ADIABATIC VACUUM DISTILLATION TO FRACTIONATE
PARAFFIN HYDROCARBON MIXTURES (C_8-C_{14})

By

Dawn L. Mulligan

and

C. T. Stubblefield
NORCUS Faculty Appointee

Separations Chemistry Laboratory
Research and Development
Chemical Processing Division

September, 1969

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

FIRST UNRESTRICTED
DISTRIBUTION MADE JUL 2 '70

ATLANTIC RICHFIELD HANFORD COMPANY
RICHLAND, WASHINGTON

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Key

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U.S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
SUMMARY	2
EQUIPMENT	2
EXPERIMENTAL	3
DISCUSSION	4
CONCLUSIONS	6
FIGURES	8

ABSTRACT

A pure, straight-chain paraffin hydrocarbon mixture (C_8-C_{14}) is the diluent for tri-n-butyl phosphate extractant used in reprocessing spent uranium fuel elements. Precise adiabatic vacuum distillation, following a density fractionation, provided more sensitive qualitative analysis of industrial paraffin mixtures. Trace contaminants were concentrated to enhance further identification. Conclusions were supported by gas-liquid chromatography and ultraviolet spectrophotometry.

ADIABATIC VACUUM DISTILLATION TO FRACTIONATE
PARAFFIN HYDROCARBON MIXTURES (C_8-C_{14})

INTRODUCTION

In the Hanford Purex process of extraction of plutonium, uranium, and neptunium from the fission products, a solvent which is a mixture of normal paraffin hydrocarbons (NPH) serves as a diluent for the nitrates of plutonium, uranium, and neptunium in tri-n-butyl phosphate (TBP). Normal paraffin hydrocarbon is essentially a mixture of the straight-chain paraffins between n-octane and n-tetradecane. The mixing ratios of the hydrocarbons vary considerably with the source of the commercial product; therefore, differences in boiling points and densities are common. The presence of any olefinic and aromatic bonds would be undesirable because the absorption of high-energy radiation would fracture these bonds, leading to polymerization and general degradation in the NPH.

The purpose of this research was to develop a scheme whereby a profile analysis of hydrocarbon composition would be established for any commercial product in the NPH class. Special emphasis was to be placed on establishing the relative amounts of the individual paraffin hydrocarbons, and on isolating and identifying impurities. Careful fractional distillation of NPH was to be used to isolate its constituents; gas-liquid chromatography (GC) and ultraviolet (UV) spectrophotometry were to be used to identify components.

The commercial NPH currently being used in the Hanford Purex process was chosen to serve as a reference working standard for this research; the bulk of the report deals with its profile. The label "NPH-R" is assigned to the reference solvent.

SUMMARY

Purex process solvent (NPH-R) was separated by adiabatic vacuum distillation into its major paraffin components. Olefinic and aromatic components were concentrated in the high-density, high-boiling point fractions; more efficient concentrations of these non-paraffin hydrocarbons were effected by a preliminary density fractionation to remove light components, followed by distillation of the high-density fraction.

Normal paraffin hydrocarbon now in use at Hanford was found to be remarkably pure of branched-chain and non-paraffinic hydrocarbons. The still, when efficiently combined with a density fractionator and GC, was able to concentrate such trace contaminants as much as 25 times.

More complex materials were found to require several successive distillations to isolate even one pure component; however, separation of pure-component mixtures (containing fewer than five components per fraction) was relatively simple and made possible further identification.

EQUIPMENT

Precise fractionation of NPH was carried out in the Auto Annular Teflon Spinning Band Distillation Column (Figure 1, page 8) made by Nester/Faust Manufacturing Corporation of Newark, Delaware. A vacuum jacket and silvering make it an adiabatic still. The spiral band, rotating up to a maximum of 7200 rpm, extends the column's fractionating ability; band rotation also prevents flooding by pumping liquids downward to the pot. At 760 mm Hg, the adiabatic still is said to produce the equivalent of 250 theoretical plates, which enables it to separate liquids whose boiling points differ

by only 0.5 C.

In these experiments, fractional distillation was carried out under reduced pressure. The preset pressure was maintained by the Gilmont Cartesian diver-type vacuum control. A vacuum take-off system on the column allowed for changing the distillate receiver without disturbing equilibrium. Distillate collection was automatically limited to occur only within a pre-selected range of the head temperature, and the collection rate was adjustable.

A rotating evaporator manufactured by Labline Company accomplished preliminary density fractionating. Paraffin components in these and all fractions analyzed were identified on a Perkin-Elmer Model 810 gas chromatograph with flame-ionization detector.

The Beckman DK-2 ultraviolet spectrophotometer was used to search for aromatic structure in the fractions.

