1. The Process

You are part of a team looking at the production of methyl acetate, a commodity chemical with many uses. The first step in the production of methyl acetate is the dehydration of methanol (CH_3OH) to produce dimethyl ether (CH_3OCH_3):

$2CH_3OH \leftrightarrows CH_3OCH_3 + H_2O$

This reaction can take place in either liquid or vapour phases.

The team has requested that you individually prepare and evaluate an initial design for this first step by applying your extensive knowledge of the Douglas hierarchy for design.

A stream, consisting of 99% (by mole) methanol and 1% water at ambient conditions, is available as a feed. The rate of this feed stream is $(450 + 10d)$ kmol h^{-1}. d should be replaced by the last digit of your student number. For instance, if the last digit of your student number were 3, the flow rate of the feed would be 480 kmol h^{-1}. This feed has a cost of 0.4 € kg^{-1}. Dimethyl ether is considered to have a value of 1.15 € kg^{-1} to the company.

The fractional conversion of methanol in this reaction depends on the residence time. The chemist in your team has undertaken some experimental analysis and has generated the data shown in Table 1. The chemist has also determined that these conversion values are achievable when the reaction takes place at a temperature of 600 K ± 10 K and suggests that the temperature for the reaction should be limited to this range of values.

The chemist suggests that the conversion follows a relationship of the form

$$\text{conversion} = \alpha + \beta \log t \tag{1}$$

where α and β have yet to be determined.

2. The design task

A process needs to be designed to make most effective use of the methanol feed available while producing dimethyl ether with a molar fractional purity of 0.99. The design of the process flowsheet will be based on the application of the full Douglas approach, levels 1 through 5. You will be expected to identify and to model all the main processing units, along with sizing information, and their interconnections including possible heat exchanges.

Table 1: Data provided by the chemists in the company, showing single pass fractional conversion of methanol as a function of the residence time for the reaction.

Residence time [s]	Fractional Conversion
0.77	0.146
1.41	0.600
1.82	0.771
2.32	0.781

3. Cost models

Table 2 presents the cost models for various types of units. The costs of the different utilities available, for heating, cooling, and electricity, are given in Table 3.

Table 2: Cost models for processing units for estimating the total annualised cost, TAC, in millions of €, of buying, installing, and maintaining the equipment.

Unit type	TAC	Notes
Distillation	$\frac{1}{100(1-r)}\frac{1.0}{\alpha_{lh}-1}\sqrt{F_d}$	F_d flow of feed to the column in kmol h^{-1}, α_{lh} relative volatilities of light to heavy keys, r recovery of keys $\in [0.9,0.998]$.
Reactors	$0.001tF$r	F_r flow of feed to the reactor in kmol h^{-1}, t residence time in seconds.
Heat exchangers	$0.09A_{0.65}$	A = heat exchanger area [m^2].
Flash vessels	$0.001F_v$	F_v = flow rate to the vessel [mol h^{-1}].
Compressors	$0.02F_c$	F_c = vapour flow rate to the compressor [mol h^{-1}].

Table 3: Cost data for utilities.

Utility	T_{in} [°C]	T_{out} [°C]	Cost [€ GJ^{-1}]
High pressure steam (30 bar, superheated)	450.0	425.0	7.00
Low pressure steam (8 bar)	170.4	170.4	2.50
Cold water	10.0	15.0	0.60
Electricity			60.00

4. Things to do

Given the chemistry data, the process requirements, and the cost data and models above, develop a full process flowsheet for the production of dimethyl ether by following these steps. In attempting each of the following steps, fully itemise and justify all the decisions taken. Marks allocated to each step are indicated in the right margin, for a total of 100.

1. Using the data provided by the chemists, Table 1, fit the equation suggested (equation 1 above) using regression to define a relationship for the single pass fractional conversion of methanol as a function of the residence time, in seconds. You will be using this equation in the modelling below. Suggest the time domain for validity for your equation and comment on how accurate this fitted equation may be. [5]
2. Apply levels 1 through 4 of the Douglas approach so as to develop a process flowsheet consisting of the main process units. In your report, summarise the questions in the Douglas hierarchy that you considered and the key decisions you took, including the identification of potential design variables, with justification for these decisions. There is no need to include any discussion of elements of the Douglas hierarchy that do not apply to your case. Do not perform any economic potential analysis at this point. Sketch the final process structure obtained after level 4 of the hierarchy, labelling all input, output, and recycle

streams; diagrams for each of levels 1-3 are not required. [20]

3. Implement a process and cost model based on the process identified in the previous step. Use one of GAMS (recommended), MATLAB, or a spreadsheet calculator. The model should include costing information sufficient to calculate the economic potential for the process design obtained after level 4. Details on how to model the various potential processing units are given in the Appendices below.

