

# Application of Pressure-Controlled Advanced Distillation Curve Analysis: Virgin and Waste Oils

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**ABSTRACT:** One of the most important properties measured for liquid fuels is the volatility, usually expressed by the distillation curve. In previous work, we introduced the composition-explicit or advanced distillation curve (ADC) metrology, which we have applied to a wide variety of liquid fuels including biodiesel fuels. Application of this method to high-boiling-point fluids such as oils has required the addition of an inert-gas purge in the apparatus. Despite this precaution, there is clear evidence of thermal decomposition or polymerization at high distillation temperatures. To address this complication, a low-pressure version of the ADC was introduced. In this work, we have applied the low-pressure ADC method to the study of virgin and waste engine (motor) oils (5W-30, 10W-30, 20W-50), reclaimed comingled oil, reclaimed cutting oil, and used transformer oil. The results parallel similar measurements performed at atmospheric pressure, but with little evidence of chemical decomposition.

## INTRODUCTION

In the United States alone, over 200 million gallons (approximately  $7.6 \times 10^8$  L) of used lubrication oil are improperly disposed each year.<sup>1</sup> The oil from even one improperly disposed automotive oil change (approximately 4–5 L) can contaminate up to one million gallons of fresh water.<sup>2</sup> Proper collection, storage, and reuse of used oils is of great environmental importance. In addition to recovery efforts, the chemical energy contained within the used oils is becoming apparent, and efforts are being made to convert these used oils into usable transportation fuels. Similarly to the refining of crude oils, more efficient methods are being developed that can, through pyrolysis, effectively convert the heavy components contained within these used oils into shorter molecules typical of those found in diesel and gasoline fuels.<sup>3–5</sup> In addition to these efforts to convert used oils into transportation fuels, many reclaimed used oil streams are being directly combusted in boilers for power generation. Thus, effective collection and subsequent efficient refining of these fluids is important because such processes can remove contaminants from the environment while providing an additional product or fuel stream.

The majority of used lubricant oil generated is automotive crankcase oil (sometimes called drain oil). This oil can be recycled and treated for subsequent use by re-refining, although this is a multistep, complex, and expensive process.<sup>6</sup> First, the lightweight impurities are removed, and then middle-weight impurities (such as components of gasoline) are removed by fuel stripping. Next, vacuum distillation is employed to separate the heaviest impurities. The cleaned oil is then hydrotreated, and an appropriate additive package is added to complete the re-refining process. The totality of these individual steps results in a very energy-intensive process, and any improvements in either the process or product are critical to ensuring the viability and economic acceptability of re-refining. The re-refined oil must meet the same specifications as virgin oil for the re-refined product to be of value. A number of standards and specifications are used to ensure the quality of lubricating oils; among them is ASTM D-4485,<sup>7</sup> which incorporates by

reference other ASTM methods (such as flash and fire point, ASTM D-92;<sup>8</sup> corrosivity, ASTM D-130;<sup>9</sup> and foaming tendency, ASTM D-892).<sup>10</sup> The boiling behavior (i.e., the distillation curve) of the oil is typically determined by ASTM D-2887, a gas chromatographic method that calculates the distillation-curve boiling temperatures based on standardized retention times,<sup>11</sup> but this is a poor substitute for a direct measurement. The D-2887 method has a stated uncertainty of up to 11.8 °C in the determination of the boiling points near the end of the distillation curve. This large uncertainty in temperature and the ambiguity in the pressure at which the measurement is performed makes the boiling behavior for crankcase oil calculated with D-2887 unsuitable for fundamental applications such as equation-of-state development. This disconnect with theory is a major disadvantage, because all process design simulations require an equation of state for the fluid being treated, even if that fluid is a highly complex mixture.

The distillation curve is one of the most important properties that can be measured for any complex fluid, because it is the only practical avenue to assess the volatility or the vapor–liquid equilibrium (VLE).<sup>12–14</sup> Moreover, it can be directly correlated to many engine operating parameters.<sup>15–20</sup> Consequently, a method for measuring the distillation curve of automotive oils, lubricant oils, and other heavy oils with a much lower uncertainty is desirable.

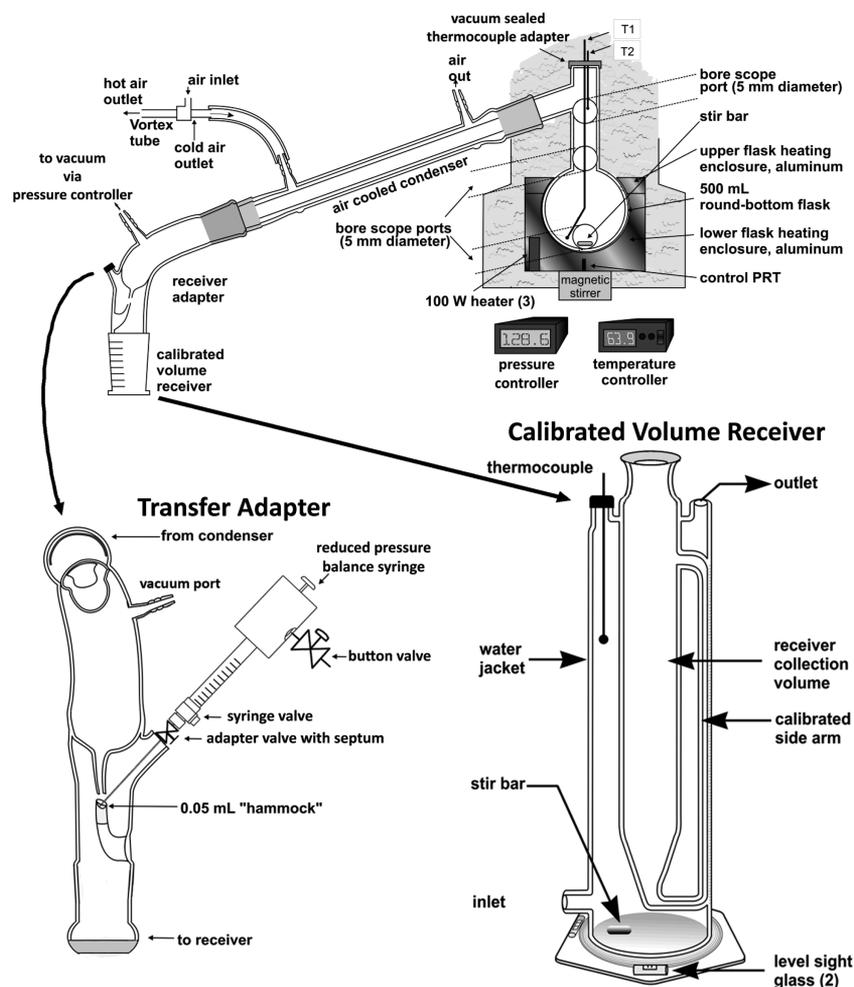
In earlier work, we described a method and apparatus for an advanced distillation curve (ADC) measurement that is especially applicable to the characterization of complex fluids such as fuels and lubricants.<sup>21–23</sup> This method is a significant improvement over current approaches,<sup>24</sup> featuring (1) a composition-explicit data channel for each distillate fraction