EXPERIMENTAL

Normal paraffin hydrocarbon-R (Figure 2, page 9) was first compared with a synthetic standard (Figure 3, page 10) containing equal volumes of the pure normal paraffins C_{10} - C_{14} . Chromatograph oven and detector temperatures were chosen to optimize resolution, symmetry of peaks, and reasonable retention times. All analyses were made on 2- μ l samples.

Major components had been identified before, by gas chromatography; adiabatic distillation was expected to separate trace components.

A 100-ml portion of NPH-R was placed in the 200-ml pot of the adiabatic still and cuts taken at 70 mm Hg until about 50 ml remained in the pot. Half this residue was then further fractionally distilled from the 50-ml pot.

Each fraction was compared with a series of GC standards (Figures 4 through 7, pages 11 through 12); each standard contained equal volumes of three successive normal paraffins.

A second method of fractionating the NPH-R involved concentrating the lightest and heaviest fractions. The original GC pattern Figure 2, page 9, has suggested this procedure. A 500-ml stock sample was distilled in the rotating evaporator at room temperature and a pressure of less than 1 mm Hg. The first distillate, very much enriched in n-octane and n-nonane, was caught in a dry ice-acetone trap; after an hour, the cold trap was replaced with an ordinary condenser and a receiver of 1-liter capacity. Careful distillation was continued in the evaporator until only a few ml of residue remained in the pot. The first and last partial fractions were distilled separately in the adiabatic still, as were 25 ml of the large middle fraction.

In a third method, 500 ml of NPH-R were separated into twenty 25-ml fractions in the Labline evaporator. Gas chromatography was used to select those fractions to be separated further in the adiabatic still. This procedure was attempted with both NPH-R and another, more complex diluent (Figure 8, page 13).

DISCUSSION

The adiabatic still was an effective but demanding research instrument. An extensive preparatory study was necessary to familiarize the operator with controls, the effects of vacuum variations, the necessity for constant attention to the still to prevent flooding, sudden boilups, and inadvertent collection of distillate mixtures during such boilups. The still efficiently separates pure fractions when the distillate can be quickly, accurately analyzed on a research gas

chromatograph; oven temperatures for optimum GC separation of the distillate must be chosen in advance for the components expected. The adiabatic still is limited to 275 C at atmospheric pressure, and boiling points at reduced pressures cannot be accurately estimated before distillation. It is necessary to do a number of detailed preliminary distillations (Method 1) on any new material to become familiar with its major boiling points under vacuum and to learn the best GC conditions for resolving each major component.

The first, simple distillation of NPH-R revealed the presence of previously unsuspected paraffins--C₈, C₉, and possibly C₇ and C₁₄. Before distillation, the quantitative analysis from GC data by graphical means showed the approximate composition of NPH-R to be 10 percent decane, 27 percent undecane, 31 percent dodecane, 28 percent tridecane, and 4 percent tetradecane by volume. Figure 9, Page 14, is the GC pattern of a synthetic sample of NPH-R which was prepared in the laboratory to these concentrations.

Fraction 1 contained both n-octane and n-nonane, both of which "creep" through the still's closed reflux valve at approximately 86 to 98 C. The GC analysis of this mixture at 180 C oven temperature is given in Figure 10, page 15; its GC profile at 120 C compared favorably with Standard B, Figure 4, page 11.

The purest cuts were n-decane at 104 C, n-undecane at 123 C, n-dodecane at 140 C, and n-tridecane at 155 C. Each of the GC patterns for these individual fractions showed a single component.

The GC pattern of the residue at 180 C is shown in Figure 11, page 16; and at 210 C in Figure 12, page 17. Temperature effect is vivid. The comparison of Figure 12 with Standard E, Figure 7, showed that C₁₃ is present. Retention

time for the second peak of this fraction is shown to be displaced somewhat from that of pure n-tetradecane, suggesting the presence of aromatics. A sample was analyzed on the Beckman DK-2 spectrophotometer at 273 mμ with 1,2,3,4-tetrahydronaphthalene serving as a reference. The distillation residue was shown to contain one to two percent aromatics. Apparently this second peak represented n-tetradecane contaminated with aromatics.

Results of the second method, dividing NPH-R into light, middle, and heavyweight fractions by density-vacuum fractionation, indicated an improved concentration of trace components. Aromatics, which had been estimated by UV to be less than 0.2 percent by weight in the original NPH-R, increased to ~5 percent in the heaviest of three density fractions. This mixture yielded a variety of high-boiling, non-paraffinic hydrocarbons when separated in the adiabatic still. The lightest and the middle density fractions both contained less than 0.05 percent aromatics.

Method 3, the distillation of 20 density fractions, did not improve our ability to concentrate trace impurities in NPH-R. It was useful in identifying normal paraffin components of the complex diluent whose original GC profile is shown in Figure 8, page 13. However, further identification of this mixture was not attempted because the majority of its hydrocarbons were clearly *not* paraffinic and therefore not suitable for use in the Purex process.

