Dimer Acids: Gas Chromatographic Analysis

J.P. NELSON and A.J. MILUN, General Mills Chemicals, Inc., Minneapolis, Minnesota 55413

ABSTRACT

A gas chromatographic method is described for analyzing commercial polymerized fatty acids. The method determines unpolymerized acid, dimerized acid, and trimerized acid. Involved is an esterification to the methyl esters, followed by programed temperature gas liquid chromatography. Several years experience with this analysis has demonstrated its utility as a tool for quality control and research.

INTRODUCTION

Dimer acid is the common name for the commercial product manufactured by polymerizing unsaturated fatty acids, such as tall oil fatty acids. It has utility as a coreactant in the manufacture of polymers and a variety of specialty chemicals. Actually, dimer acid is a complex mixture of structures covering a range of mol wts (1). The predominant species is dicarboxylic, dimerized fatty acid (dimer) with a mol wt averaging ca. 560. Also present are monocarboxylic, unpolymerized acids, (monomer) with mol wts ca. 280 and tricarboxylic, trimerized acids (trimer) with mol wts ca. 840. Properties of products made from dimer acid often depend upon how much of these species are present. Thus, an assay for monomer, dimer, and trimer is very useful for quality control of the dimer acid.

Several publications describe the analysis of polymerized fatty acids. The earlier ones employ time consuming vacuum distillation (2,3). More recent ones use liquid column chromatography and gas liquid chromatography (4-7). The last two measure monomer and dimer concentrations, with trimer calculated by difference. Our GLC procedure has the advantage of measuring all three components directly. In our method, programed temperature GLC is carried out on samples after esterification with boron trifluoride-methanol. We have used this method successfully now over several years for monitoring dimer acid composition.

EXPERIMENTAL PROCEDURES

Reagents and Apparatus

Boron trifluoride-methyl alcohol reagent: 25 g Boron trifluoride is dissolved in 200 g ice-cold absolute methyl alcohol. A detailed description of reagent preparation is presented by Metcalfe, et al. (8).

Silicone septums: Silicone septums are packed loosely in a glass tube and heated at 320 C for 3 days while purging with helium at 20 cc/min. Septums are removed from the tube, cooled and wiped with an absorbant tissue.

Petroleum ether: Petroleum ether is distilled before use, discarding a 10% heel (bp 95-140 F).

Column packing: 100 ml Toluene solution containing 0.6 g SE-30 silicone gum rubber (General Electric Co., Schenectady, N.Y.) is added to a 500 ml round bottom flask containing 10 g 100-120 mesh Gas Chrom Q (Applied Science Laboratories, State College, Pa.). The mixture is degased ca. 1 min with a water aspirator and immediately poured into a Whatman no. 1 filter cone. When filtration stops, the wet packing is transferred to a glass dish heated at 70 C on a hot plate. The dish is heated until no toluene odor remains.

Chromatographic column: A 4 ft length of stainless steel tubing (1/4 in. outside diameter, 22 gauge wall thickness) is filled with the packing. Both ends of the tubing are closed with glass wool. The packed column is cured by heating for 2 days at 350 C while purging with 50 cc/min of helium.

The cured column is installed in the gas chromatograph and heated to 350 C. On cooling the column to 100 C, a recorder baseline shift of 35% or less of the chart width indicates a satisfactory column bleed rate. A shift larger than 35% signifies the column should be cured longer.

The column is heated to 350 C and 5 μliter of a 10% petroleum ether solution of trimer methyl ester is injected 10 times at 10 min intervals. This conditions the column. Then, a sample of distilled dimer methyl ester is analyzed, and the area percent of monomer, dimer, and trimer is calculated. The injections of trimer methyl ester (column conditioning) followed by the analysis of the dimer methyl ester are repeated until the conditioning produces an increase in trimer content of less than 0.1%. At this point, the column is satisfactory for analyses.

Trimer methyl ester for column conditioning: The residue is esterified from a wiped film evaporator distillation of dimer acid with boron trifluoride-methyl alcohol reagent.

Standard monomer methyl ester: Monomer acids were stripped with heat and vacuum from crude polymerized fatty acids and esterified with boron trifluoride-methyl alcohol reagent.

Standard dimer methyl ester: A crude polymerized fatty acid was distilled in a molecular still, and the middle fraction was esterified with methyl alcohol using sulfuric acid catalyst. Area percentage analysis by GLC gave 0.4% monomer, 98.5% dimer, and 1.1% trimer.

