CH402 Capstone Project - Atmospheric Distillation of Crude Oil

<u>Objectives</u>

- (1) Given a specific crude oil, cadets will design a process that separates the crude into light ends, naphtha (or raw gasoline), kerosene, gas oils, and residuum.
- (2) Given a specific crude oil, cadets develop realistic constraints for allowed sulfur and water content in refined products and implement these constraints in their design.
- (3) The process will be refined to reduce or eliminate redundant equipment through consolidation of process steps.
- (4) The process will be refined to reduce overall energy consumption through integration of heat exchangers for energy recovery.
- (5) Cadets will determine the number and diameter of distillation trays, the diameter and thickness of column shells, the size of the reflux drums, the heat transfer areas of the condensers and reboilers, pump capacities, and pipeline dimensions.
- (6) Cadets develop a strategy for safe control of the process by identifying major control points and key relief devices.
- (7) Cadets will produce a table of purchased equipment including costs.
- (8) Cadets will perform an economic analysis of the process based on PBP, ROI, NPW, and DCFR.
- (9) Cadets will prepare a safety and environmental impact assessment of the process.
- (10) Cadets will produce a detailed design report for the project that meets specifications in Chapter 11 and includes research into regional political and economic impact on sustainability of the source crude oil.

Introduction

Crude oil is an extremely important raw material that forms over millions of years from the remains of plants and animals. This "fossil fuel" is pumped from the ground in oil fields located in the Middle East, West Africa, North and South America, and Asia. It is then transported by pipeline, railroad, and ocean-going tanker ships to refineries all over the world. The refineries convert the crude oil into fuels and basic chemicals. The Energy Information Administration estimates that that 36% of the energy used worldwide comes from petroleum and its refined products.[1] Almost all synthetic chemicals used on a commercial scale originate from molecules derived from crude oil.

Crude oil is a mixture of hundreds of hydrocarbon molecules.[2,4] The hydrocarbon molecules range in size from the smallest, methane, with one carbon atom, to large compounds containing 300 or more carbon atoms.

The major fraction of these compounds are alkanes, such as n-butane and i-butane, n-pentane, n-octane, and so on. Most of the remaining hydrocarbons are either cyclic alkanes or aromatics. Only the simplest molecules are purified on a commercial scale. Generally, in a refining process, isolation of pure products is restricted to those compounds lighter than C7's. The majority of hydrocarbon molecules present in crude oil have been isolated but only under laboratory conditions. In refining processes, the products are characterized by boiling point ranges and not molecular structure. For example, a major product in a refinery is naphtha, which would be identified as a "90 to 140 °C cut."

Not all compounds in crude oil are hydrocarbons. Small quantities of sulfur, nitrogen, and metals are also present. By far, the most important of these is sulfur. Sulfur is present in the form of hydrogen sulfide and organic compounds of sulfur. These organic compounds are present through the entire boiling range of the hydrocarbons in the They are similar in structure to the hydrocarbons themselves. but with the addition of one or more sulfur atoms in the structure. simplest of these is ethyl mercaptan, which has a structure similar to ethanol, but with the oxygen atom replaced by sulfur. The higher carbonnumber ranges of these compounds are thiophenes, which are found mostly in the heavy residuum ranges, and disulfides, which are found in the middle distillate range of the crude oil. The sulfur from these heavier compounds can only be removed by converting the sulfur to H₂S in a hydrotreating process operating under severe conditions of temperature and pressure and in the presence of a suitable catalyst. The lighter sulfur compounds are usually removed by extraction with caustic soda or other proprietary solvents.

Organic chloride compounds are also present in crude oil. These are not removed as such, but the process equipment must be designed to withstand attack by HCl, specifically in the primary distillation processes. This protection is in the form of monel lining in the sections of the process most susceptible to chloride attack. Injection of ammonia is also used to neutralize the HCl in those sections.