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**Figure 1.** Schematic diagram of the ADC apparatus used for the measurement of reduced-pressure distillation curves.

(for both qualitative and quantitative analysis);<sup>25–28</sup> (2) temperature measurements that are true thermodynamic state points that can be modeled with an equation of state;<sup>29–34</sup> (3) temperature, volume, and pressure measurements of low uncertainty suitable for equation of state development; (4) consistency with a century of historical data; (5) an assessment of the energy content of each distillate fraction;<sup>35</sup> (6) trace chemical analysis of each distillate fraction;<sup>36,37</sup> and (7) a corrosivity assessment of each distillate fraction.<sup>38–40</sup> We have applied this metrology to azeotropes, gasolines, aviation fuels, diesel fuels, crude oils, and rocket propellants.<sup>36,37,41–64</sup>

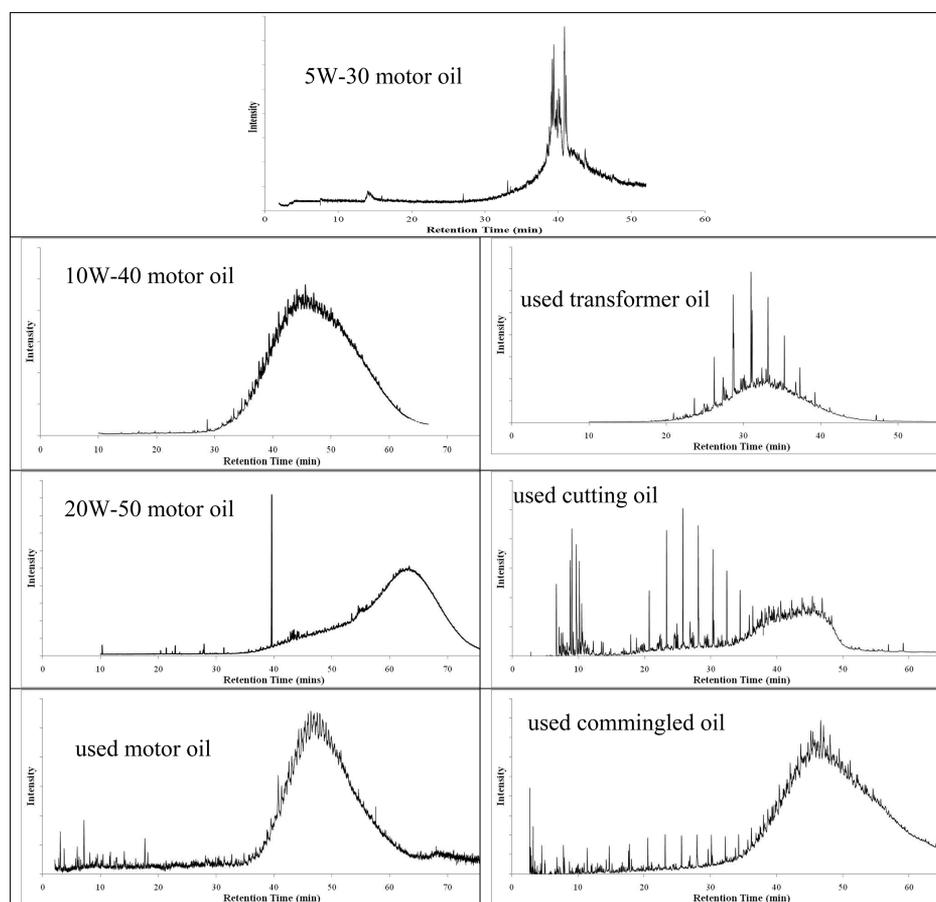
In subsequent development work, we extended the applicability of this method to heavier fluids (such as heavy crude oils) and thermally unstable fluids by introducing a reduced-pressure ADC apparatus.<sup>65</sup> The new reduced-pressure apparatus and method provides temperature and volume measurements with precision comparable to the atmospheric-pressure apparatus while allowing for measurement and control of the pressure down to 0.1 kPa. Moreover, the reduced-pressure apparatus also provides a composition-explicit data channel with a pressure-balanced sampling syringe that was introduced concurrently.<sup>66</sup> Thus, the changing composition of the fluid can be measured during the distillation curve measurements even at pressures as low as 0.1 kPa. The low-pressure apparatus is shown schematically in Figure 1. Reducing the pressure of the measurement lowers the boiling temperatures of the mixture components and, thereby, shifts the distillation curve to lower

temperatures. Assuming that the composition remains unchanged (i.e., no thermal decomposition occurs), the reduced-pressure distillation curve will typically have little or no modification in shape compared to the higher-pressure distillation curve. The subtle sigmoidal character caused by a complex mixture will simply be shifted to lower temperatures.

## EXPERIMENTAL DETAILS

The *n*-hexane used as a solvent in this work was obtained from a commercial supplier and was analyzed by gas chromatography (30-m capillary column of 5% phenyl/95% dimethyl polysiloxane having a thickness of 1  $\mu\text{m}$ , with a temperature program from 50 to 170  $^{\circ}\text{C}$  at a heating rate of 5  $^{\circ}\text{C min}^{-1}$ ) with flame ionization detection and mass spectrometric detection.<sup>67,68</sup> These analyses revealed the purity to be approximately 99%, and the fluid was used without further purification.

