

CENG 102 Chemical Process Project Description

Plant for Hydrodealkylation of Toluene to Benzene

Introduction:

During World War II, large quantities of toluene were necessary for the production of the explosive, TNT. After the war, with the reduced need for explosives, alternative uses were sought. It soon became favorable to convert this toluene to benzene to manufacture various precursors for nylon.¹ The primary technique used initially was the hydrodealkylation of toluene to benzene, or HDA process. Alternative techniques have been developed since then, including light oil distillation, catalytic reforming or steam cracking of liquid petroleum, and toluene disproportionation (TDP). Currently, HDA plants are usually used to maintain the balance of benzene supplies when all other sources of benzene cannot meet demand.²

Your Assignment:

You will utilize material and energy balances, as learned in CENG 100, and modify them with the new knowledge you have developed in CENG 102. As before, our goal is to design a system that (1.) separates the desired and undesired products, (2.) optimizes the recycle structure of the process, and (3.) maximizes the production of benzene.

Project Goal:

The purpose of this project is to modify the basic assumptions we made in this plant from CENG 100 and correct our calculations. You will compare how this plant operates under idealized conditions (ideal reactors, ignoring kinetics, ideal separation units, - all from CENG 100) with more realistic conditions. This is the first time we are continuing this project since CENG 100, and it will be expanded upon again in your future classes.

(1.) Product and Process Design Principles by Seider, et al, 3rd edition

(2.) <https://www.icis.com/resources/news/2007/11/01/9075160/benzene-production-and-manufacturing-process/>

Process Description:

Toluene and hydrogen are reacted in a high temperature and pressure reactor to produce benzene and methane. An unavoidable and undesired side-reaction is the further reaction of benzene into biphenyl ($C_{12}H_{10}$). If the reactor operating temperature is too low, the benzene can become hydrogenated and produce cyclohexane. Although this is a common precursor for nylon, it has a similar boiling point as benzene, yielding an azeotrope and extreme difficulty in separation. Increased temperature can mitigate this reaction, but lead to hydrocarbon decomposition, known as coking. The product is subsequently sent through a complex separation train to purify the benzene product, purge the biphenyl, and recycle unused toluene and hydrogen. The exact structure of the separation train depends on the desired purity and can vary between one and three different types of distillation columns.

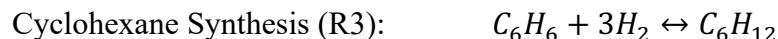
Process Steps:

Hydrodealkylation (HDA) of Toluene to Benzene:

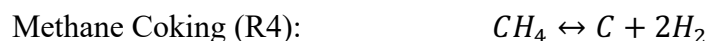
Fresh toluene is fed with hydrogen (in large excess) into the HDA Reactor, where the two primary reactions take place:



If the reactor temperature is too low, a third (undesired) reaction takes place, producing cyclohexane, which would require extremely expensive separations downstream:



If the reactor temperature is too high, the various hydrocarbons will decompose into carbon and hydrogen – a process known as coking. The primary coking reaction that is of concern is the breakdown of methane:



This process typically takes place in packed bed reactors, using a chromium, molybdenum, or platinum oxide catalyst. With catalyst, reactors are typically operated between 950°F-1150°F. Higher temperatures (as high as 1400°F) are sometimes used instead of catalyst. Operating pressures can range between 30 and 60 atm. Although extremely high toluene conversion and benzene yield/selectivity can be achieved, for practical purposes, industrial operating conditions are typically set to guarantee conversions near 75%.

Removal of Light Ends:

The reactor effluent is typically sent to a low temperature flash drum, also referred to as a partial condenser. The goal of this step is to remove the light ends (light gases, such as H_2 and CH_4) from the heavier materials, such as toluene, benzene, and biphenyl, which condense out of the mixture and are sent forward to be separated. The light ends are not separated from each other (too expensive for the minimal benefits) but are most recycled to the reactor feed. Since the reactor feed has H_2 in large excess, this recycle stream significantly reduces the amount of fresh H_2 that needs to be purchased and fed to the process. Maintaining high concentrations of H_2 in the reactor can help reduce biphenyl production (reaction R2). This ultimately improves the benzene yield and selectivity, which more than compensates for the slight reduction in toluene conversion (reaction R1) caused by the methane recycle.

