**Imperial College London**
**Reaction Engineering 1 Design Project**
**Spring Term 2023**

# Reactor Design Project: Reduction of Ethyne

## Introduction

Before ethene became the key synthetic building block in the petrochemical industry, produced by large steam crackers, it was ethyne that formed the backbone of that industry.

Recent thoughts on how to decarbonise the chemicals industry have turned to ethyne again as an interesting reactant because the process of generating ethyne from natural gas is based on an electric arc converting methane to ethyne and hydrogen – this means that in this process electricity and natural gas are employed to generate two desirable feedstocks.

Although there is a major integrated project on its way to demonstrate the electrification of steam crackers[1] it will be important to learn whether ethyne hydrogenation to yield ethene and therefore directly feed into the existing infrastructure may be an alternative pathway to follow.

Your team has been tasked to design and evaluate the reactor required for the conversion of ethyne to ethene using the effluent gas of a Hüls arc furnace as feedstock[2]. This evaluation will need to be conducted in a number of steps, starting with a simple model and step by step increasing the complexity of the model until a fairly representative and realistic simulation of the reactor is arrived at.

Unfortunately, ethyne hydrogenation to ethene is a complex reaction involving heterogeneous catalysts and the need to maximise the intermediate (ethene) rather than the end product of hydrogenation (ethane). Not much reliable literature is available regarding rate equations and data and many investigations rely on one key publication[3] by Dr. Rene Bos (Bos *et al.*) who is now a Principal Scientist at Shell plc (he is currently also involved with Imperial, supervising LINK projects in Chemical Engineering). You will therefore need to base your reactor model on that publication and the proposed rate equations therein.

Your task is to design a catalytic reactor to produce ethene from ethyne in a reaction mixture. MATLAB will be used to carry out the calculations and simulations. The inlet conditions to be used are given in Table 2. Data for ethyne hydrogenation (rate equations, heat capacities, equilibrium constant etc) are given below.

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[1] https://www.basf.com/global/en/who-we-are/sustainability/whats-new/sustainability-news/2022/basf-sabic-and-linde-start-construction-of-the-worlds-first-demonstration-plant-for-large-scale-electrically-heated-steam-cracker-furnaces.html (accessed 10th January 2023)

[2] https://collections.nlm.nih.gov/ext/dw/101709483/PDF/101709483.pdf (accessed 10th January 2023)

[3] Bos, A. N. R., Botsma, E. S., Foeth, F., Sleyster, H. W. J., & Westerterp, K. R. (1993). A kinetic study of the hydrogenation of ethyne and ethene on a commercial Pd/Al2O3 catalyst. *Chemical engineering and processing: process intensification*, *32*(1), 53-63.

## The Design Project

Your team should design a catalytic reactor system to produce 100 tonnes per day of ethylene with heterogeneous reactors, using the inlet conditions given in Table 2. You might be required to use **parallel reactors and inlets** to achieve the required throughput.

### REACTION KINETICS

There are two reactions occurring in parallel. One is ethyne hydrogenation to ethene (desired) and the other is over-hydrogenation of ethene to ethane (undesired):

$$C_2H_2 + H_2 \leftrightarrow C_2H_4 \qquad \Delta H = -172\ kj/mol \tag{1}$$

$$C_2H_4 + H_2 \leftrightarrow C_2H_6 \qquad \Delta H = -137\ kj/mol \tag{2}$$

1) If the concentration/partial pressure of ethene is substantial in the feed the two rates of reactions can be expressed using the Langmuir-Hinshelwood mechanism. Bos *et al* found the following rate expressions using a Berty reactor at 310K. All pressures in bar.

$$r_{C_2H_4} = \frac{k_{1,0}P_{C_2H_2}P_{H_2}}{\left(1 + b_{2,0}P_{C_2H_2} + b_{O,0}P_{CO}\right)\left(1 + b_{H,0}P_{H_2}\right)} \quad \frac{mol}{kgCat \cdot s} \tag{3}$$

$$r_{C_2H_6} = \frac{k_{2,0}P_{C_2H_4}P_{H_2}}{\left(1 + b_{22,0}P_{C_2H_2} + b_{42,0}P_{C_2H_4} + b_{O2,0}P_{CO}\right)^3} \quad \frac{mol}{kgCat \cdot s} \tag{4}$$