The most common metal impurities found in crude oils are nickel, vanadium, and sodium. These are not volatile, and usually end up in the residuum or fuel oil products of the crude oil. These are typically not removed from the oil, and normally they are only a nuisance if they affect further processing of the oil or if they are a deterrent to sales. For example, these metals are known to cause a reduction in catalyst life in the catalytic sections of the refinery, in which case they would need to be removed to the extent possible. As another example, high concentrations of nickel and vanadium are unacceptable in fuel oils used in the production of certain steels.

Although the majority of hydrocarbons found in crude oil are alkanes, cyclic alkanes and aromatics, there is a fourth group of compounds also present. These are the unsaturated or "olefinic" hydrocarbons. They are not naturally present in any great quantities in most crude oils, but are often produced in significant quantities during the processing of the crude oil to refined products. This occurs in those processes that subject the oil to high temperature for a relatively long period of time. Under these conditions, the saturated hydrocarbon molecules break down or "crack," losing one or more of the atoms attached to quadrivalent carbon. The remaining atoms are rearranged to form unsaturated compounds. An example is the thermal cracking of n-butane to form ethane and ethene (ethylene):

CH3-CH2-CH3 + heat
$$\rightarrow$$
 CH3-CH3 + CH2=CH2 (n-butane) (ethane) (ethylene)

Crude oil also contains water and suspended solids. This is not surprising since the oil is extracted from underground reservoirs in the oil field. The water content can vary greatly from field to field, and may be present in large quantities if oil extraction is enhanced using water injection technology. Most of the water and suspended solids is separated at the field to minimize the amount that would otherwise need to be transported to refineries. However, there will always be residual amount of these unwanted impurities. Refiners deal with this by purchasing crude oil with a specification on the allowed content of water and suspended solids, and they will have process units that reduce the quantities to acceptable limits.[3]

Finally, methane is also present in crude oil, and can be as high as 65% of the material coming out of the well.[4] The vast majority is removed in the field. As the crude oil emerges from the well, there is a significant decrease in pressure, causing the gases dissolved in the oil to flash off. The gas is either collected for processing and sales, or is flared in the field.[5] However, a residual amount of dissolved methane will always be present in the oil entering the refinery.

Although all crude oils contain the types of compounds and impurities described above, rarely are there two crude oils with the same characteristics. This is because crude oils from different geographic locations contain different quantities of the various compounds and minerals described earlier. Crude oils produced in Nigeria, for example, contain high amounts of cyclic alkanes. On the other hand, crude oil from Venezuela has a relatively low amount of material boiling below 350°C. The difference in the character of the various crudes enables refiners to improve their operation by selecting the best crude or crudes that meet their product marketing requirements.

To simplify this project, we will not consider chlorides, alkenes, metals, water, suspended solids, or methane in the crude oil. The crude oil being processed in your design can be considered to have been "pretreated" to remove these components. Sulfur will be considered to be in the form of hydrogen sulfide only. This is to simplify design your work. That is, mercaptans such as ethyl and methyl mercaptan are not present in the oil by assumption.

Cadets will be provided with a type of crude oil, specified by its name as it appears in the CHEMCAD database. Cadets will then use CHEMCAD to calculate "pseudo components" from the information contained in the database. The output of this calculation is a report that contains the boiling point curve and other useful parameters that help CHEMCAD model the fluid. This report must be formatted and submitted as an appendix with the final report. The pseudocomponents can then be used to model the fluid traffic through the distillation column, allowing equipment size and heat duties to be calculated. A procedure for activating this feature in CHEMCAD 7 will be provided by your instructor.

<u>Assignment</u>:

Each cadet team will be assigned one crude oil from the CHEMCAD database. Cadets will then use CHEMCAD's thermophysical tools to create a series of "pseudocomponents" that model the properties of the crude oil. This is accomplished in "Thermophysical," "Pseudocomponent Curves." Simply step through the menus until you come to bulk properties, and enter your crude in the "Distillation Curve" dropdown menu. CHEMCAD will calculate all of the physical properties needed. Your assignment is to process 10,000 BPSD of crude oil into light ends, naphtha, gas oils, and residuum. The "cuts" that you must prepare are shown in Table 1.

