0.166	0.110	0.107	0.048	

Assume ideal gas law for vapor density.

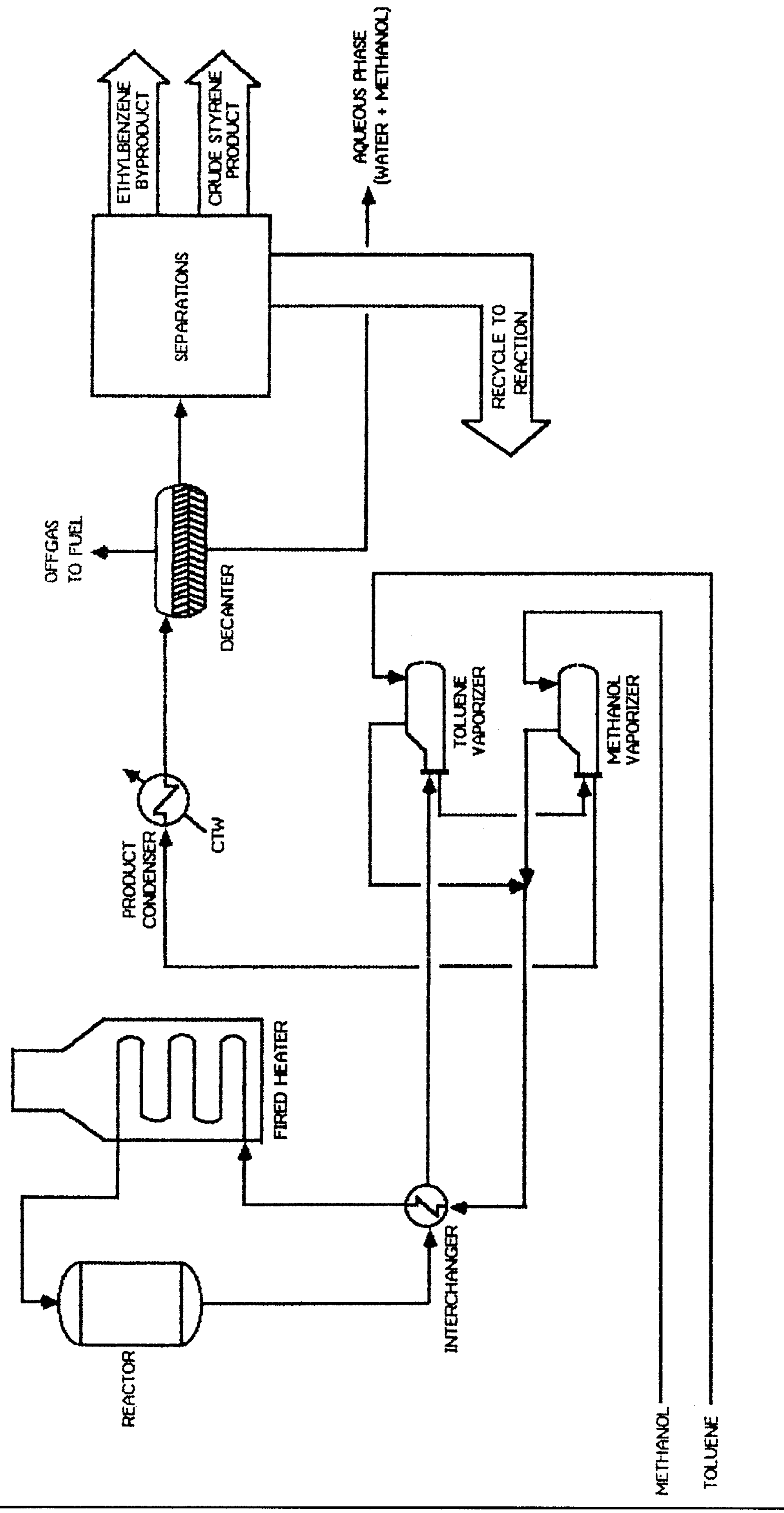

FIG. 1 PROCESS FLOW DIAGRAM