The parameters for this model at 310K are given below:

$$k_{1,0} = 15.80 \times 10^{0}$$
$$k_{2,0} = 15.60 \times 10^{-3}$$
$$b_{2,0} = 1.80 \times 10^{+3}$$
$$b_{H,0} = 3.95 \times 10^{0}$$
$$b_{O,0} = 2.46 \times 10^{+6}$$
$$b_{22,0} = 28.7 \times 10^{0}$$
$$b_{42,0} = 0.04 \times 10^{0}$$
$$b_{O2,0} = 19.1 \times 10^{+3}$$

2) The data and rate expression in 2) was further fitted to multiple temperatures in the range between 299 and 330K and considering a total pressure of 0.3 to 2.1 MPa. The temperature dependency of the above parameters was assumed to be of Arrhenius type using 310K as reference temperature and the following activation energies were arrived at:

$$k_i = k_{i,0} \exp\left\{\frac{-E_{k,i}}{R}\left(\frac{1}{T} - \frac{1}{310}\right)\right\} \tag{5}$$

$$b_i = b_{i,0} \exp\left\{\frac{-E_{b,i}}{R}\left(\frac{1}{T} - \frac{1}{310}\right)\right\} \tag{6}$$

$$E_{k1} = 10.1 \times 10^{3}$$
$$E_{k2} = 26.9 \times 10^{3}$$
$$E_{b2} = -14.4 \times 10^{3}$$
$$E_{bH} = 0$$
$$E_{bO} = -84.4 \times 10^{3}$$
$$E_{b22} = -8.0 \times 10^{3}$$
$$E_{b42} = -36.4 \times 10^{3}$$
$$E_{bO2} = -10.7 \times 10^{3}$$

YOUR TASK

1) Considering dimensions, convert the Langmuir-Hinshelwood rate expressions to volumetric rate expressions, which could be solved numerically to find the reactor volume.

2) Using MATLAB, solve the mass balance for this system at 330K (isothermal) using the Langmuir-Hinshelwood rate expressions and explain the effects of CO and $H_2$ partial pressures (sensitivity analysis). You should include the following plot: Catalyst weight vs. conversion of reaction 1 and discuss.

3) Using MATLAB, solve the mass and energy balances for this system and investigate the temperature profile of a single adiabatic reactor, using your group's inlet conditions. You should create a plot of the **rate** of reactions 1 and 2 vs temperature and discuss.

4) Using MATLAB, incorporate the Ergun equation (9) into your balance to account for the pressure drop along the catalyst bed, making your assessment more realistic. As a result you should create a plot of the pressure drop along the length of your reactor and discuss.

5) Using MATLAB, design a system of adiabatic reactors to produce **100 tonnes per day** of ethene, achieving **over 80% overall conversion of ethyne**. To prevent catalyst degradation, it is necessary to keep the reactor below the **Maximum Allowable Working Temperature (MAWT)**. Interstage cooling can be used, which can cool down the gas-side flow by $T\Delta$ = 150K. You should include the total duty of the interstage cooling system. Create a plot of the temperature profile along the reactors and a plot of extent of reactions 1 and 2 and discuss and contrast with your earlier results.

Consider the operating conditions in the single adiabatic catalyst bed. Pay attention to the efficient/cost effective use of the catalyst i.e. ethene production/weight of catalyst. Consider and discuss ways in which this can be improved. Use additional simulations as necessary.

**ASSUMPTIONS**

*a) The gas is perfect at all temperatures and pressures*

*b) The gas is in plug flow in the reactor (1D model)*

*c) The pressure drop can be modelled using the Ergun equation for turbulent flow*

*d) The pressure drop across the interstage cooling can be neglected*

**MATLAB Notes**

a) You will be required to use an ODE solver function in MATLAB. The recommended solvers are ODE45 and ODE15, for which you can find documentation online.

b) The ODE solver options are commonly used to tune the solver and deal with numerical errors. The Event function, AbsTol and MaxStep can be used to improve convergence of your model.

**DATA**

*a) Heat Capacity [Shomate Equation]*

$C_p$ (in units of $J \cdot mol^{-1}K^{-1}$) of each pure component is a function of temperature only, given by the Shomate equation where **t = T [K] /1000**:

$$C_P = \mathrm{a} + \mathrm{bt} + \mathrm{ct}^2 + \mathrm{dt}^3 + \mathrm{et}^{-2} \quad (7)$$

