An Automated Transesterification Technique for Quantitation of Acid Precursors of Ester-Based Oils

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Abstract

A novel automated transesterification (ATE) technique has been developed for the quantitative determination of acid components used in synthesizing ester-based oils. The ATE technique has been successfully tested over a period of more than five years using several commercially available ester-based new and used refrigeration oils and jet oils. In this automated technique, the ester-based oil is transesterified using a commercially available SAP-Ester kit, and the resulting methyl ester mixture is then extracted and analyzed by gas chromatography (GC). During the transesterification, the large number (50–100) of oil-ester components are significantly reduced to a much smaller group of easily resolvable and quantitatable methyl esters (mostly < 6, depending upon the number of acids used).

Introduction

A high-temperature capillary gas chromatographic (GC) analysis of an ester-based oil can provide only qualitative and semiquantitative information about the multiester components. However, no detailed quantitative compositional information can be obtained by a capillary GC analysis regarding individual acids or alcohols (or both) used in synthesizing these multiester components. The most common polyol esters used in commercial applications (e.g., jet engine oils) are synthesized using various acid molecules ranging from mostly C_5 to C_{12}. In order to identify and quantitate the acid molecules of these esters, the ester oils are transesterified using a commercially available BF_3–methanol reagent. During the transesterification, the large number (50–100) of ester components are significantly reduced to a much smaller group of easily resolvable and quantitatable (by GC) methyl esters (mostly < 6, depending upon the number of acids used). The transesterification method in which fatty acid methyl esters (FAMEs) are generated has been in use for the last several years for different applications such as characterizing fats and oils and determining the total fat content in foods. The manufacturer provides the method details along with the SAP-Ester kit (Alltech, Deerfield, IL). In the manual procedure, the reaction mixture is heated/refluxed to ≥ 65°C in an open test tube for approximately 5–10 min, which results in loss of a significant amount of low boiling methyl esters (e.g., C_5 acid methyl esters), and, therefore, the accuracy and reproducibility of the results are jeopardized. The manually operated transesterification method is also described in the published literature (1–3).

A novel automated transesterification (ATE) technique has been developed for quantitative determination of acid substituents of esters present in polyol-based oils (e.g., jet engine oils). The ATE technique has been successfully tested over a period of approximately five years using several commercially available ester-based new and used refrigeration and jet engine oils. In this automated technique, the ester-based oil is transesterified using a SAP-Ester kit, and the resulting methyl-ester mixture is extracted using methylene chloride and then analyzed by GC.

However, the ATE technique has been developed using an HP 7686 PrepStation coupled with an HP gas chromatograph (Agilent Technologies, Palo Alto, CA); it should be adaptable to any commercially available preparative system with similar capabilities. To the best of our knowledge, the ATE technique is the first application of the PrepStation for reaction chemistry in the petroleum industry.

The PrepStation and GC are run unattended. Although it takes approximately 1 h to complete the transesterification and GC analysis of a sample, it requires less than 1 h to prepare the system and the GC vials for 10–15 samples, reagents, and sample solutions. Because the transesterification reactions and extraction of the resulting methyl esters in the ATE technique are performed in a sealed GC vial, losses of low boiling methyl esters are eliminated. Also, the manually operated method requires approximately 1 h/sample.

Additionally, the undesirable/unidentified reaction products detected in the GC analysis of the transesterified methyl esters from the manually operated method are almost completely eliminated in the ATE technique.

Experimental

A typical manually operated transesterification was performed, according to the manufacturer's instructions, in an open 20-mL test tube using one SAP-Ester kit per oil sample. In general, the ester-based oil was saponified by heating/refluxing with methanolic sodium hydroxide. The resulting mixture was then treated with a specified amount of a boron trifluoride–methanol reagent. Finally, the FAMEs were extracted using a nonaqueous solvent (e.g., methylene chloride or petroleum ether), dried, and then analyzed using a capillary GC. Several transesterification reagents, which could be used for so-called simplified procedures(4), are available from Alltech. One of the alternative derivatization reagents was trimethyl-sulfonium hydroxide, and the major advantage of this reagent is that the derivatization can be performed in a single fast reaction step. The transesterification method developed for the PrepStation is given in Table I. It is highly recommended that the PrepStation is primed just before its use. The prime method given in Table II worked well to clean up the system. Some minor differences between the two transesterification procedures are given in Table III.