Table 1. Approximate carbon number and boiling range for products.		
Component	Composition	Normal Boiling Range
	(Carbon Number)	(degrees C, approx.)
Light ends ^a	C1 to C4	-162 to -1
Naphtha	C5 to C12	+30 to +200
Gas oils	C12 to C20	+200 to +371
Residuum	C20 to C70	+371 to +540
^a Includes tail gas and liquid petroleum gas (LPG)		

In addition to the cuts specified in Table 1, you are also responsible for further processing the light ends into purified methane, ethane, propane and butane. Purified propane and butane should be blended to produce liquefied petroleum gas (LPG). Purified ethane and methane that result from producing LPG can be blended to produce fuel for fired heaters if needed, or you may take a credit for these products in your economic analysis. Purified hydrogen sulfide should be further processed into sulfuric acid. A detailed design of the sulfuric acid plant is not required at this time, but the capital investment must be included in your economic analysis.

The light hydrocarbons in the crude oil must be entered manually before you enter your assigned crude oil. These components include water, methane, ethane, n-propane, i-butane, n-butane, and hydrogen sulfide. CHEMCAD will then automatically populate the relative amounts of these components using information obtained from the database. The water and H_2S can be entered as zero when creating the pseudo-components, and later added to the feed in the amount specified for your crude oil.

Please be aware of all design heuristics in Appendix E of the Peters, Timmerhaus, and West textbook, especially pumps, heat exchangers, and distillation columns. Use of typical design conditions specified in these heuristics, especially for distillation columns, is strongly encouraged. You may also use the heuristics for preliminary design of heat exchangers, subject to the comments below.

(Changed 4-23-19.) You are responsible to determine sufficient pipe pressure drops to size all pumps. You must also design all condensers, reflux drums and reboilers for each distillation column. You are also required to design any ancillary equipment such as fired heaters, dewatering vessels, etc. The 3-step design method is required for each heat exchanger. In the even that you cannot get the 3-step method to work, or as a preliminary design, you may assume that the heat transfer coefficient (U) for entry into CHEMCAD is 850 W/($m^2 \cdot K$) for all condensers and 1100 W/($m^2 \cdot K$) for all reboilers. Cooling water for the condensers is available at 5°C and 5 atm and must be returned to central facilities no higher than 65 °C. Reboilers are to be heated with steam, and saturated steam is available from an existing steam plant at pressures of 150, 790, or 3550 kPa. All utilities available in the colorful worksheet may be assumed to be available for use in your design.

You must complete an economic analysis using the colorful worksheet. The timeline for your evaluation is 10 years with MACRS depreciation and with 1% inflation. You must evaluate the return on investment (ROI), payback period (PBP), net present worth (NPW) and

discounted cash flow rate of return (DCFR) for the project. A table showing a summary of purchased equipment costs is required and must be included in your report (see DP3 for a simplified example). All equipment pricing must be in May 2019. Pricing of raw materials and finished products can be obtained from current internet sources, and must be documented carefully. Pricing of utilities is available in the colorful worksheet.

Costs or raw materials and products are determined as follows: Costs of products (LPG, naphtha, and gas oil) should be 90% of current market values (since products are not quite finished) at the refinery location. Crude oil (raw material) price is determined from international market values and must include transportation costs. Transportation costs by sea (tanker) are \$1.00 per barrel per 1000 miles. Railroad shipping costs are \$5.50 per barrel per 1000 miles. Pipeline shipping costs are \$0.75 per barrel per 1000 miles. (Added 4-23-19.)

<u>Deliverables</u>:

You are responsible for producing a design report for this project. The report must follow the guidelines in Chapter 11 of your textbook. A printed paper report is due by the date specified below. The report can be stapled or clamped, but no brown bombers, please. Electronic copy of your final files must be archived in your SharePoint directory, to include any word documents, excel spreadsheets, and CHEMCAD files.