Standard trimer methyl ester: A stripped dimer acid was esterified with methyl alcohol and sulfuric acid as the catalyst. A molecular still distillation fraction of this material analyzed 0.4% monomer, 5.7% dimer, and 93.9% trimer.

Methyl behenate solution: 0.4 g Methyl behenate is dissolved in 25 ml petroleum ether.

GLC: Analyses were performed on a model 609 flame ionization gas chromatograph equipped with a model 50 automatic attenuator manufactured by F&M Scientific Corp., Avondale, Pa. Operating conditions were: injection port temperature, 350 C; detector temperature, 370 C; program start, 100 C; program finish, 350 C; program speed, 13 C/min; helium flowrate, 100 cc/min, air flowrate,

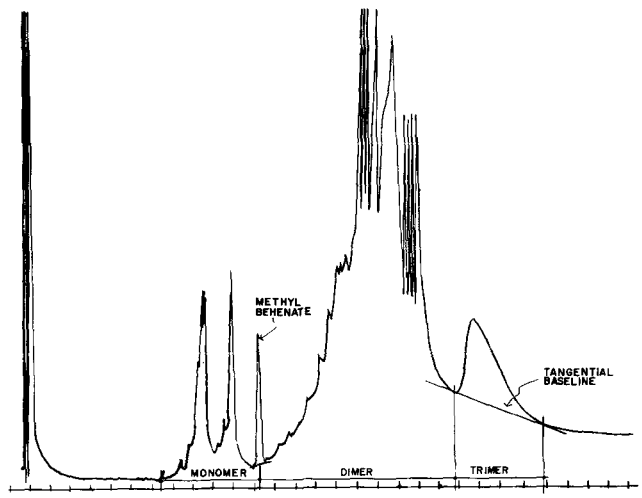

FIG. 1. Gas liquid chromatogram of methyl ester of distilled dimer acid.

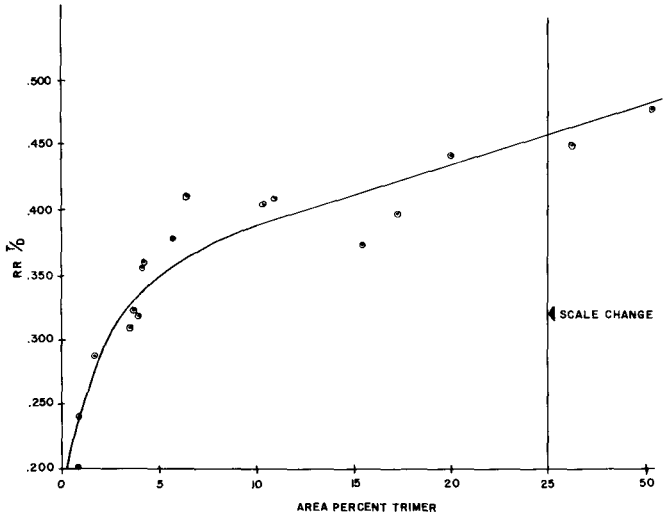

FIG. 2. Calibration curve, relative response of trimer to dimer.

350 cc/min; hydrogen flowrate, 55 cc/min; and chart speed, 20 in./hr.

Peak areas were measured with a model CRS-40 electronic integration system, manufactured by Infotronics Corp., Houston, Tex. In this system, the signal from the gas chromatograph is recorded on magnetic tape. Then, the tape is played back to an electronic integrator which is actuated manually at the beginning and end of each area (see below). The monomer and dimer areas are integrated using the baseline position just before monomer begins eluting. For the trimer areas, only the part appearing above the tangential baseline (Fig. 1) is integrated.

Procedure

Ca. 0.2 g (± 0.01 g) sample is weighed into a 50 ml round bottom flask. 10 ml Boron trifluoride-methyl alcohol reagent is added along with several boiling chips, and an air condenser is attached to the flask. The solution is heated at reflux temperature for 5 min. After cooling the flask under tap water for 1 min, the contents are transferred to a 250 ml separatory funnel. The flask is rinsed once with 10 ml petroleum ether, transferring the rinsings to the same separatory funnel. Then 100 ml distilled water and 40 ml petroleum ether are added to the separatory funnel and the mixture is shaken. After the phases separate, the bottom phase is withdrawn. The top phase is filtered through Whatman no. 1 filter paper filled with anhydrous sodium sulfate. The bottom layer is extracted 2 more times with 50 ml portions of petroleum ether using the same separatory funnel and filter. The combined petroleum ether extracts are reduced to a volume of ca. 2 ml by heating on a steam bath while blowing nitrogen over the surface. This is done by evaporating most of the petroleum ether from the solution in the beaker, then transferring the remaining solution to a 2 dr vial, and completing the evaporation to 2 ml. After adding 1 drop methyl behenate solution to the concentrate, ca. 4 μliter this solution is injected into the gas chromatograph and analyzed under the operating conditions described above.