Three commercially available virgin (unused) motor oils were investigated in the current study and consisted of three different viscosity ranges: SW-30, 10W-40, and 20W-50. No synthetic motor oils were selected for this work; synthetic fluids are far simpler in composition (fewer components with similar properties) than lubricants prepared from petroleum stocks. The SW-30 sample was a typical winter motor oil, the 10W-40 sample was a typical summer oil, and the 20W-50 sample was a specialty oil used in high-performance racing engines and also in worn engines with larger-than-optimal surface clearances. The used oils investigated in this study consisted of used motor



**Figure 2.** Chromatograms of the neat used and unused oils investigated in this study. Details of the chromatography are discussed in the text.

oil (crankcase oil from motor vehicles), used transformer oil, used cutting oil (from metal machining operations), and a sample of commingled oil (miscellaneous lubricating and penetrating oils) that were obtained as process streams from a commercial oil re-refining facility. The re-refiner typically uses vacuum distillation as a means of clean up and segregates process streams to facilitate that process. All the lubricant oils (new and old) were translucent but dark in color, with the viscosity of typical oils, and each consisted of a single phase. The used transformer and cutting oils had amber casts but were nevertheless translucent. Like the used lubricant oils, they were single-phase fluids, but both were noticeably less viscous than the used lubricant oil.

The oils were examined by high-temperature gas chromatography with flame ionization detection (GC-FID) and mass spectrometric detection (GC-MS). The samples were analyzed on a 30 m  $\times$  0.25 mm i.d. capillary column with a special high-temperature-resistant 0.1- $\mu$ m coating of dimethyl polysiloxane. Initially, the temperature was maintained isothermally at 50  $^{\circ}$ C for 5 min, followed by a 5  $^{\circ}$ C  $\text{min}^{-1}$  ramp to 400  $^{\circ}$ C. The column was then held at 400  $^{\circ}$ C for 10 min. An inlet temperature of 350  $^{\circ}$ C, a constant head pressure of 69 kPa, and a split injection with a 10:1 split ratio were applied. The high-temperature GC program allowed for the elution of large molecules with low volatility. The chromatograms for all of the neat fluids can be seen in Figure 2. These analyses revealed the expected cluster of hydrocarbon compounds having the usual Gaussian-like distribution (sometimes called an unresolved envelope). It is possible to “stretch” out each of the Gaussian

distributions and, in fact, assign many of the peaks. Familiar families include normal and branched hydrocarbons, mono-nuclear and polynuclear aromatics, esters, and naphthenes. The composition of the virgin oils consisted of branched and linear hydrocarbons, with approximately 10% ester, although the precise formulation is proprietary. Low concentrations of antioxidants (alkyl-substituted phenols) were noted as well. Somewhat unusual is the chromatogram for the sample of 20W-50 oil, which shows a singular large, sharp peak at a retention time of approximately 39 min. This is a proprietary antioxidant compound.<sup>69</sup> The used crankcase oil showed an early-eluting suite of components that are typical in that they result from contamination by engine blow-by. This contamination consists of the heavier constituents of gasoline (primarily alkyl aromatics) and moisture. In addition to this early suite, contaminants included some noticeable oxidation products (acetaldehyde, butanal, benzaldehyde, and benzoic acid) and also ethylene glycol. The latter contaminant, from coolant, is a result of engine failure. We note that the used crankcase oil had a separate water phase in equilibrium comprising approximately 5% of the total volume of this fluid. Only traces of water were actually dissolved or entrained in the oil phase. The used transformer oil consisted of linear and branched hydrocarbons, with many of the expected polyethers. The used commingled oil was similar to the used crankcase oil, with many light contaminants (more of which were branched aliphatics rather than alkyl aromatics),

**Reduced-Pressure ADC.** The experimental apparatus (Figure 1) and procedure for the reduced-pressure advanced

distillation curve were previously reviewed in detailed elsewhere;<sup>65</sup> therefore, only new features and details pertinent to this study are provided herein. Although the apparatus for reduced-pressure ADC is substantially the same as that used in prior work, we have incorporated the concept of CO<sub>2</sub> control for added safety in the event of an upset condition leading to unexpected venting to atmospheric pressure. This was done by adding a reservoir of CO<sub>2</sub> to the vent line of the low-pressure controller such that a nonflammable, nonoxidizing atmosphere is aspirated into the apparatus during pressure control. The CO<sub>2</sub> in this reservoir was continually replenished during a measurement, to ensure the absence of air. Moreover, in the unlikely occurrence of a catastrophic venting, only nonflammable, nonoxidizing gas would be aspirated into the apparatus. The volume of available CO<sub>2</sub> during operation was approximately 3 times the internal volume of the ADC apparatus.

For each experiment with the lubricant oils, 100 mL of the sample was placed into the boiling flask with a 100 mL pipet. The thermocouples were then inserted into the proper locations to monitor  $T_k$ , the temperature in the fluid, and  $T_b$ , the temperature at the bottom of the takeoff position in the distillation head. As with all ADC measurements, the  $T_b$  measurement is used primarily as a diagnostic. The combined uncertainty in the thermocouple measurements was 3 °C. This uncertainty estimate contains the repeatability of the measurements and the calibration of the thermocouples. Note that this uncertainty is higher than that of ADC measurements performed at atmospheric pressure and is the result of the higher variability in measured temperatures at the controlled low pressures. Temperature measurements made at atmospheric pressure are typically performed in less than 1 h, a period of time too short to affect the measured pressure appreciably.

Once the apparatus was prepared with sample, enclosure heating was commenced with a four-step program based on a previously measured distillation curve or on the basis of the expected volatility following the gas chromatographic analysis of the neat fluid. The corresponding fluid and vapor temperatures were recorded at predetermined distilled volume fractions, which also included the initial boiling behavior of the fluid. Distillate volume measurements were made in a level-stabilized receiver.