   The model should be fully commented and must be included as an Appendix in your report and must also be submitted as a separate file in its native format to allow us to run your model. Up to 10 of the marks may be deducted due to insufficient commentary in the model itself regardless of what modelling language you use.

   If you developed your model in either GAMS or MATLAB, the actual text of the module should be included as an appendix in the report. If you used a spreadsheet calculator, include two screenshots in the appendix: one showing typical values for some combination of design variable values and one showing all the equations in the spreadsheet. For a spreadsheet, you must ensure that there is sufficient commentary in the spreadsheet itself to understand the model and its outcomes. [20]

4. For the final flowsheet obtained with level 4 of the Douglas approach, use your model to investigate the behaviour of the economic potential in terms of the chosen design variable(s), considering annual hours of operation as indicated in the lecture notes for the type of process operation expected (level 1 of the Douglas hierarchy). Discuss how the design variables and the decisions you made in levels 1 to 4 impact on the economic potential. Plots of the economic potential with respect to the design variables will be required to support your discussion. [10]

5. Prepare a full stream table for the final process design from level 4 for your choice of design variable value(s). Fully justify your choice of values for the design variable(s) for this stream table. [5]

6. Use Aspen Plus to simulate the process identified in the first step. Use this simulation to

   a) fill in a stream table for the process and

   b) determine the heating and cooling duties of all of the units.

   Discuss the possible reasons for the differences you may observe between the stream tables from the previous step (step 4) and this step and also comment on any implications arising from these differences. If you were unable to prepare a stream table for either of the steps, discuss what you may have expected to see when comparing the stream tables. In your report, include a screenshot of the process flow diagram in Aspen and a screenshot of the stream table. The Aspen model must also be submitted as a separate file in Moodle. [10]

7. Another member of your team has also been investigating the process for the dehydration

Table 4: List of hot and cold streams in an alternative process design where the hot streams must be cooled to their desired outlet temperature and the cold streams heated.

Label	Heat duty	T_{in}	T_{out}

	(kW)	(°C)	(°C))
H1	10500.5	326.9	76.8
H2	3764.03	31.8	31.0
H3	9621.94	64.3	64.2
H4	1441.3	331.85	321.85
C1	12109.7	41.4	326.9
C2	4183.16	129.4	131.3
C3	8690.03	91.0	97.7

of methanol. As part of their investigation, they have identified a set of cooling and heating requirements for their particular design (which may or may not be similar to those you may have obtained in answering the above questions), presented in Table 4. Knowing your expertise in the *Pinch* method, they have asked you to design a heat exchanger network for them.

Therefore, apply the Pinch method, as taught in the lectures and tutorial sessions and showing all the work, to design and cost a heat exchanger network for the heating and cooling requirements given in Table 4. Use $\Delta T_{\min}$ = 15 °C for the pinch analysis and U = 1.5 kW m^{-2} °C^{-1} for the overall heat transfer coefficient for the design of any exchanger in the network. Sketch the resulting heat exchange network.
Assuming that the heating and cooling requirements are of the same order of magnitude as your own design would have, discuss the economic implications of the heat exchanger network you have designed on your previous conclusions in step 4 regarding the economic potential of the process. [25]

8. Which decisions taken in levels 1 to 4 of the Douglas hierarchy had the most impact on the final design and why? Draw alternative process diagram(s) to illustrate your reasoning. [5]

5. Submission

The submission, via Moodle, will consist of three parts, each of which is submitted under a separate tab in the submission page (see the top of the submission page on Moodle):

1. A report which answers the above questions, written using a word processor and submitted as a PDF document. This report must include your model (step 3) as an appendix as described above and also two screenshots of your Aspen simulation, one showing the full process flow diagram and one for the stream table. If you have used a spreadsheet calculator for the modelling in step 3, please insert two screenshots of the spreadsheet, one with values and one showing the equations, in the report as the appendix.
2. The model for level 4 from step 3, in your chosen modelling language, including the economic potential calculations for that level. The model should be submitted in the form of the original file (e.g. as a .gms file for a GAMS model); a text version of the model must also be included in the report as an appendix, as noted above.
3. Your Aspen Plus simulation model should be included in the form that Aspen can read. Also include, as noted above, screenshots of Aspen showing your process flow diagram and

   a screenshot of the stream table within your report.