| | a | b | c | d | e |
|---|---|---|---|---|---|
| $C_2H_2$ | 40.6869 | 40.7328 | -16.1784 | 3.66974 | -0.658411 |
| $C_2H_4$ | -6.3879 | 184.4019 | -112.9718 | 28.49593 | 0.315540 |
| $C_2H_6$ | -6.1401 | 212.0843 | -103.5428 | 19.82347 | 0.361453 |
| $H_2$ | 33.0662 | -11.3634 | 11.4328 | -2.77287 | -0.158558 |
| CO | 25.5676 | 6.0961 | 4.0547 | -2.67130 | 0.131021 |
| $N_2$ | 26.0920 | 8.2188 | -1.9761 | 0.15927 | 0.044434 |
| $CH_4$ | -0.7031 | 108.4773 | -42.5215 | 5.86279 | 0.678565 |
| $O_2$ | 29.6590 | 6.1373 | -1.1865 | 0.09578 | -0.219663 |
| $CO_2$ | 24.9974 | 55.1870 | -33.6914 | 7.94839 | -0.136638 |
| $H_2O$ | 30.0920 | 6.8325 | 6.7934 | -2.53448 | 0.082139 |

Assume the heat capacity of the mixture is a mole fraction weighted sum of the individual heat capacities. For a mixture with mole fractions $y_i$:

$$\mathrm{C}_p = \sum_i y_i \mathrm{C}_{p,i} \quad (8)$$

*e) Catalyst data*

The catalyst particles are cylinders of diameter 5.5 mm and length 16 mm (equivalent particle diameter of 7.04 mm) and have a (particle) density of 1400 $kg/m^3$.

The bed voidage may be taken as 0.4. **The void fraction is the fraction of the total packed bed (reactor) volume that is taken up by the void (gas/empty space).**

*f) Pressure drop*

It can be assumed that the pressure gradient in a fixed-bed of particles governed by the Ergun equation which, for these Reynolds numbers, reduces to:

$$\frac{dP}{dz} = -\frac{1.75G^2(1-\varepsilon)}{D_p \rho \varepsilon^3} \quad (9)$$

where G is the superficial mass velocity of the fluid (mass/(time*area)).

$\varepsilon$ is the bed voidage

$D_p$ is the equivalent particle diameter

$\rho$ is the gas density

## Project Logistics

1. **Duration and assistance.** The project is available now (otherwise you could not read this). The project will run for two term weeks (27 February until 10 March). There will be GTA assistance available in person and *via* TEAMS on Mondays, Tuesdays, Thursdays and Fridays from 09:00-12:00 only.
2. The following rooms have been reserved for you to work on your project: ACEX 252, ACEX 400A, ACEX 400B, RODH 303 and RODH 403. The GTAs will be available for consultation in ACEX 400 A&B. Your course coordinator will be available *via* the RE1 TEAMS channel, or you can make an appointment *via* email to discuss any group issues.
3. **Groups.** Your boss has assigned you to a group of (normally) 4 engineers for the duration of the project. Because of your boss's abhorrence of paperwork, there will be no switching permitted.
4. **Assessments.** The project will be assessed in the following ways:
    a. MATLAB programme for reactor design (1 per group!) – 40%
    b. Reactor design report (1 per group!) – 60%
5. **Notes**
    a. You MUST use MATLAB version R2021b for your design and simulations
6. **Deliverables**
    a. Submit your best Matlab code by 10/03/22 at 16:30
    b. Submit your report by 10/03/22 at 16:30

**Marking scheme for the reactor report:**

- Presentation: overall style, clarity and organisation 20%
- Description of theory 20%
- Results and discussion of the initial simulations 25%
- Results and discussion of the advanced/sensitivity analyses 35%

Report Guidelines

The following items are to be submitted:

(a) **One report**

The submission of one report by each group of students will be required. Please use the normal departmental template for report writing. A penalty will be imposed on reports exceeding the page limit. Arial 11-point font (minimum) and 2 cm margins (minimum). Single spacing is acceptable.

Each report should not exceed 10 pages, including main body text and all figures (introduction through conclusions, inclusive), but excluding the title page, author names, abstract, references or table of contents.

Do not try to include all of the results you generate but do include meaningful analyses to go with the figures or tables. Adopt compact and efficient ways to present the results. A compare-and-contrast approach may be helpful with overlaid plots from different simulations

shown on the same graph with appropriate legends (you can programme Matlab to do this for you or manually transfer the data).

The following is a **suggested** structure for the report and the topics for inclusion under the major headings. There is also a **suggestion** of an appropriate page limit for the different headings.

**Table 1.** Report structure.

| Section | pages |
|---|---|
| Abstract | - |
| Introduction | 1 |
| Theory and Methodology | 3 |
| Results and discussion of basic design | 2 |
| Results and discussion of sensitivity analysis | 3 |
| Conclusions | 1 |

**Overall page limit – 10. No addendum permitted.**

(i) Abstract and Keywords: The abstract must summarize the content of the report and the main conclusions. This is normally a short paragraph.