NOTE: Flash separation is a technique that separates components in a mixture based on differences in volatility (ease to vaporize). This will be covered in CENG 102 and 122.

Separation of Toluene, Benzene, and Biphenyl:

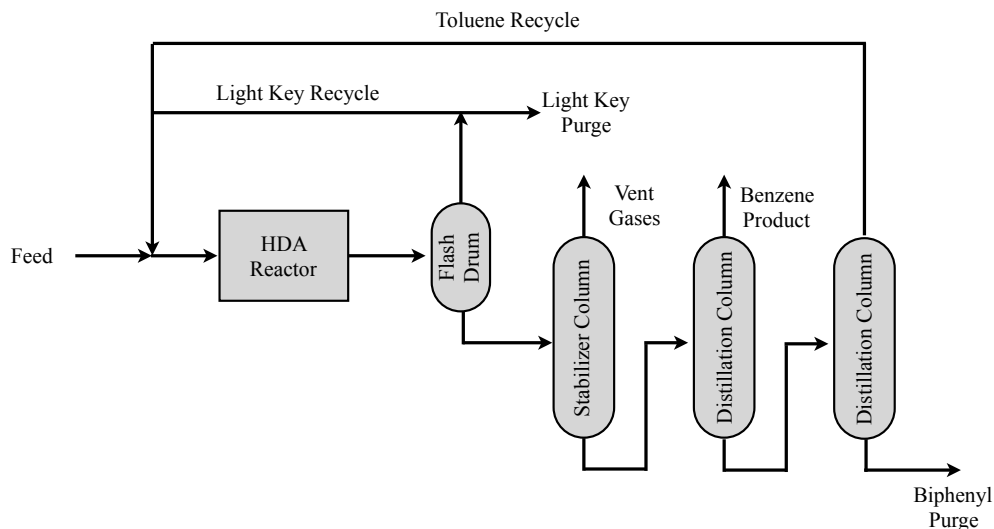
The liquid heavy ends (toluene, benzene, and biphenyl) are taken from the condenser and sent to a separation train to separate into their individual components. Typically, the first column, known as a stabilizer column (a specialized distillation column) is a relatively short column where any residual dissolved light gases (H_2 and CH_4) are completely removed to be recycled. This step is sometimes accomplished simply by the use of a second flash drum. The number of columns that follows the stabilizer depends on the desired extent of separation and is typically designed based entirely on economic justifications. Three typical configurations are described on the next page:

Option 1: 3 Columns with no Biphenyl Recycle

First column removes light ends (stabilizer column)

Second column separates benzene product out (desired product)

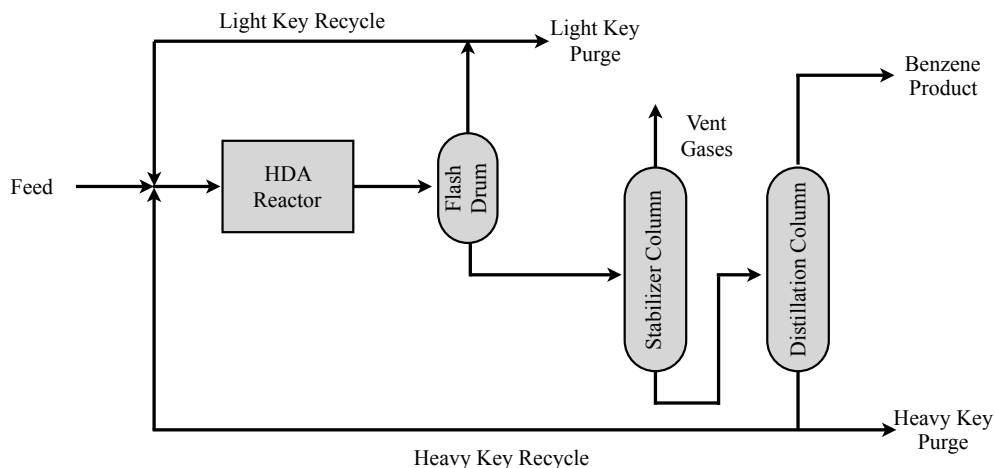
Third column separates toluene from biphenyl – toluene is recycled to reactor to reduce the amount of fresh toluene needed for the process; biphenyl is waste or a secondary product (low resale value)