Grading, Grading Rubrics, and IPRs:

Grading for this project is rubric-based. A grading rubric has been linked to the course web site. The rubric contains 15 grading components (15 columns). You are expected to fully understand each column in the rubric. You are also strongly encouraged to develop a detailed plan of attack for each column, to review your plan with your instructor, and to maintain frequent communication with him regarding any changes to your plan during the development of your project. This will assist you in preparing for the IPRs. For IPR grades, your instructor will assess your progress on the rubric against a reasonable level of progress (instructor expectation) at the time of the IPR, and your grade will reflect that progress.

<u>Due Dates</u>:

The completed project is due by 1600 Friday 10 May 2019. This includes a paper printout of your final report as well as completed electronic files saved in SharePoint. In-Progress Reviews (IPRs) are by appointment with your instructor. IPR1 is due no later than 1600 on

5 April and IPR2 is due no later than 1600 on 25 April. You are encouraged to meet with your instructor at least once a week outside of normal class hours to ensure adequate progress.

References Used in This Handout

- 1. "Primary Energy Consumption by Source and Sector, 2012," http://www.eia.gov/totalenergy/data/monthly/pdf/flow/primary_energy.pdf, accessed 18 March 2019
- 2. D.S.J. Jones and P.R. Pujado, Handbook of Petroleum Processing, Dordrecht, The Netherlands: Springer Science and Business Media B.V, pp. 1-6.
- 3. http://en.wikipedia.org/wiki/Basic_sediment_and_water, accessed 18 March 2019.
- 4. P.J. Daniel, S. Smuk, R. Taherian, J.J. Pop, Patent Number w02010059601 (US 20120000279), May 27, 2010.
- 5. M. Sunmoni, "Gas Flaring in Nigeria," The environmentalist, http://ecoremediation.blogspot.com/2012/06/gas-flaring-in-nigeria-what-are-harmful.html, accessed 18 March 2019.

Other Useful Resources

- Glossary of Petroleum Industry Common Terms and Symbols, http://www.alken-murray.com/fuel-glossary.htm
- 2. Online Unit Converter, http://www.onlineconversion.com/
- 3. Glossary of Units, http://sizes.com/units/index.php
- 4. McKetta's Encyclopedia of Chemical Processing http://www.tandfonline.com/doi/book/10.1081/E-ECHP#.VElERX10yRs
- 5. Ullmann's Encyclopedia of Industrial Chemistry http://onlinelibrary.wiley.com/book/10.1002/14356007
- 6. Kirk-Othmer Encyclopedia of Chemical Technology, http://o-nlinelibrary.wiley.com.usmalibrary.usma.edu/book/10.1002/04712389
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<u>Checklist</u>
Determination of the number of separation steps required
 For each distillation column, cadets must determine number of trays tray diameter column shell thickness column height
 For each distillation column, cadets must separately determine Condenser area given heat transfer coefficient Reboiler area given heat transfer coefficient Reflux drum size Pump capacities for any required pumps
<pre>Integrated process flow diagram that includes separate working units for each unit including:</pre>
 Include properly formatted CHEMCAD reports for each column: Each column and its supporting equipment must be in a separate appendix (one appendix per column). CHEMCAD spec sheets for condenser, reboiler, reflux drum, distillate pump, reflux pump, and bottom product pump Heat exchanger spec sheets are "tabulated data." Column Profile Tray Compositions Tray Properties Table of tray number, diameter, and P-drop. (Added 4-23-19)
 Safety and Environmental Impact Assessment in an appendix: CHEMCAD environmental report along with discussion of meanin of report contents NFPA 704 fire diamond entries for each stream UFL and LFL for each stream Completed "Safety Design Checklist"
Written design report consistent with Chapter 11 of PTW:

See Chapter 11 for details, especially Table 11-1.
Letter of transmittal addressed to Professor Andrew Biaglow,

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