Reduced-pressure distillations of the used cutting oil and the used commingled oil were performed at 20 kPa, whereas the distillations of the remaining fluids were performed at 1 kPa. The difference in the experimental pressure conditions was chosen with consideration of the difference in initial volatility of the two sets of fluids. The used cutting and commingled oils contained a much higher content of volatile components and

**Table 1. Initial Boiling Temperature Data for the Used and Unused Oils Measured at Reduced Pressure<sup>a,b</sup>**

	IBT (°C)
SW-30 (1 kPa)	233.0
10W-40 (1 kPa)	247.5
20W-50 (1 kPa)	269.4
used motor oil (1 kPa)	131.5
used transformer oil (1 kPa)	165.8
used cutting oil (20 kPa)	73.1
used commingled oil (20 kPa)	94.0

<sup>a</sup>Pressures at which measurements were made in parentheses.

<sup>b</sup>Uncertainty discussed in the text.

would be expected to undergo rapid vaporization at room temperature when exposed to pressures as low as 1 kPa, so a higher operating pressure was used. In fact, it can be clearly seen from the chromatograms of the neat fluids (Figure 2) that the used cutting and commingled oils did, in fact, have a much higher concentration of light, more volatile molecules, eluting at much lower retention times than the other lubricant oils.

For each of the fluids, sample aliquots were withdrawn for selected distillate volume fractions to provide the composition channel information as an accompaniment to the temperature data grid of the distillation curves. To accomplish this, aliquots of approximately 7 μL of emergent fluid were withdrawn from

**Table 2. Distillation Curve Data Recorded at 1 kPa for Unused Motor Oils and Waste Motor and Transformer Oils<sup>a</sup>**

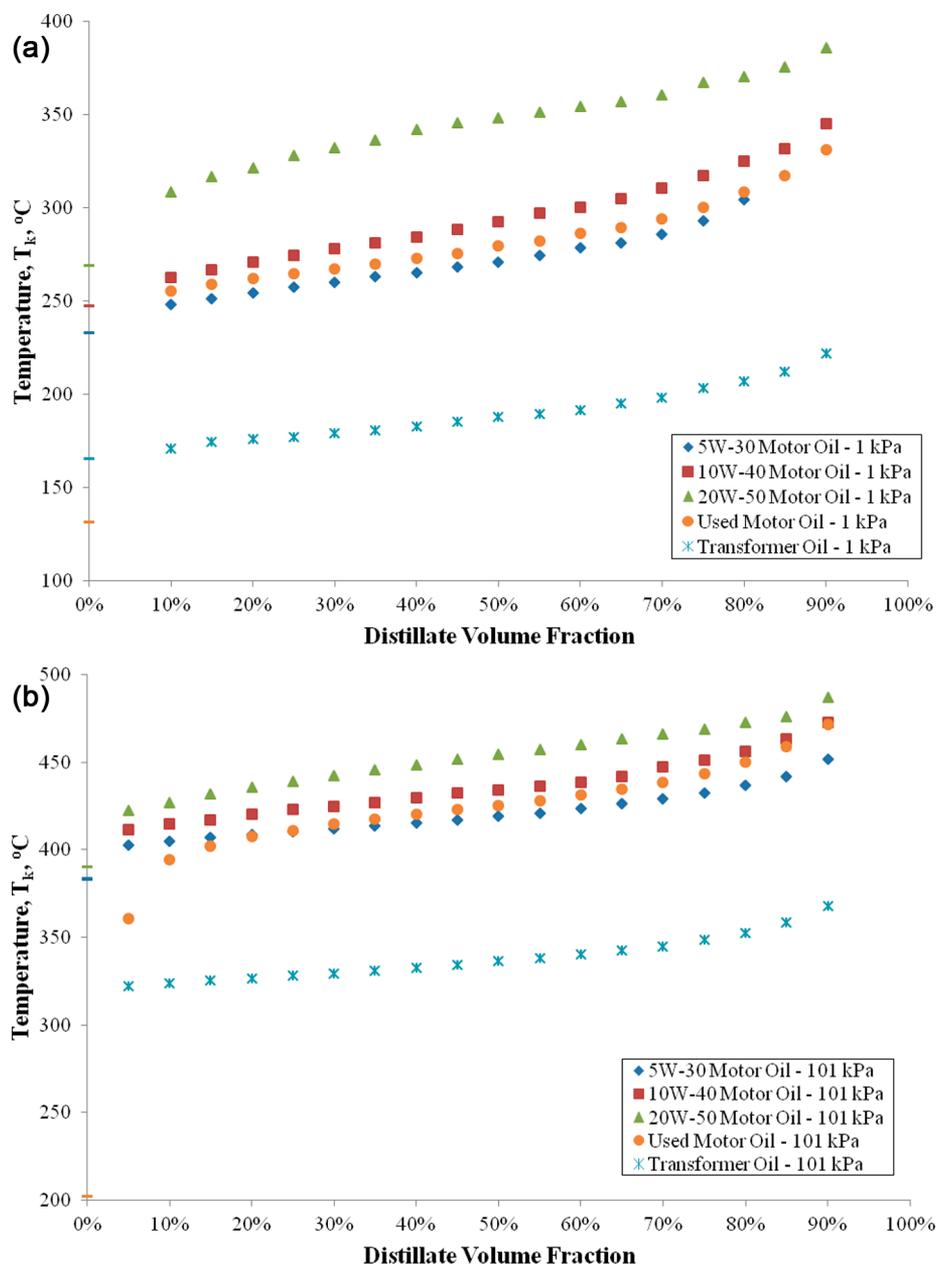
vol fraction (%)	$T_k$ (°C)				
	SW-30	10W-40	20W-50	used motor oil	used transformer oil
0.025	238.1	255.7	284.3	188.3	166.8
10.0	248.4	262.9	308.7	255.5	171.0
15.0	251.6	267.0	316.6	259.4	174.6
20.0	254.3	271.0	321.4	262.2	176.2
25.0	257.7	274.5	328.2	265.0	177.1
30.0	260.3	278.4	332.5	267.4	179.4
35.0	263.1	281.5	336.3	270.2	180.7
40.0	265.4	284.2	342.1	272.9	183.0
45.0	268.6	288.7	345.5	275.5	185.5
50.0	271.2	292.5	348.3	279.5	187.8
55.0	274.8	297.3	351.6	282.5	189.5
60.0	278.9	300.5	354.3	286.5	191.6
65.0	281.3	305.0	357.3	289.5	195.4
70.0	286.1	310.7	360.9	294.2	198.4
75.0	293.0	317.1	367.4	300.5	203.5
80.0	304.7	325.2	370.4	308.8	207.0
85.0	317.5	332.0	375.8	317.4	212.3
90.0		345.0	386.0	331.5	222.0

<sup>a</sup>Uncertainty discussed in the text.