Calculations: The peak areas, measured by electronic integration, are defined as follows (Fig. 1): monomer area includes all peaks eluted prior to the methyl behenate peak; dimer area includes all peaks eluted after methyl behenate and up to the valley between the dimer and trimer peaks; and trimer area includes all material eluting after the dimer peak. (This is the area over a tangential baseline [Fig. 1]. The limits of the integration area are at the points where the baseline touches the GLC curve at each end of the trimer peak.)

The first step in the calculation corrects peak areas for response differences. This is accomplished by summing all three areas, then calculating area percent trimer. Using Figure 2, the appropriate relative response of trimer is obtained, and this value is divided into the trimer area to yield the corrected trimer area. Next, division of the monomer area by its relative response yields the corrected monomer area. Finally, the following equation calculates the wt percent of monomer, dimer, and trimer:

$$\text{monomer dimer or trimer} = \frac{A_{(M,\ D,\ \text{or}\ T)}}{A_M + A_D + A_T} \times 100,$$

where: M = monomer, D = dimer, T = trimer, A_M = corrected monomer area, A_D = dimer area, and A_T = corrected trimer area.

Calibration: Six known mixtures of standard monomer dimer, and trimer methyl esters were weighed to have the following: 1-20% monomer, 60-90% dimer, and 1-20% trimer.

The mixtures were dissolved in enough distilled petroleum ether to make 10% (w/v) solution, and these were gas chromatographed as described above. Peak areas were measured as described above, and relative response values for monomer and trimer relative to dimer were calculated by the following equation for each mixture:

$$\text{relative response of monomer or trimer} = \frac{A \times W_D}{W \times A_D},$$

where: A = area of monomer or trimer, W = mg monomer or trimer, A_D = area of dimer, and W_D = mg dimer.

The relative response values for monomer were summed and their mean calculated to yield the final relative response for monomer.

For each calibration chromatogram, the area percent trimer was determined and plotted against the calculated trimer relative response to give a calibration curve for trimer similar to the one shown in Figure 2. A computer was used to plot this curve.

DISCUSSION

Good precision and accuracy require careful attention to column performance, because the high operating temperatures cause substrate bleeding. The following precautions enabled us to attain satisfactory results over an extended period: (A) calibration mixtures are chosen with chromatogram shapes similar to those of samples analyzed; (B) baseline shift on column cooling is not allowed to exceed

TABLE I

Analysis Reproducibility

Type of dimer acid	Percent monomer		Percent dimer		Percent trimer	
	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation
Crude	32.1	±0.7	55.6	±0.6	12.3	±0.7
Stripped	6.8	±0.3	77.3	±0.8	15.9	±0.7
Distilled	1.6	±0.2	94.0	±0.6	4.4	±0.2

35% of the chart width, thus keeping substrate bleeding within reasonable limits; (C) a secondary standard (a distilled dimer acid) was analyzed daily. The results [percentages of monomer and trimer] must be within ± 10% relative standard deviation. Incidently, we have observed that when these percentages are too low, the doublet in the main monomer peak has disappeared.); and (D) at least once each week, a calibration mixture containing 15-20% monomer is analyzed and monomer relative response is calculated. (This is necessitited by the gradual decrease in monomer relative response over a period of time.)

The reproducibility of this method has been checked for several years with three different types of dimer acid. Reproducibility data are in Table I.

REFERENCES

1. Cowan, J.C., JAOCS 39:534 (1962).
2. Harrison, S.A., and D.H. Wheeler, J. Amer. Chem. Soc. 76:2379 (1954).
3. Paschke, R.F., J.R. Kerns, and D.H. Wheeler, JAOCS 31:5 (1954).
4. Zielinski, W.L., Jr., Ibid. 41:249 (1964).
5. Payler, R.A.E., R. Feinland, and N.H. Conroy, Anal. Chem. 40:1358 (1968).
6. Arlt, H.G., Jr., U.S. Pat. 3,367,952 (1968).
7. Firestone, D., JAOCS 40:247 (1963).
8. Metcalfe, L.C., and A.A. Schmitz, Anal. Chem. 33:363 (1961).

[Received May 22, 1974]