Option 2: 2 Columns with Biphenyl Recycle

First column removes light ends (stabilizer column)

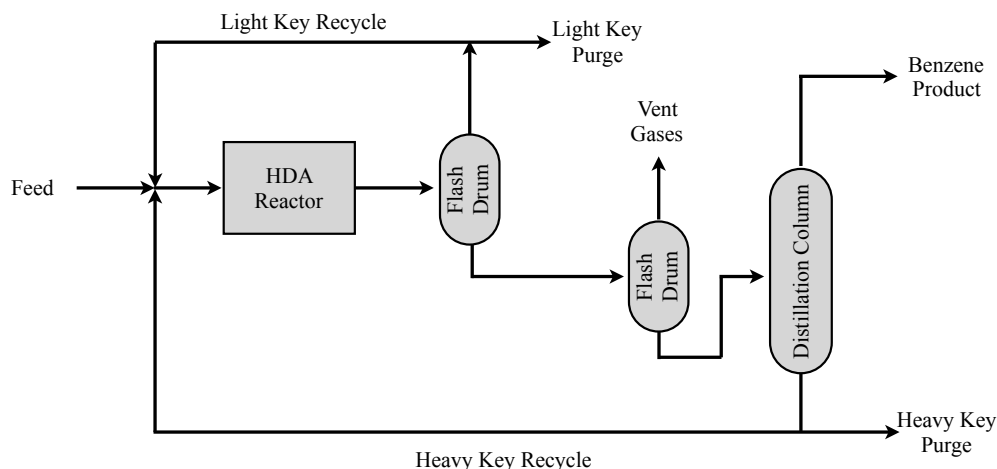
Second column separates benzene product out as one stream & secondary stream containing toluene and biphenyl is mostly recycled; toluene is the primary reactant and biphenyl serves to hinder reaction 2 and improve benzene yield



Option 3: 1 Column with Biphenyl Recycle

Stabilizer column is replaced with a second flash drum

Lone column separates out the benzene product and recycles the toluene and biphenyl



The fewer columns there are in the separation train, the fewer that need to be built (reducing capital/construction costs). However, this also likely requires the remaining columns to be taller (slightly higher capital costs) and more energy-intensive processes (higher energy/utility costs). In CENG 102, we still cannot analyze distillation columns, but we can focus on the flash drums to determine the efficiency of separation.

Energy Considerations:

As with all industrial processes, energy integration is of key importance in HDA plants. High power compressors and pumps are necessary to achieve the necessary high pressures in the reactor. Work can be recaptured through turbines and expanders where the streams are decompressed. Heating/cooling utilities and heat exchangers are necessary to pre-heat the reactor feed and subsequently cool its exhaust. And the separation train (depending on the types of columns) generally incorporate reboilers, condensers, and more heat exchangers. In this project, the students will be asked to determine various energy/work requirements, throughout the whole process. Energy analysis of the separation train will mostly be saved for CENG 122, whereas energy optimization/saving methods will be developed in CENG 101B and 124A.

PROJECT:

Answer the questions on the following pages. Use the Project Cover Page document (to be posted separately) as your cover page when submitting.