**Table 3. Distillation Curve Data for Used Cutting Oil and Used Commingled Oil Recorded at a Pressure of 20 kPa<sup>a</sup>**

vol fraction (%)	$T_k$ (°C)	
	used cutting oil	used commingled oil
0.025	85.2	104.0
10.0	230.1	115.0
15.0	249.9	220.0
20.0	273.5	339.1
25.0	292.4	346.7
30.0	303.2	350.0
35.0	311.3	353.0
40.0	319.7	356.0
45.0	325.9	361.5
50.0	333.0	364.5
55.0	339.3	368.0
60.0	344.0	373.2
65.0	348.4	381.5
70.0	352.0	389.5
75.0	361.5	399.0
80.0	372.6	408.0
85.0	391.5	-

<sup>a</sup>Uncertainty discussed in the text.



**Figure 3.** Distillation curves of the used and unused motor oils and the used transformer oil for data collected (a) at a pressure of 1 kPa and (b) at local atmospheric pressure (approximately 83 kPa) and adjusted to standard atmospheric pressure by use of the modified Sydney Young equation. The uncertainties of the measurements are discussed in the text.

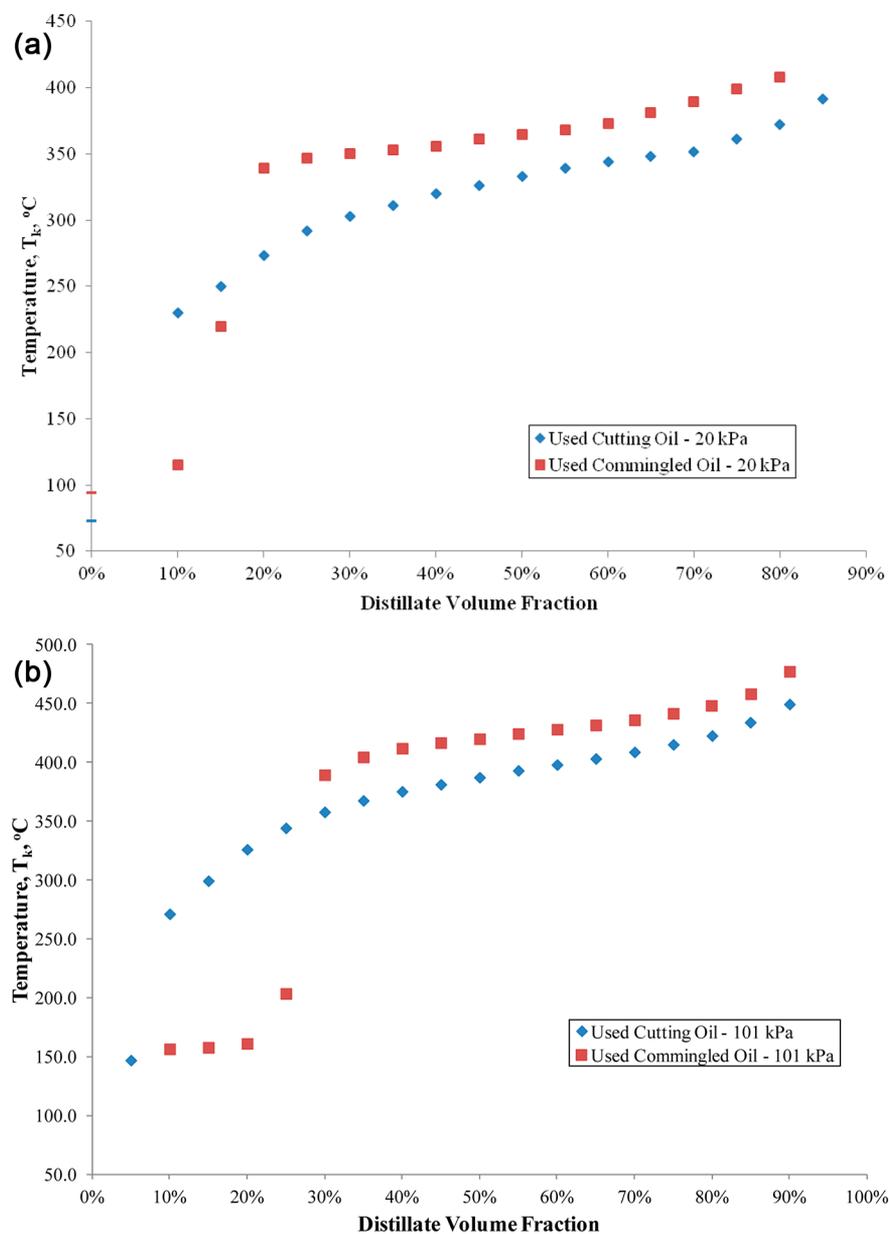
the sampling hammock in the receiver adapter with the pressure-balanced syringe and added to a crimp-sealed vial containing a known mass (approximately 1 mL) of *n*-hexane solvent. The withdrawn distillate samples were chemically analyzed using GC-FID. The same GC program as described for the neat sample analysis was used for all of the distillate samples.

## RESULTS AND DISCUSSION

The initial boiling temperatures (IBTs) of the new and used lubricant oils are provided in Table 1. The IBTs presented in Table 1 represent the fluid temperatures at the onset of vaporization marked by a sudden increase of the vapor temperature,  $T_h$ . These data represent an average of three to four measurements. Consistent with the description outlined in the Experimental Details, the combined uncertainty of these

measurements was somewhat less than 3 °C. First, the difference in the initial volatility of the used cutting and commingled oils as compared with the rest of the fluids is clear. Despite being measured at higher pressures (20 kPa), the used cutting and commingled oils had much lower IBTs than the other fluids, which were measured at 1 kPa. Second, it is of interest to note the significantly reduced IBT for the used motor oil compared to the unused motor oils. It is very likely that this is due to the presence of gasoline (from engine blow-by), moisture, and other contaminants, although this source cannot be confirmed because of the uncertain provenance of a waste oil sample.