(ii) Introduction: The hydrogenation process description; general aims and objectives of the reactor design and specific aims for this hydrogenation process.

(iii) Theory and Methodology: Only the theory and methods used in the work should be presented (the report is not a tutorial). It can cover the chosen reactor design elements and any required details on mass balances, reactor modifications, etc., with salient equations as appropriate; methodology to implement these strategies or any experimental simulations.

(iv) Results and analysis: Results and analysis (not all cases, but the ones that you judge as the most important); sample calculations; clear statements of parameters used and simulations performed. The use of multiple plots on one set of axes is useful for showing comparisons.

(v) Discussion: The discussions must give insights. It is not enough to just describe the results. One way is to make tables or graphs showing trends and to provide an explanation for the observed trends.

(vi) Conclusions and suggestions for future work to improve your design.

**Report Marking**

Reports are due to be submitted electronically (BlackBoard) by ***16:30 on Friday 10$^{th}$ March***. Late submissions will be penalized. It is wise to allow plenty of time when attempting submission at peak times in case the electronic submission system becomes overloaded.

Marks will be awarded for quality of the results and presentation of the report. The assessors will look for: Good English and proper grammar including appropriate punctuation marks; organisation of the report in a coherent and logical manner with sections and sub-sections as necessary under the major headings; inclusion of proper citations and references; good formatting including figures with legible lines, appropriate background, legend positioned appropriately and figures of proper size (neither too big nor too small); titles for figures and tables placed appropriately (below the figures and above the tables) and labelled accordingly. Proofread carefully to identify typos (I did!)

Reports are checked against each other as well as those from previous years, and against other electronic sources worldwide using the TurnItIn service.

Reports showing evidence of plagiarism are always penalized.

(b) **Program listing**

**ONE** copy of the Matlab program files should be sent in a single .zip file by e-mail to (ce-exams-submission@imperial.ac.uk **please do not cc the module leader**) indicating all group member names. The computer program should be well documented, and in particular, units of calculated quantities should be added in comments. Due by 16:30 on Friday, 10th March.

File type and naming

- Reactor design
    - Ideally please submit one MATLAB file (e.g. 'Hydrogenation_reactor_design group x') that can be executed
    - Otherwise – please ensure all files are appropriately named and collected in a single zip file:
        - Compress this folder to a .zip and rename it to 'RD Group [Group number].zip'. So for example group 54 would submit 'RD Group 54.zip'
- Submission
  Submit one .zip file to (ce-exams-submission@imperial.ac.uk) with the subject line 'Group [Group Number] - files'. Send **ONE** email per group. **Please do not cc the module leader.**

(c) **Data files**

All additional calculations that were carried out in spreadsheets, etc. should be included in a data file and e-mailed along with the program files in the .zip folder.

(d) **Individual reactor design derivations**

At the beginning of the course, all students will be expected to individually derive the PFR design equation for the reactors. Please note that you are not expected to analytically solve this design equation, as it is likely impossible.

It is also suggested to check your initial reactor design with the GTAs with an initial rate check (i.e. the rate at the reactor inlet) using the initial conditions only. This is possible before programming any loops into the programme and can be verified by hand calculation.

**Other information**

- Please post any questions on the Discussion Board on Blackboard. Please do not e-mail questions to the module leader – he is likely to just tell you to post it on Blackboard because he is rude.
- Please do not send your project files (code, report) to the module leader or cc him, as this will cause his inbox to crash and make him sad.
- Table 2 (each group's inlet conditions for the reactor design) is on the next page