To show work:

- Provide hand-written sample calculations for each part.
- **CLEARLY WRITE OUT THE ENERGY BALANCE** or any other critical relevant equations (equilibrium constant, etc.) you use **FOR EACH QUESTION**.
- For mixture heat capacities or pseudocritical parameters, perform the calculation for each once in the project, and then provide tables of the mixture properties (in other words, we don't need to see the work for those mixture calculations dozens of times – only once).
- Box your solutions in your work pages and label the work with each Question #!
- If you use MATLAB to help you solve, provide the code you used for each question, with clear labels for all equations defined. Ask instructors for more details.
- If you use Excel to help you solve, provide print-outs of all your data calculations, but clearly box and label sections for different calculations. Ask instructors for details.
- If you complete all calculations by hand, please write out all species balances for all your calculations and provide all necessary solutions to these balances that are relevant to answer the questions on the following pages.
- For any/all questions that require iterations – you are expected to perform one iteration by hand (including the % change), but can then provide a table of all subsequent iterations and can report your final desired answer. If you only use a solver, you will receive very little partial credit. NOTE: some questions, you will be explicitly told to simply use a solver (since you have not been taught how to iterate those cases).
- For any/all problems that require interpolation – you do not need to show the interpolation work by hand EVER. You ARE expected to show which values you are interpolating around (the closest Pr columns and Tr rows, as well as the 4 values within the table you're interpolating around).

EXTRA CREDIT: There are several opportunities for extra credit. Note that extra credit only cancels points lost and your total score maxes out at 100%. In other words, if you get 390 out of 400, and earn 40 points extra credit. Your final score maxes out at 400.

GROUPS:

You are allowed (AND ENCOURAGED) to work on this project in groups of 4 to 6. Groups CANNOT be any larger. Also, NO ONE can work alone. This is supposed to be a collaborative effort, so you have to find fellow engineers to work with. All group members are expected to contribute equally and the work provided should label clearly which person contributed to what parts. Each group is expected to turn in a single completed project.

NOTE: LEGIBILITY AND CLEAR ORGANIZATION OF SOLUTIONS ARE NECESSARY FOR PROPER GRADING.

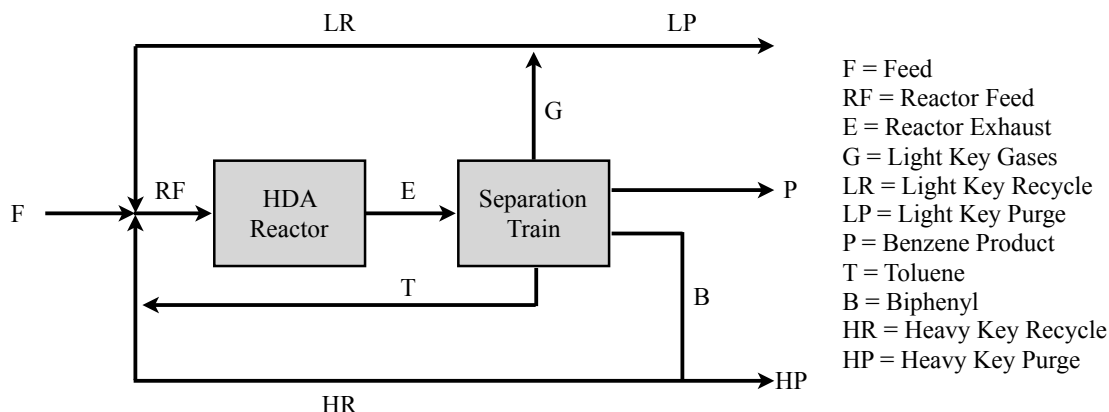
WORTH: 10% of the overall course grade. DO NOT WAIT UNTIL THE LAST MINUTE TO START THIS PROJECT. YOU WILL REGRET IT.

DUE: Friday, March 15, at 11AM (beginning of 1st class).

Project Questions:

Part I: General Process with Biphenyl Recycle (Separation Options 2 or 3):

See the simplified Block Flow Diagram (BFD) for the analysis in this part.