The resulting methyl ester mixtures were analyzed by an Agilent GC model HP-5890 Series II equipped with an oncolumn injector, automatic sampler (HP-7673), and flame ionization detector (FID). Although one of the Carbowax-type capillary columns is most commonly used for FAMEs analysis, we found that the DB1-type column resolved FAMEs equally well. Additionally, we found the MXT-1 column to be highly suitable for FAMEs analysis, and it was employed under the operating conditions given in Table IV.

The GC method (described previously) required 38 min/sample to complete the separation and quantitation of the methyl ester components. The method is fully automated and requires no additional analyst time.

The HP-7886 PrepStation and the HP-5890 GC were coupled through HP Bench Supervisor software (Agilent Technologies). Bench Supervisor was used to create a fully automated lab bench. Using the methods from the instruments (PrepStation and GC) to build a Bench Supervisor method, samples could be automatically processed and analyzed from start to finish. The Bench Supervisor software tells each instrument when to run a particular method. Also, the Bench Supervisor software tracks the movement and location of all vials, data files, and other resources needed by each instrument method. Figure 1 displays the Bench Supervisor software system screen as it looks when ready for use.

The automated technique provided highly reproducible and accurate quantitation of acid components of the esters because all transesterification steps were performed in a sealed GC vial.

The PrepStation and GC were run unattended. Although it took approximately 1 h to complete the transesterification and GC analysis of a sample, it required less than 1 h to prepare the system and the GC vials for 10–15 samples, reagents, and sample solutions. The manually operated method required

Table I. Transesterification Method for the PrepStation

PrepStation method: PREFAME.TSP 30-min run

1. Fatty acid methyl ester method
2. For Alltech SAP-Ester kit #18026
3. Preheat at 90°C
4. Rinse system with 5.00 mL methanol using entire system flow path
5. Aspirate 0.200 mL from NaOH–MeOH
6. Transfer 0.015 mL from neat sample to oil sample (solution) and 0.235 mL from sample loop
7. Mix oil sample at medium speed for 0.30 min
8. Evaporate oil sample at 90°C for 3.00 min
9. Mix oil sample at medium speed for 0.30 min
10. Transfer 0.300 mL from BF_3–MeOH to oil sample
11. Mix oil sample at medium speed for 0.30 min
12. Evaporate oil sample at 90°C for 3.00 min
13. Preheat off
14. Rinse system with 2.500 mL water using aspirate flow path
15. Transfer 0.400 mL from 50% sat'd NaCl to oil sample
16. Rinse system with 2.500 mL water using aspirate flow path
17. Rinse system with 2.500 mL methanol using aspirate flow path
18. Rinse system with 5.000 mL of $MeCl_2$ using entire system flow path
19. Dispense 0.800 mL of $MeCl_2$ into oil sample
20. Mix oil sample at medium speed for 0.50 min
21. Wait 2.00 min
22. Sample ready oil sample
23. Rinse system with 5.000 mL methanol using entire system flow path

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Vial/cartridge information table

Name	Type	Number of uses
Oil sample	Empty vial	1
BF_3–MeOH	Reagent	3
50% sat'd aq. NaCl	Reagent	3
Neat sample	sample	N/A
NaOH–MeOH	Reagent	3

Solvent information

Station 1	SPE* module	2.5-mL syringe	
Station	**Port**	**Solvent**	**Size**
Station 1	1	Water	500.0 mL
Station 1	2	Methanol	500.0 mL
Station 1	3	Methylene chloride	500.0 mL
Station 1	–	Air	N/A

* SPE, solid-phase extraction.

approximately 1 h/sample. One SAP-Ester kit was used per oil sample in the manually operated method, whereas in the automated technique, 10–15 oil samples could be transesterified using only one SAP kit.

In addition to analysis speed and reproducibility and accuracy of the results, the undesirable reaction products detected in the GC traces of the transesterified methyl-ester mixtures from the manually operated method were almost completely eliminated in the automated technique. Because the automated technique provided highly reproducible and accurate quantitation of acid components of the ester-based oils, it was well suited to replace the manually operated transesterification method.

Results and Discussion

The GC traces are very useful for quickly obtaining the qualitative and semiquantitative compositional information on a petroleum sample. Depending upon the type of polyol and the number of acids used in the preparation of the polyol-based ester product, the number of ester components could be very large. Because 50–100 similar ester components are likely to be present in a synthetic polyol-based ester oil, it becomes almost impossible to obtain quantitative compositional information from its GC analysis. A GC trace for a typical commercial jet oil is given in Figure 2.

