

Fractional Distillation and GC Analysis of Hydrocarbon Mixtures

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Background

A general chemistry sequence targeted at undergraduate engineering majors was recently launched on our campus. The curriculum for this two-course sequence was designed to better meet the needs of engineering students (a topic recently addressed in this *Journal* [1]) and reflects the reality that these courses are the only college-level chemistry courses the students complete.¹ Consequently, some of the traditional general chemistry topics were abandoned or their treatment curtailed, and some topics historically absent from general chemistry are now covered. To support this new curriculum and to make the material more relevant to this audience, the theme of “Chemistry and the Automobile” is woven into all the topics covered.

At the beginning of the second semester, there is a three-week unit on organic chemistry. Included in this is a discussion of the use of IR and ¹³C NMR spectroscopy to identify organic functional groups. This unit is followed by a second unit on fossil fuels, which discusses how crude oil is converted into gasoline and also covers motor oil, greases, alternative fuels, and petrochemicals. The next unit, synthetic polymers, includes the preparation, structure, different classification schemes, and physical properties of synthetic polymers.

To support this new curriculum, new lab experiments have been developed. The experiment described herein is one of them. It is performed after the unit on organic chemistry has been completed and the students have had some practice interpreting IR and ¹³C NMR spectra, and while the unit on fossil fuels is underway. At this point in the semester, the students have already synthesized an organic compound and performed a simple distillation. They have also been exposed to the operation of a gas chromatograph and have used it to examine the product of an ether synthesis before and after its purification.

In addition to the type of general chemistry sequence described above, this lab is also well suited to an introductory organic chemistry laboratory course. It gives students practice interpreting the IR and ¹³C NMR spectra of organic compounds and illustrates how several pieces of information (IR and ¹³C NMR spectra and experimentally measured boiling points) can be combined to identify a compound. The tandem operation of fractional distillation and GC analysis not only demonstrates how fractional distillation is performed but also illustrates how successful the separation was. Finally, this procedure is used to model, in a very simplified way, the fractional distillation process to which crude petroleum is subjected in the process of obtaining straight-run gasoline, ligroin, kerosene, and other fractions.

Previous Work

Although no previous article in this *Journal* has packaged the themes of hydrocarbons, fractional distillation, and gas

chromatography in quite this way, previous authors have addressed these topics. Gasoline (2–4) has been examined by gas chromatography, as have the accelerants used in arson cases (5). Used engine oil has been subjected to fractional distillation and the fractions examined by IR spectroscopy (6). Technical-grade xylene have been examined by GC and IR (7). The species present in different batches of ligroin have also been examined by GC (8). The hydrocarbon mixture obtained as a result of a chemical reaction has been examined by GC; this includes the products of the dehydration of 2-methyl-2-butanol (9) and the isomerization of xylene by AlCl₃-HCl (10). Hydrocarbon combustion products have been examined by GC (11). Binary phase diagrams of liquid organic species have been generated with the aid of a fractionating column only (12) or coupled with inspection of the fractions by GC (13). Fractionating column efficiency has been explored by GC analysis of distillates (14). Hydrocarbon mixtures have been used to explore GC operating parameters and the Kovat Retention Index System (15–17). Organic unknowns have been used to illustrate various separation and characterization techniques (18, 19).

Summary of the Experiment

The students are advised that they will be working with a three-component mixture consisting of equal volumes of three different liquid hydrocarbons. They are given the information in Table 1 and told that in every case, the mixtures contain