Design Parameters:

- (1) All flow rates and compositions, as found in CENG 100, are provided in a separate document with flows related to the streams in the diagram above.
- (2) Since compression equipment typically needs to be of a single phase, the fresh feed toluene and H₂ must come in separate streams. Each stream enters at 1 bar & 10°C.
- (3) Each fresh feed stream must be heated and compressed to 570 psia.
- (4) The compressor for the hydrogen stream operates at 80% efficiency, while the toluene (vapor) compressors operate at 75% efficiency.
- (5) The reactor feed stream compressor operates at 85% efficiency.
- (6) The single-pass conversion of the reactor is 75%, with a benzene yield of 95%.
- (7) The reactor is fed at 1200°F and 570 psia – established such that R3 and R4 are (initially) assumed to be shut off.
- (8) The reactor exit stream is at 1270°F and 570 psia.
- (9) For all flash columns with more than two components, the K-value values of the individual species are provided in a separate document.
- (10) For all flash columns with only binary mixtures, K-values are not provided.
- (11) Assume all gases DO NOT behave as ideal gases unless specified otherwise!
- (12) Assume no heat of mixing.

Questions:

PART I: Fresh Feed Processing

- 1.) Hydrogen Compression: How much work is required to compress the fresh H₂ stream from 1 bar to 484 psia? What is the final temperature after compression? Assume ideal gas.

EXTRA CREDIT I: In reality, standard compressors can only compress to by 3x, and hence multiple compressors in series are required. Also, compressors can break down if they overheat, so the process is typically cooled in between compressors, in a process known as inter-stage cooling. As extra credit, you must determine:

- a.) the work of each compressor (operating at a pressure ratio of 3, except the last);
- b.) the exit temperature from each compressor;
- c.) the amount of heat removed in each inter-stage cooling step, if the intermediate streams are cooled back to 30°C.

NOTE: a cooling step IS NOT used after the final compressor because the stream is to be subsequently heated to high temperature.

ALSO NOTE: all the compressors satisfy Design Parameter #4.

- 2.) Hydrogen Non-Ideality: Assuming the final temperature found in #1 (*not* the extra credit) is correct, modify the work found by accounting for non-idealities (i.e. evaluate the residuals and find the modified work). Was it safe to assume an ideal gas?

NOTE: This actually should have led to a change in final temperature, which you do not need to calculate.

- 3.) Toluene Heating: Determine the heat required to heat the feed toluene from 10°C to 600K at 1 bar. Assume any vapors in this process act as ideal gases.

- 4.) Toluene Compression: How much work is required to compress the (now) vapor toluene stream from 1 bar and 600K to 484 psia? What is the final temperature after compression? Assume ideal gas.

- 5.) Toluene Vapor Non-Ideality: Assuming the final temperature found in #4 is correct, modify the work found by accounting for non-idealities (i.e. evaluate the residuals and find the modified work). Was it safe to assume an ideal gas?

NOTE: This actually should have led to a change in final temperature, which you do not need to calculate.

PART II: Reactor Feed Pre-Treatment

- 6.) Mixing Temperature: Determine the temperature of stream RF after streams LR, F, T, and HR are mixed. Stream LR will be at 100°F while stream(s) F will be at the temperatures found in #1 and #4. Streams T and HR are superheated vapors, each 100°C above their respective saturation temperatures. All streams are at 484 psia. Assume ideal gases and no heat loss.

EXTRA CREDIT II: Include the residuals of all the entering streams and the residual of the exit stream (using pseudocritical properties) to solve for the true final temperature. Do not attempt to iterate – just use some solver and the B-correlations (despite the pressure).

- 7.) Pre-Reactor Compression: If the reactor feed stream, RF, is compressed to 570 psia, how much work is required? What is the final temperature after compression? Assume ideal gases (and compressor efficiencies account for residual effects).
- 8.) Pre-Reactor Heating: How much heat is required to heat the compressed RF stream (now at 570 psia) from the compressor exit temperature up to 1200°F? Do NOT assume ideal gases.