The distillation curve results, expressed in  $T_k$  from the reduced-pressure ADC measurements, are reported in Tables 2 and 3 and graphically presented in Figures 3a and 4a. The fluids investigated at 1 kPa (Table 2, Figure 3a) are presented



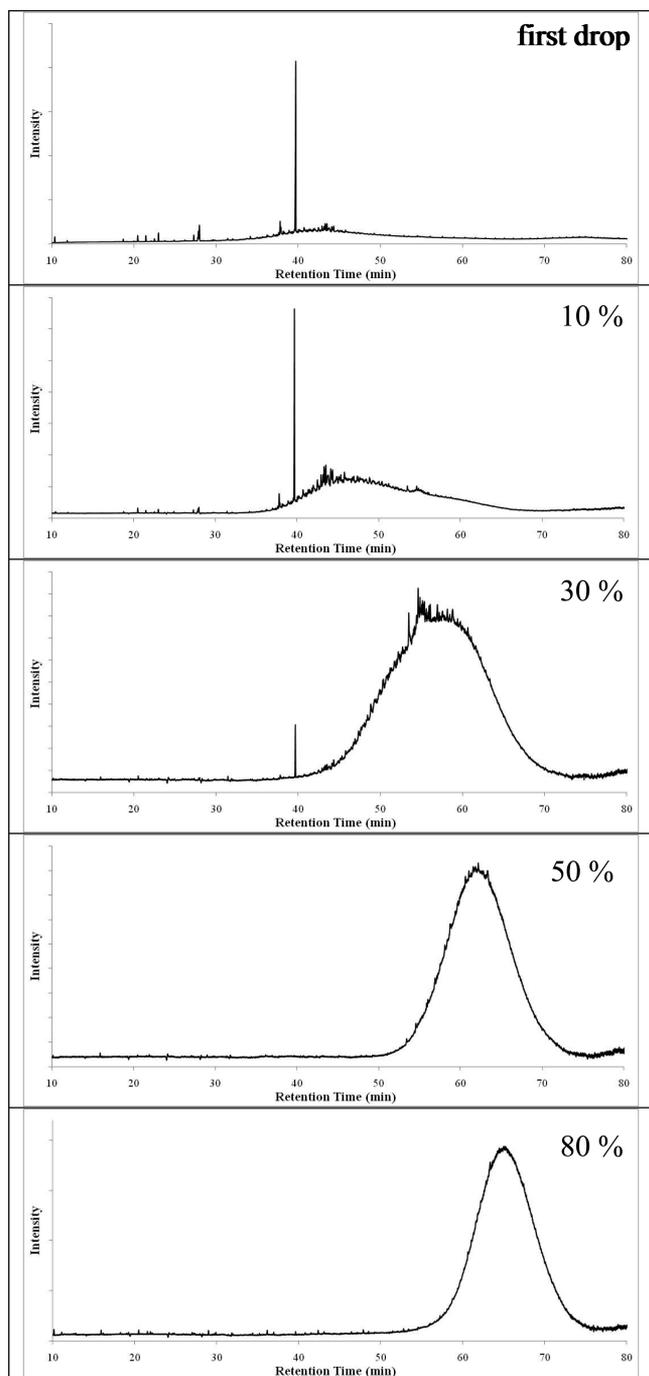
**Figure 4.** (a) Distillation curves of the used cutting and commingled oil for data collected (a) at a pressure of 20 kPa and (b) at local atmospheric pressure (approximately 83 kPa) and adjusted to standard atmospheric pressure by use of the modified Sydney Young equation. The uncertainties of the measurements are discussed in the text.

separately from the fluids analyzed at 20 kPa (Table 3, Figure 4a) to avoid confusion. All of the distillation curves presented are averages of three or four separate measurements. The combined experimental uncertainty was less than 3 °C for all temperatures reported. We show hash marks (on the y axis of the distillation curve figures) representing the measured initial boiling temperatures (IBTs). Also provided are distillation curves previously reported from the same fluids at atmospheric pressure (101 kPa).<sup>70</sup> These data, which were adjusted from our experimental pressure of approximately 83 kPa by use of the modified Sydney Young equation, can be seen in Figures 3b and 4b.<sup>71</sup>

We note that the distillate volume fractions measured in that prior work are slightly different from those reported here, and in that earlier work, the IBTs could be determined only for the SW-30 and 20W-50 virgin oils and the used motor oil. The comparison between the two pressure regimes, performed with

two ADC instruments, offers additional information regarding the fluids' volatilities and compositions at high temperatures. For example, it was previously shown that differences in the shapes and relative temperatures of distillation curves of biodiesel fuel made at different pressures can be used to track thermally induced sample composition transformations.<sup>72</sup>