Table 1. Identity of Hydrocarbons in Mixtures

Compound		Accepted bp/ °C
Name	Formula	
Category 1: Alkanes and Cycloalkanes		
n-Pentane	CH ₃ (CH ₂) ₃ CH ₃	36
n-Hexane	CH ₃ (CH ₂) ₄ CH ₃	69
Cyclohexane	C ₆ H ₁₂	80
2,2,4-Trimethylpentane	(CH ₃) ₂ CHCH ₂ C(CH ₃) ₃	98–99
n-Octane	CH ₃ (CH ₂) ₆ CH ₃	125–127
Category 2: Alkenes and Cycloalkenes		
1-Pentene	CH ₃ CH ₂ CH ₂ CH=CH ₂	30
1-Hexene	CH ₃ CH ₂ CH ₂ CH ₂ CH=CH ₂	64
Cyclohexene	C ₆ H ₁₀	83
1-Octene	CH ₃ (CH ₂) ₅ CH=CH ₂	122
cis-Cyclooctene	C ₈ H ₁₄	145
Category 3: Alkyl-Substituted Aromatics		
Toluene	C ₆ H ₅ CH ₃	111
Ethylbenzene	C ₆ H ₅ CH ₂ CH ₃	136
para-Xylene	1,4-C ₆ H ₄ (CH ₃) ₂	138
meta-Xylene	1,3-C ₆ H ₄ (CH ₃) ₂	138–139
ortho-Xylene	1,2-C ₆ H ₄ (CH ₃) ₂	143–145

Table 2. Identity of the Unknown Mixtures and Retention Times of Their Constituents

Mixture	Species					
	Lowest Boiling		Intermediate Boiling		Highest Boiling	
	Compound	R_t /min	Compound	R_t /min	Compound	R_t /min
1	<i>n</i> -Pentane	3.3	Cyclohexene	6.8	<i>ortho</i> -Xylene	11.3
2	<i>n</i> -Hexane	5.1	1-Octene	8.6	Ethylbenzene	10.6
3	Cyclohexane	6.2	Toluene	8.7	<i>cis</i> -Cyclooctene	11.3
4	1-Hexene	5.0	<i>n</i> -Octane	8.7	<i>para</i> -Xylene	10.7
5	1-Pentene	3.2	2,2,4-Trimethylpentane	7.5	<i>meta</i> -Xylene	10.8

one compound from among those listed under category 1 (alkanes and cycloalkanes), one compound from category 2 (alkenes and cycloalkenes), and one compound from category 3 (alkyl-substituted aromatics). Each group is also given a copy of the IR and ^{13}C NMR spectra of the three compounds (unknowns) in their particular mixture.

The students complete this lab in preassigned groups. The fractional distillation apparatus is preassembled for the students and each group performs the fractional distillation in their own hood. Five three-component unknown hydrocarbon mixtures are used and each of the 15 compounds is used only once. The five mixtures used and the retention times of the components are summarized in Table 2. In every case, the difference in retention times between any two species in a mixture is 2.0 minutes or more. The difference in retention times of the lowest- and highest-boiling components in each mixture is 5 minutes or more. For mixture 1, ΔR_t is 8.0 minutes; for mixture 2, ΔR_t is 5.5 minutes; for mixture 3, ΔR_t is 5.1 minutes; for mixture 4, ΔR_t is 5.7 minutes; and for mixture 5, ΔR_t is 7.6 minutes.

The students transfer their unknown mixture (containing 40 mL of each compound) into a 250-mL round-bottom flask. The mixture is heated with the aid of a heating mantle and five fractions are collected. The volumes of fractions 1, 3, and 5 are approximately 30 mL each, and the volumes of fractions 2 and 4 are approximately 10 mL each. Graduated cylinders are used to collect the fractions. The fractionating column is packed with glass helices to a height of six inches. The boiling point range of each fraction is recorded. The composition of fractions 1, 3, and 5 is examined by gas chromatography. The students are not given the retention times of the individual pure liquid hydrocarbons. That is, they are not given the information in Table 2. Small amounts of each group's fractions 1, 3, and 5 are turned in at the end of lab in sealed vials and the gas chromatograms of their samples are obtained for the students outside of lab. The students report the retention times of all the observed species and the approximate percentage composition detected (which are uncorrected for detector response) of each species for each chromatogram.