PART III: Reactor Operation

- 9.) Reactor Heat: Assuming ideal gases, how much heat is added/removed for the reactor, if the feed enters at 1200°F and exits at 1270°F?
- 10.) Adiabatic Temperature: From your results in (9.), you'll find heat was added overall to an exothermic reaction – which may not be cost-efficient. What is the exit temperature if the reactor is operated adiabatically? Assume ideal gases again.
- 11.) Influence of Non-Idealities on Equilibrium: We found in CENG 100 that the reactor IS NOT operating at equilibrium. You will find in CENG 113 that equilibrium can still influence reaction kinetics (rate), and hence reactor sizing.
- a.) Determine the equilibrium constant for reactions 1 and 2.
- b.) If the reactor mixture are actually not ideal gases, but form an ideal solution of gases, will accounting for fugacity promote or hinder either reaction's equilibrium? Hint: evaluate the "effective" equilibrium constant.

PART IV: Separation Section

- 12.) Pre-Separation Pressure Reduction: To reduce the necessary operating temperatures, the reactor exhaust (stream E) pressure must be reduced to 484 psia. This can be done by two methods: throttling or a turbine (to extract some work). Let's evaluate each case separately.
- a.) Throttling: Assuming a non-ideal gas, determine the final temperature if the stream passes through a throttle valve.
 - b.) Turbine: If, instead, the stream passes through a turbine with efficiency 80%, how much work can get extracted from the process? What is the final temperature at the turbine exit? Assume ideal gases (with residuals accounted for by the efficiency).
- 13.) Flash I: If stream E (with 5 components) enters a flash column that operates at 484 psia and 100°F, determine the following:
- a.) The total molar flow rate of the liquid and vapor exit streams.
 - b.) The compositions of the liquid and vapor streams.
 - c.) The recovery fractions of H₂ and CH₄ (each separately) in the vapor stream.
 - d.) The recovery fractions of toluene, benzene, and biphenyl in the liquid stream.
- NOTE: Recovery fraction is defined as the total moles of a species in an exit stream divided by the total moles of that species in the feed stream. This is a measure of how much of a component is recovered (vs how much lost) in a given stream.
- 14.) Flash II (AKA Stabilization Column): From your results to #13, you should have found there is still a moderate amount of CH₄ dissolved in the liquid stream. This needs to be removed to make subsequent separations easier. It is suggested to feed the liquid exit from Flash I to a 2nd flash column (as described in Option 3 on page 5), as opposed to using a stabilization column (larger and more expensive). If Flash II operates at 484 psia and 200°F, determine the following:
- a.) The total molar flow rates of the liquid and vapor exit streams.
 - b.) The compositions of the liquid and vapor streams.
 - c.) If the vapor exit streams of Flash I and Flash II are combined (to form stream LG), and 5.86% of this stream is purged (the bulk is recycled as stream LR), how much benzene is being purged (lost forever) from the system?

- d.) Did Flash II successfully eliminate (or reduce significantly) the CH_4 from the liquid stream? Explain. If the answer is yes, then the “cheap” Flash II was a success. If the answer is no, then the more expensive stabilization column may be necessary.
- 15.) Flash III (Ideal): After several separation columns, the last of the light gases and all the benzene can be removed by the distillation column. Eventually, a stream flowing at 140 mol/s is produced with composition: 92% biphenyl and 8% toluene. It is desired to separate these components in a flash column operating at 2 bar and 500°F. Assuming ideal gases and ideal solution behavior, find the following:
- a.) The compositions of the liquid and vapor streams.
 - b.) The total molar flow rates of the liquid and vapor exit streams.
 - c.) If it is desired for the liquid composition to be 99% biphenyl, what pressure would be required? What are the corresponding vapor compositions? What are the total flow rates of the two exit streams in this case?
- 16.) Flash III (Non-ideal): Re-answer problem 15 parts (a.) and (b.), but assume non-ideal gases. For this system, it is safe to assume (i.) the vapors are non-ideal, but for an ideal solution of vapors, and (ii.) the liquid can be treated as an ideal solution.
- EXTRA CREDIT III: Re-answer Problem 15 (c.) under the non-ideal conditions described in Problem 16.
- 17.) Final Question: Looking at the process, as a whole, explain if Flash III is even necessary. If it is, explain its purpose. If it is not, explain why.