CONCLUSIONS

The adiabatic still with its spinning band has been found to be an excellent tool for isolating the components of complex hydrocarbons such as NPH. Identification of the individual components may require other instruments; *e.g.*, the gas

chromatograph and ultraviolet spectrophotometer. Trace impurities can be isolated and identified. A GC analysis of the stock material helps determine the method of attack.

Extremely fine cuts can be obtained from the adiabatic still, but it would be very time-consuming to take such fine cuts unnecessarily. Distillation with a good, but less precise, fractionation column could precede the application of the adiabatic still. When as in NPH-R, trace contaminants to be identified can be concentrated by such preliminary work, the still is able to isolate useful quantities of individual fractions from what had been a minute percentage of the original material.

FIGURE 1
AUTO ANNULAR TEFLON SPINNING BAND
DISTILLATION COLUMN (NESTER/FAUST)

NOTE: THE AREA UNDER EACH PEAK IS PROPORTIONAL TO THE VOLUME PERCENT OF THAT COMPONENT BECAUSE STANDARDS WERE MADE BY VOLUME.

FIGURE 2
GC OF NPH-R STOCK

NOTE: THE AREA UNDER EACH PEAK IS PROPORTIONAL TO THE VOLUME PERCENT OF THAT COMPONENT BECAUSE STANDARDS WERE MADE BY VOLUME

FIGURE 3
GC OF NPH (STANDARD A)
[An Equal-Volume Mixture of Paraffins]

NOTE: THE AREA UNDER EACH PEAK IS PROPORTIONAL TO THE VOLUME PERCENT OF THAT COMPONENT BECAUSE STANDARDS WERE MADE BY VOLUME

FIGURE 4

GC OF NPH (STANDARD B)

FIGURE 5

GC OF NPH (STANDARD C)

NOTE: THE AREA UNDER EACH PEAK IS PROPORTIONAL TO THE VOLUME PERCENT OF THAT COMPONENT BECAUSE STANDARDS WERE MADE BY VOLUME

FIGURE 6
GC OF NPH (STANDARD D)

FIGURE 7
GC OF NPH (STANDARD E)

NOTE: THE AREA UNDER EACH PEAK IS PROPORTIONAL TO THE VOLUME PERCENT OF THAT COMPONENT BECAUSE STANDARDS WERE MADE BY VOLUME

FIGURE 8
GC OF STOCK FROM ANOTHER SOURCE

NOTE: THE AREA UNDER EACH PEAK IS PROPORTIONAL TO THE VOLUME PERCENT OF THAT COMPONENT BECAUSE STANDARDS WERE MADE BY VOLUME

FIGURE 9

GC OF NPH SYNTHETIC
[Made to Simulate NPH-R]

NOTE: THE AREA UNDER EACH PEAK IS PROPORTIONAL TO THE VOLUME PERCENT OF THAT COMPONENT BECAUSE STANDARDS WERE MADE BY VOLUME

FIGURE 10

GC OF NPH-R FRACTION 1

NOTE: THE AREA UNDER EACH PEAK IS PROPORTIONAL TO THE VOLUME PERCENT OF THAT COMPONENT BECAUSE STANDARDS WERE MADE BY VOLUME

FIGURE 11
GC OF NPH-R FRACTION 19

NOTE: THE AREA UNDER EACH PEAK IS PROPORTIONAL TO THE VOLUME PERCENT OF THAT COMPONENT BECAUSE STANDARDS WERE MADE BY VOLUME.

FIGURE 12
GC OF NPH-R FRACTION 19

DISTRIBUTION

Number of Copies

82	<u>Atlantic Richfield Hanford Company</u> D. L. Anderson S. J. Beard L. I. Brecke L. E. Bruns M. H. Campbell (10) R. P. Corlew W. M. Harty O. F. Hill G. L. Gurwell R. E. Isaacson L. M. Knights D. E. Larson M. L. Madeen C. W. Malody D. L. Mulligan (10) L. M. Richards G. L. Ritter W. W. Schulz H. P. Shaw A. E. Smith P. W. Smith R. E. Smith R. E. Tomlinson R. L. Walser J. H. Warren N. S. Wing ARHCO Document Control (2) Extra (35)
194	<u>Division of Technical Information Extension</u>
1	<u>Pacific Northwest Laboratory</u> Technical Information Library
5	<u>Prairie View A&M College, Prairie View, Texas</u> C. T. Stubblefield (5)

Number of Copies

14

Richland Operations Office

J. T. Christy

O. J. Elgert

H. E. Parker

R. K. Sharp

Technical Information Library

1

The Northwest College and University
Association for Science

Marge Yesberger