The hydrocarbons were selected so as to be relatively inexpensive and safe to handle and to have a boiling point that falls between 30 and 150 °C. It was also desirable to have some high-boiling alkanes or cycloalkanes and alkenes or cycloalkenes, so that the aromatic species would not always be the highest-boiling member of the mixture (mixture 3) and the alkane or cycloalkane would not always be the lowest-boiling member of the mixture (mixtures 4 and 5). Benzene

Table 3. Representative GC Results from Student Fractional Distillations

Trial	Fraction 1		Fraction 3		Fraction 5	
	R_t /min	% ^a	R_t /min	% ^a	R_t /min	% ^a
<i>Mixture 1</i>						
1	3.1	92.2	3.3	25.6	—	—
	7.1	7.8	7.4	74.4	—	—
	—	—	—	—	10.8	100.0
2	2.9	93.3	3.4	16.0	—	—
	7.1	6.7	6.5	84.0	6.8	35.6
	—	—	—	—	11.3	64.4
3	3.1	95.4	—	—	—	—
	7.2	4.6	6.8	31.4	—	—
	—	—	11.1	68.6	10.9	100.0
<i>Mixture 2</i>						
1	4.8	91.2	5.4	4.6	—	—
	9.3	3.6	8.3	69.8	8.5	39.3
	11.2	5.2	10.8	25.6	10.5	60.7
2	4.6	98.6	5.3	7.9	—	—
	9.1	1.4	8.4	57.0	8.7	19.5
	—	—	10.6	35.1	10.3	80.5
3	4.6	95.1	5.3	6.9	5.4	2.1
	9.3	2.8	8.3	68.5	8.7	20.7
	11.2	2.1	10.7	24.6	10.4	77.2
<i>Mixture 3</i>						
1	5.9	90.2	6.5	10.2	—	—
	9.1	9.8	8.6	62.0	8.6	9.2
	—	—	11.4	27.8	11.1	90.8
2	6.0	79.3	—	—	—	—
	9.0	20.7	8.6	72.8	9.2	2.7
	—	—	11.5	27.2	10.9	97.3
3	6.1	81.3	5.7	19.0	6.7	1.5
	9.1	18.7	8.7	63.6	8.9	35.9
	—	—	11.1	17.4	11.0	62.6
<i>Mixture 4</i>						
1	4.7	92.8	—	—	—	—
	9.3	3.0	8.6	58.2	8.8	33.0
	11.8	4.2	10.8	41.8	10.7	67.0
2	4.6	89.4	5.4	13.1	—	—
	—	—	8.9	52.3	8.6	24.8
	11.5	10.6	11.0	34.6	10.5	75.2
3	4.7	85.1	5.3	5.7	—	—
	—	—	8.5	55.9	8.6	28.2
	11.0	14.9	10.8	38.4	10.4	71.8
<i>Mixture 5</i>						
1	3.2	100.0	3.6	1.5	—	—
	—	—	7.6	90.5	—	—
	—	—	11.3	8.0	10.8	100.0
2	3.0	84.0	3.3	1.1	—	—
	7.7	5.9	6.8	94.3	7.8	2.1
	10.9	10.1	11.1	4.6	10.6	97.9
3	3.4	53.7	3.5	2.1	—	—
	9.2	17.7	7.0	95.0	7.6	4.3
	11.0	28.6	11.4	2.9	10.4	95.7

^aPercentage of the component detected in indicated fraction.

was not used as a component because of its toxicity. Nonane, decane, cumene, mesitylene, and *tert*-butylbenzene were not included because their boiling points are above 150 °C, and *n*-octane was selected over *n*-heptane to permit the inclusion of an alkane with a high boiling point (above 100 but below 150 °C).

The gas chromatographic separations are performed on a Varian 3350 gas chromatograph equipped with a thermal conductivity detector. A 6-ft \times 1/8-in. stainless steel column packed with Chromosorb 101 (80/100) is used. The operating

conditions are as follows: the initial column temperature of 110 °C with no initial hold time is ramped at a rate of 10 °C/min to a final column temperature of 250 °C followed by a final hold time of 10 min. The helium carrier gas flow rate is 30 mL/min and the sample size is 0.5 μ L of the fraction (undiluted).