However, if the complex ester mixture was transesterified into the methyl esters, the GC analysis could provide quantitative information about the acids used in synthesizing the ester-based oil. A GC trace for the transesterified jet oil is given in Figure 3.

In order to obtain the quantitative composition of the acid precursors from a GC trace (Figure 3), the FID mass response for their methyl esters was determined using the same GC system. The acid distribution can be determined accurately by multiplying the peak areas with their respective response factors (RF). Given are the FID mass RFs for the methyl esters of C_5 to C_{14} acids: for acid I-C_5, the response factor was 0.72; n-C_5, 0.72; n-C_6, 0.78; n-C_7, 0.85; n-C_8, 0.96; n-C_9, 0.96; n-C_{10}, 0.96; and n-C_{14}, 1.00.

As shown, there are considerable variations of the GC-response factors (0.72–1.00) for the C_5 to C_{14} methyl esters. It is, therefore, essential for the quantitative analyses that the GC peak area be corrected accordingly.

In order to establish the repeatability of the automated technique, a typical polyol-based ester base stock used in the jet engine oils was transesterified using the automated technique, as well as by the manually operated method. Results (GC peak area percents) for the acid precursors (C_5 to C_{10} acids) of an ester base stock, along with those of a commercial jet engine oil are given in Table V.

As shown in the Table, the automated technique gave highly reproducible results that were similar to those obtained by the carefully operated manual method. Also, the data given previously clearly demonstrated that approximately 15% of the low boiling acid precursors (i-C_5 and n-C_5) were lost

Table II. Prime Method for the Cleaning Up of the Entire Flow Path for the PrepStation

PrepStation method:	**PRIME.TSP**		**12-min run**

1. Rinse system with 5.00 mL methanol using entire system flow path
2. Rinse system with 5.00 mL water using entire system flow path
3. Rinse system with 10.00 mL methanol using entire system flow path
4. Rinse system with 5.00 mL methylene chloride using entire system flow path

—END—

Solvent information

Station 1	SPE module	2.5-mL syringe	
Station	**Port**	**Solvent**	**Size**
Station 1	1	Water	500.0 mL
Station 1	2	Methanol	500.0 mL
Station 1	3	Methylene chloride	500.0 mL
Station 1	–	Air	N/A

Table III. Comparison between Automated and Manual Transesterification Techniques

Automated technique	Manual technique
Performed in a sealed GC vial	Performed in an open test tube
0.015-mL oil sample used	0.1–0.2-g oil sample used
0.2 mL 0.5N NaOH–CH_3OH	4 mL 0.5N NaOH–CH_3OH
Mixture heated to 90°C	Mixture heated to ≥ 65°C
0.3 mL BF_3–CH_3OH	5 mL BF_3–CH_3OH
0.4 mL 50% sat'd aqueous NaCl	5 mL sat'd aqueous NaCl
0.8 mL methylene chloride	5 mL petroleum ether
Extract not dried	Extract dried over anhydrous sodium sulfate

Table IV. GC Operating Conditions

Column	MXT-1, 15- × 0.53-mm i.d., 0.15-µm film thickness
Oven temperature	40°C to 400°C at 10°C/min, final time = 2 min
Injector	Oncolumn, 50°C to 400°C at 60°C/min, final time = 100 min
Detector temperature	400°C
Injection size	0.1 µL
Carrier gas	helium, flow 2 mL/min, constant flow

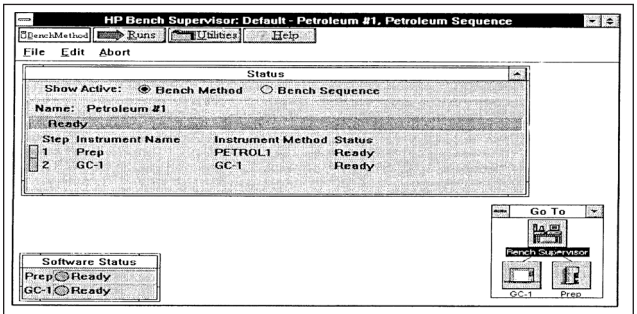

Figure 1. HP Bench Supervisor screen display.