Please note that parts 2 and 3 must be submitted as original files (e.g. .gms for a GAMS model) and not a PDF document. We must be able to load your model into the appropriate software to verify that it works.

All work must be your own and you must not discuss the project with anybody else. You may use material from the lectures and the various tutorials to discuss relevant topics with others in your class.

A. Appendices

Separation units For separation based on rectification distillation, the composition of the streams can be defined according to a semi-sharp separation. For the short-cut model, suitable for the Douglas hierarchy, we will assume that all non-key species distribute wholly to either the top or bottom product. That is, species lighter than the light key go to the top; species heavier than the heavy key go to the bottom. The keys distribute according to a design variable, r, the recovery. So, rf_l will be the flow of the light key in the top product if f_l is the flow of the light key in the feed to the column and rf_h will be the flow of the heavy key to the bottom product.

Any flash vessels, on the other hand, should be modelled assuming vapour-liquid equilibrium for the separation.

For both forms of separation, Antoine's equation can be used to estimate the vapour pressure. Values for the Antoine coefficients for the species involved can be obtained from http://webbook.nist.gov/chemistry/.

Compressor Should you require a compressor for a vapour stream, you should use the model described by Biegler *et al.* [1] summarised here for the estimate of the work required, $\dot{W}$ [J s^{-1}]:

$$\dot{W} = \dot{n} \Delta H_v$$

where $\dot{n}$ is the molar flow rate in mol s^{-1} and ΔH_v is the change in specific enthalpy, J mol^{-1}. For an ideal system, and for the purposes of this project we will assume ideal gas conditions, this equation can be approximated by

$$\dot{W} = \dot{n} \frac{\gamma}{\gamma - 1} RT_1 \left[\left(\frac{P_2}{P_1} \right)^{\frac{\gamma - 1}{\gamma}} - 1 \right]$$

where the gas is being compressed from P_1 to P_2 and the inlet temperature is T_1 [K]. γ = 1.4 for an ideal system and R = 8.314 J mol^{-1} K^{-1}.

Due to efficiency losses, the actual work required will be 1.562 times the theoretical work.

Note: you should assume a 10% pressure drop from the reactor inlet to the inlet of the compressor and the pressure of the outlet of the compressor should be 10% greater than the destination's operating pressure.

Simulation in Aspen Plus For the simulation of your process flowsheet with Aspen Plus, the following are suggested:

- use the NRTL physical property method;
- for any reactors, use a plug flow reactor (RPlug) to simulate your reactors; note the following:
  - use a length to diameter ratio of 10 for any reactor design;
  - choose a kinetic reaction with reaction rate expressed in a volume basis;
  - Use a kinetic factor of 0.336 to include catalyst impact and an activation energy of 80480 kJ kmol^{-1}.

1 L T Biegler, I E Grossmann & A W Westerberg 1997, *Systematic methods of chemical process design*, PrenticeHall, pp. 125ff.

– The reaction kinetics are described by a Langmuir-Hinshelwood-Hougen-Watson (LHHW) model to account for DME adsorption as found by chemists.

  Driving force expressions (partial pressure as Ci basis)

    ∗ Term 1

      · Conc. Exponents for reactants: CH_3OH = 1

      · Conc. Exponents for products: DME = 0; H_2O = 0

      · Coefficients: A = 0; B = C = D = 0

    ∗ Term 2

      · Conc. Exponents for reactants: CH_3OH = -1

      · Conc. Exponents for products: DME = 1; H_2O = 1

      · Coefficients: A = 2.8086; B = -3061; C = D = 0

  Adsorption expression ∗ Adsorption term exponent = 1 ∗ Concentration

    exponents: Term 1: H_2O = 0, Term 2: H_2O = 0 ∗ Adsorption constants:

      · Term 1: A = -0.61395, B = C = D = 0

      · Term 2: A = -0.61395, B = C = D = 0

• for distillation units, you can initially use the DSTWU shortcut model to get estimates with regards to total number of stages or reflux ratio, depending on your input. You can then use these estimates as input to the RADFRAC rigorous distillation model which needs to be used for the simulation of any distillation columns.

END OF PAPER