Table 3 contains representative GC results from fractional distillations performed by students. The quality of the separations is a function of both the mixture itself and the care with which the students performed the fractional distillation. For mixtures 1 and 5, the separations are generally of a higher quality because there is a wider spread of retention times. Few problems are encountered with any of the mixtures. The gas chromatographic peak obtained for 2,2,4-trimethylpentane (in mixture 5) is always considerably broader than any of the other peaks. The order of elution and the relative percentages of each component in the different fractions are consistent with the boiling points of the species.

In over 85% of cases, all three components of the unknown mixture were correctly identified by the students. In the rest of the cases, one of the three components was misidentified. Distinguishing which xylene is present in a sample is one trouble spot for some students. However, examination of the out-of-plane C–H bending vibrations between 900 and 600 cm^{-1} and the weaker combination and overtone absorptions between 2000 and 1667 cm^{-1} , information the students are given, should allow them to readily distinguish *ortho*-, *meta*-, and *para*-xylene. In addition, correctly determining the number of carbon peaks the xylene molecules should exhibit in their ^{13}C NMR spectra allows them to be distinguished: the *ortho* isomer has four, the *meta* isomer has five, and the *para* isomer has three. Students have also confused 1-octene and *cis*-cyclooctene.

Hazards

All compounds used in this experiment are flammable liquids.² Twelve of them (all but *cis*-cyclooctene, toluene, and 2,2,4-trimethylpentane) are also listed as irritants. Toluene is listed as toxic and 2,2,4-trimethylpentane is listed as corrosive. The entire procedure should be performed in a well-ventilated hood. The students should be cautioned not to distill the mixture to dryness.

Conclusion

Many lessons are learned or reinforced in this lab. The students are given the opportunity to separate a mixture of intermediate complexity by fractional distillation and to examine their level of success in achieving a separation by gas chromatography. They are also given an opportunity to

practice interpreting IR and ^{13}C NMR spectra. Because of the design of the experiment, students come to recognize the value of combining information about a compound from several sources and techniques in order to identify its structure.

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Supplemental Material

Instructions for students are available in this issue of *JCE Online*.

Notes

1. Chemical engineering is not a major on the UM–D campus. The majority of the students performing this lab are mechanical engineering majors.

2. Handling precautions were obtained from the Aldrich Chemical catalog.

Literature Cited

- Hawkes, J. S. *J. Chem. Educ.* **2000**, *77*, 321.
- Nahir, T. M. *J. Chem. Educ.* **1999**, *76*, 1695.
- Tackett, S. L. *J. Chem. Educ.* **1987**, *64*, 1059.
- Cassidy, R. F.; Schuerch, C. J. *J. Chem. Educ.* **1976**, *53*, 51.
- Elder, D. M.; Kildahl, N. K.; Berka, L. H. *J. Chem. Educ.* **1996**, *73*, 675.
- Mashava, P. M.; Alonge, I. E.; Mlenga, F. J. *J. Chem. Educ.* **1989**, *66*, 1042.
- Hanrahan, E. S. *J. Chem. Educ.* **1966**, *43*, 321.
- Haynes, L. W. *J. Chem. Educ.* **1983**, *60*, 234.
- Schimelpfenig, C. W. *J. Chem. Educ.* **1962**, *39*, 310.
- Harbison, K. G. *J. Chem. Educ.* **1970**, *47*, 837.
- Tse, R. S. *J. Chem. Educ.* **1971**, *48*, 550.
- Coleman, H. M. *J. Chem. Educ.* **1967**, *44*, 476.
- Cheng, R.; Hsu, C.; Tsai, Y. *J. Chem. Educ.* **1992**, *69*, 581.
- Ault, A. J. *J. Chem. Educ.* **1964**, *41*, 432.
- Benson, G. A. *J. Chem. Educ.* **1982**, *59*, 344.
- Pacer, R. A. *J. Chem. Educ.* **1976**, *53*, 592.
- Karasek, F. W.; De Decker, E. H.; Tiernay, J. *J. Chem. Educ.* **1974**, *51*, 816.
- Burns, D. S.; Berka, L. H.; Kildahl, N. J. *J. Chem. Educ.* **1993**, *70*, A100.
- O'Hara-Mays, E. P.; Yuen, G. U. *J. Chem. Educ.* **1989**, *66*, 961.