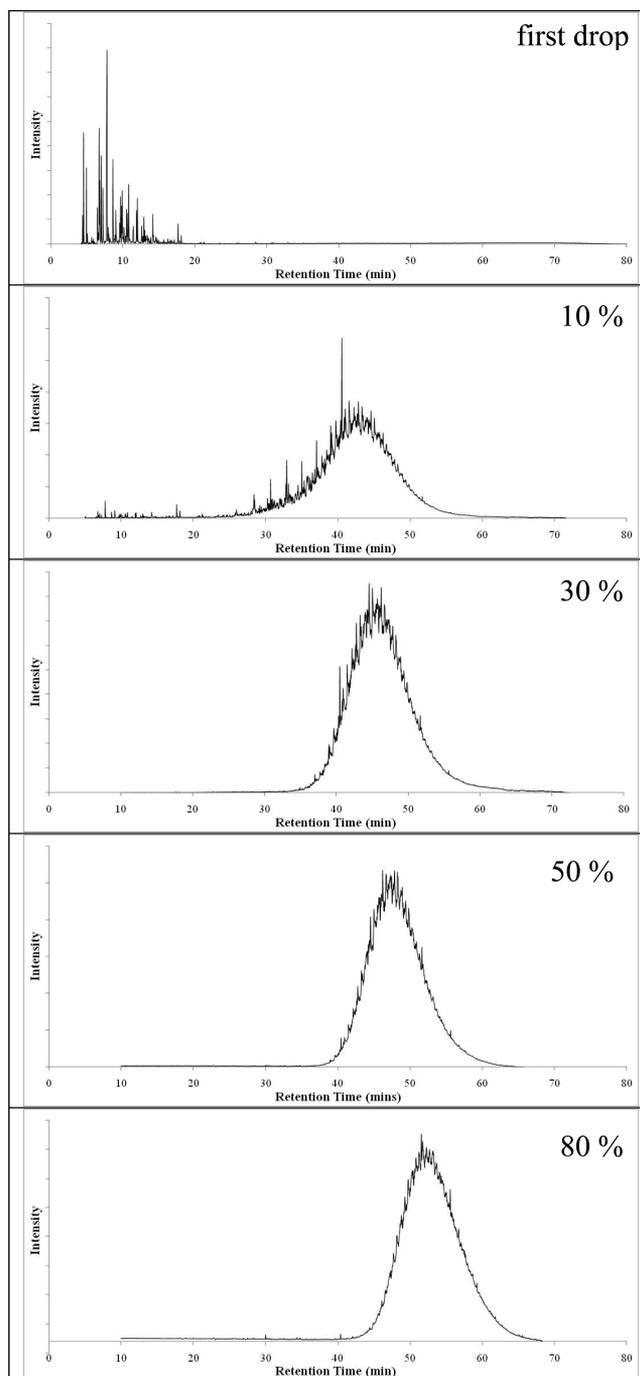
Considering first the three grades of virgin engine oils, we clearly observe the volatility decreasing with increasing viscosity range. The winter-grade SW-30 distills at lower temperatures than the 10W-40 summer-grade oil, and both distill at significantly lower temperatures than the specialty 20W-50 oil. The overall shapes of the curves at 1 and 101 kPa are very similar, with essentially the same trends. The used motor oil generally lies intermediate between the SW-30 and 10W-40 curves at both pressures. This is expected because such a stream would be expected to contain appreciable fractions of both grades of oil. Consistent with the IBT observations discussed



**Figure 5.** Distillate chromatograms for the unused 20W-50 motor oil. Details of the chromatography are discussed in the text.

earlier, the distillation temperatures of the early distillate volume fractions are markedly low, probably because of gasoline blow-by and moisture contamination.

The distillation curves measured at 1 kPa show reduced temperatures of approximately 150 °C from the corresponding temperatures measured at atmospheric pressure, except for the unused 20W-50 motor oil, which decreased by only approximately 100 °C. This fluid has the highest-boiling temperatures of any of the fluids investigated in this study, and we suspect that the extreme temperatures (400–500 °C) required for vaporization of this fluid at atmospheric pressure might have resulted in thermal cracking of the fluid, leading to the



**Figure 6.** Distillate chromatograms for the used motor oil. Details of the chromatography are discussed in the text.

flattening of the distillation curve that was observed between 40% and 65% distillate volume fractions.

The distillation curves of the used cutting and commingled oils at 20 kPa are shown in Figure 4a, and for comparison, the prior results at atmospheric pressure are shown in Figure 4b. We observe a decrease in temperature of approximately 50 °C from those measured at atmospheric pressure. The shape of the commingled oil curve measured at 20 kPa (Figure 4a) is slightly different from that measured at atmospheric pressure (Figure 4b). For the reduced-pressure measurements on this fluid, the temperature rise occurs sooner than observed in the atmospheric-pressure measurements. This indicates a lower concentration of

the more volatile components that result in the depressed temperatures at the beginning of the curve. This might be due to outgassing of the sample during the time between the two measurements (approximately one year). Another source of this variation could be sample loss through the vacuum system during the distillation at reduced pressure. A cryogenic trap in-line with the vacuum system would occasionally collect some fluid carryover, although this was typically less than 1 mL, and often no carryover was observed at all. Aside from the differences in the early part of the used commingled oil curve, no other substantive differences were observed between the reduced-pressure and atmospheric-pressure measurements for the commingled and cutting oils.

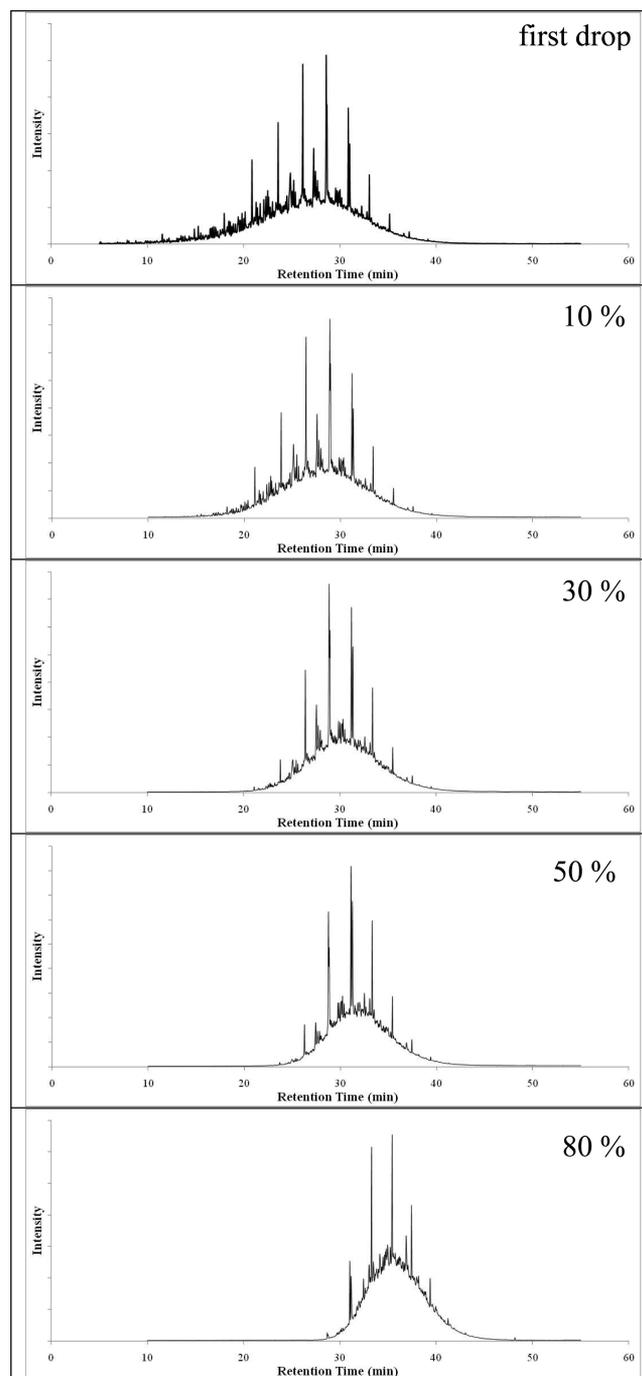
An extremely valuable feature of the reduced-pressure ADC measurement is the composition-explicit data channel: the ability to sample distillate at any desired point during the distillation. The distillate sample that is withdrawn can then be subjected to further analysis by use of any analytical method of interest, to provide information regarding the sample as a function of volatility. For the used and unused oils investigated in this study, samples were withdrawn at the first drop and 10%, 30%, 50%, and 80% volume fractions and subjected to a GC-FID analysis to help us more clearly understand the evolving composition of the sample during the distillation and its role on the observed distillation curves. Herein, we present several particularly instructive series of chromatograms drawn from the ADC measurements to illustrate the utility of the composition-explicit data channel.