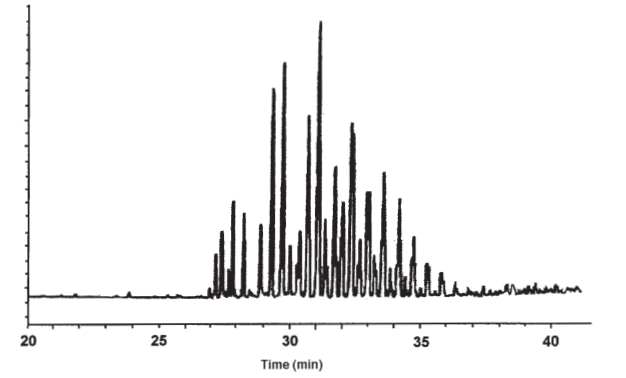

Figure 2. A GC trace of commercial jet engine oil.

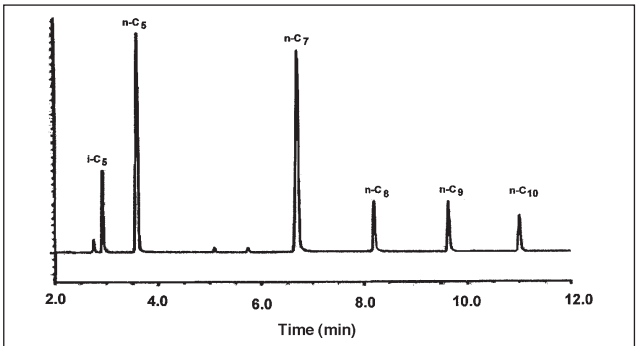

Figure 3. A GC trace of methyl esters of the acid precursors.

in the manually operated method. Additionally, the undesirable reaction products detected in the GC analysis of the transesterified methyl-esters mixture from the manually operated method (GC trace not shown) were minimized in the ATE technique.

Conclusion

An automated and cost-effective transesterification GC technique has been developed for the accurate determination of the acid components of ester-based oils. To the best of our knowledge, this technique is a first application of the PrepStation for reaction chemistry in the petroleum industry. A similar technique can also be developed for the quantitation of phenol precursors used in synthesizing tricresyl-phosphate-type ester additives.

Table V. GC Peak Area Percents of Acid Precursors of Ester-Based Base Stocks

	$i\text{-}C_5$ (3.7)*	$n\text{-}C_5$ (4.30)*	$n\text{-}C_7$ (7.0)*	$n\text{-}C_8$ (8.3)*	$n\text{-}C_9$ (9.7)*	$n\text{-}C_{10}$ (10.9)*	Others
Ester-based base stock							
Automated technique							
	8.1	32.2	38.6	7.7	7.5	5.4	0.5
	8.5	32.5	37.5	7.5	7.4	5.4	1.2
	8.1	32.1	37.8	7.6	7.6	5.6	1.2
	8.2	32.3	38.1	7.7	7.7	5.5	0.6
	8.4	32.3	37.3	7.6	7.4	5.4	1.5
	8.4	32.1	37.5	7.8	7.7	5.3	1.4
Ave.	8.3 ± 0.2	32.3 ± 0.2	37.8 ± 0.5	7.7 ± 0.1	7.6 ± 0.1	5.4 ± 0.1	1.1 ± 0.4
RSD	2.4	0.6	1.3	1.3	1.3	1.9	36.4
Manual technique							
	7.0	28.4	40.0	8.2	8.6	6.1	1.7
Ester-based jet engine oil							
Automated technique							
	9.3	32.0	37.5	6.9	9.3	5.0	0
Manual technique							
	7.8	27.6	39.2	7.6	10.1	5.7	2.4

* In parentheses are the GC retention times (under the previously mentioned GC conditions) in minutes for the methyl esters.

References

1. AOCS. *Official Methods and Recommended Practices of the AOCS*, 5th ed. American Oil Chemists Society, Champaign, IL, 1998.
2. Official Methods of Analysis, 17th ed. AOAC International, Gaithersburg, MD, 2000.
3. European Pharmacopoeia Commission. "Method 2001". In *European Pharmacopoeia*, 4th ed. European Pharmacopoeia Commission, Strasbourg, France, 2001, p. 1352.
4. K.S. Liu. Preparation of fatty acid methyl esters for gas-chromatographic analysis of lipids in biological materials. *JAOCS* **71(11):** 1179 (1994).

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