**Table 2. Inlet conditions: Adapted from Huels report (1945)**

| Group | Feed rate [kg/s] | Feed composition (mol) *[$O_2$ = 2 – CO] | | | | | | | | Feed temp. [K] | Feed press. [bar] | Reactor Diameter [m] | Reactor MAWT [K] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | C2H2 | C2H4 | C2H6 | H2 | CO | N2 | CH4 | $O_2$* | | | | |
| 1 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.00005 | 11.4 | 14.9 | 2.00 | 323 | 16.8 | 0.10 | 480.00 |
| 2 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.0005 | 11.4 | 14.9 | 2.00 | 323 | 16.8 | 0.10 | 480.00 |
| 3 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.005 | 11.4 | 14.9 | 2.00 | 323 | 16.8 | 0.10 | 480.00 |
| 4 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.01 | 11.4 | 14.9 | 1.99 | 323 | 16.8 | 0.10 | 480.00 |
| 5 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.00005 | 11.4 | 14.9 | 2.00 | 323 | 16.8 | 0.10 | 500.00 |
| 6 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.0005 | 11.4 | 14.9 | 2.00 | 323 | 16.8 | 0.10 | 500.00 |
| 7 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.005 | 11.4 | 14.9 | 2.00 | 323 | 16.8 | 0.10 | 500.00 |
| 8 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.01 | 11.4 | 14.9 | 1.99 | 323 | 16.8 | 0.10 | 500.00 |
| 9 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.00005 | 11.4 | 14.9 | 2.00 | 323 | 16.8 | 0.10 | 520.00 |
| 10 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.0005 | 11.4 | 14.9 | 2.00 | 323 | 16.8 | 0.10 | 520.00 |
| 11 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.005 | 11.4 | 14.9 | 2.00 | 323 | 16.8 | 0.10 | 520.00 |
| 12 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.01 | 11.4 | 14.9 | 1.99 | 323 | 16.8 | 0.10 | 520.00 |
| 13 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.00005 | 11.4 | 14.9 | 2.00 | 323 | 16.8 | 0.10 | 540.00 |
| 14 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.0005 | 11.4 | 14.9 | 2.00 | 323 | 16.8 | 0.10 | 540.00 |
| 15 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.005 | 11.4 | 14.9 | 2.00 | 323 | 16.8 | 0.10 | 540.00 |
| 16 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.01 | 11.4 | 14.9 | 1.99 | 323 | 16.8 | 0.10 | 540.00 |
| 17 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.00005 | 11.4 | 14.9 | 2.00 | 323 | 16.8 | 0.10 | 560.00 |
| 18 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.0005 | 11.4 | 14.9 | 2.00 | 323 | 16.8 | 0.10 | 560.00 |
| 19 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.005 | 11.4 | 14.9 | 2.00 | 323 | 16.8 | 0.10 | 560.00 |
| 20 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.01 | 11.4 | 14.9 | 1.99 | 323 | 16.8 | 0.10 | 560.00 |
| 21 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.00005 | 11.4 | 14.9 | 2.00 | 364 | 21.9 | 0.10 | 480.00 |
| 22 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.0005 | 11.4 | 14.9 | 2.00 | 364 | 21.9 | 0.10 | 480.00 |
| 23 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.005 | 11.4 | 14.9 | 2.00 | 364 | 21.9 | 0.10 | 480.00 |
| 24 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.01 | 11.4 | 14.9 | 1.99 | 364 | 21.9 | 0.10 | 480.00 |
| 25 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.00005 | 11.4 | 14.9 | 2.00 | 364 | 21.9 | 0.10 | 500.00 |
| 26 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.0005 | 11.4 | 14.9 | 2.00 | 364 | 21.9 | 0.10 | 500.00 |
| 27 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.005 | 11.4 | 14.9 | 2.00 | 364 | 21.9 | 0.10 | 500.00 |
| 28 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.01 | 11.4 | 14.9 | 1.99 | 364 | 21.9 | 0.10 | 500.00 |
| 29 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.00005 | 11.4 | 14.9 | 2.00 | 364 | 21.9 | 0.10 | 520.00 |
| 30 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.0005 | 11.4 | 14.9 | 2.00 | 364 | 21.9 | 0.10 | 520.00 |
| 31 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.005 | 11.4 | 14.9 | 2.00 | 364 | 21.9 | 0.10 | 520.00 |
| 32 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.01 | 11.4 | 14.9 | 1.99 | 364 | 21.9 | 0.10 | 520.00 |
| 33 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.00005 | 11.4 | 14.9 | 2.00 | 364 | 21.9 | 0.10 | 540.00 |
| 34 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.0005 | 11.4 | 14.9 | 2.00 | 364 | 21.9 | 0.10 | 540.00 |
| 35 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.005 | 11.4 | 14.9 | 2.00 | 364 | 21.9 | 0.10 | 540.00 |
| 36 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.01 | 11.4 | 14.9 | 1.99 | 364 | 21.9 | 0.10 | 540.00 |
| 37 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.00005 | 11.4 | 14.9 | 2.00 | 364 | 21.9 | 0.10 | 560.00 |
| 38 | 0.10 | 16.8 | 3.9 | 0.3 | 50.7 | 0.0005 | 11.4 | 14.9 | 2.00 | 364 | 21.9 | 0.10 | 560.00 |