First, in Figure 5, we examine the changing composition of the racing motor oil, 20W-50, as a function of distillate volume fraction. For a given distillate volume fraction, the components of this fluid eluted at longer retention times than those of the SW-30 and 10W-40 oils (chromatograms not shown in the interest of brevity). This is an expected result (based on the distillation curve results) because the primary separation mechanism for the GC column is based on boiling temperature, with a small contribution from polarity and polarizability. The chromatogram of the virgin 20W-50 oil (Figure 2) contained a large concentration of a single component, an antioxidant. In Figure 5, we observe this peak at a retention time of approximately 39 min for the 10% and 30% distillate volume fractions. We note that this component decreases in concentration as the distillation progresses and, by the 50% distillate volume fraction, it is no longer present. We also observe the Gaussian-like distribution shift to progressively longer retention times.

The distillate chromatograms of the used motor oil (Figure 6) are particularly beneficial in explaining the observed distillation curve, particularly the markedly reduced boiling temperatures at early distillate volume fractions compared to the unused motor oils. The GC analysis of the first drop of the used motor oil revealed a high concentration of volatile components (components eluting at retention times less than 20 min). These compounds are composed of a suite of branched alkanes and many alkyl aromatics. This early-eluting suite of components explains the much lower IBT of the used motor oil compared to the unused motor oils. The compositions of the remaining distillate fractions resemble those of the unused motor oils (with the Gaussian-like distribution shifting to progressively longer retention times), thereby explaining the convergence of the distillation curves of the used and unused motor oil following the 10% volume fraction. We note that the same antioxidant peak that is observed in high concentration in the 20W-50 motor oil can also be seen in the 10% and 30% distillate

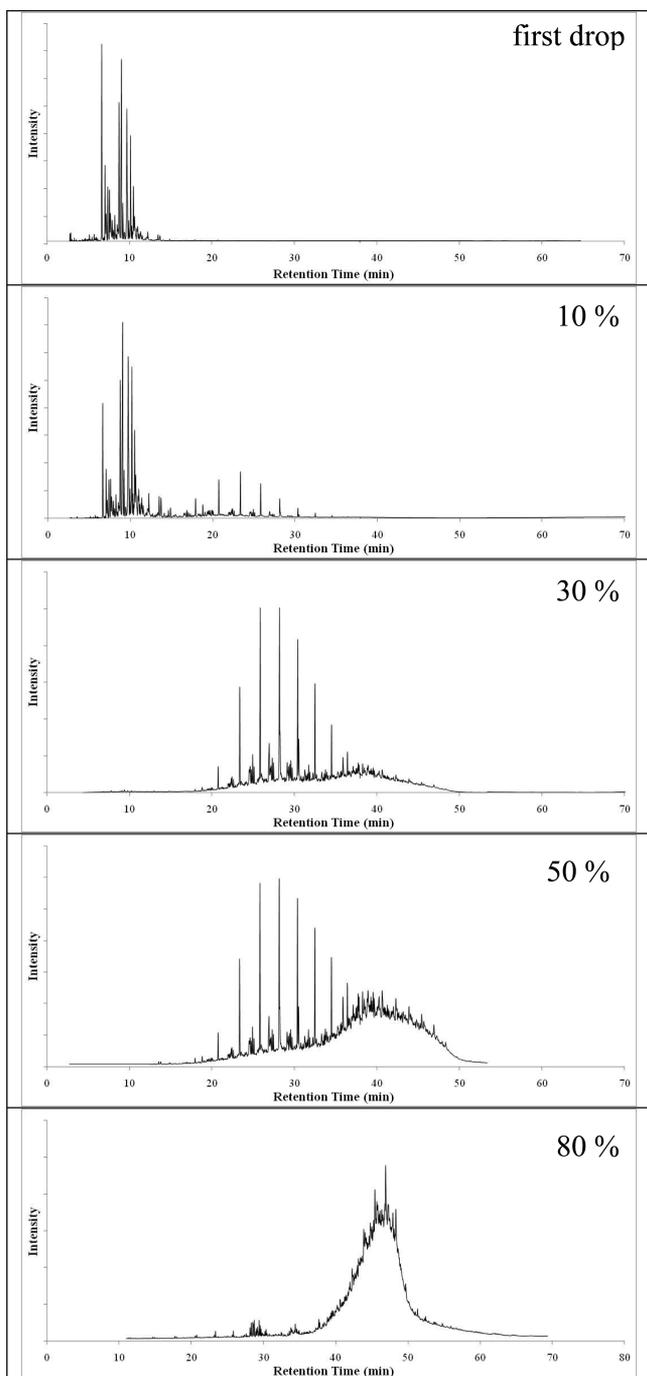
fractions for the used motor oil. We also note that no signs of sample cracking or polymerization were observed from the distillate chromatograms of any of the analyzed motor oils at reduced pressure.

The GC analysis of the distillate samples collected during the distillation of the used transformer oil (Figure 7) revealed little



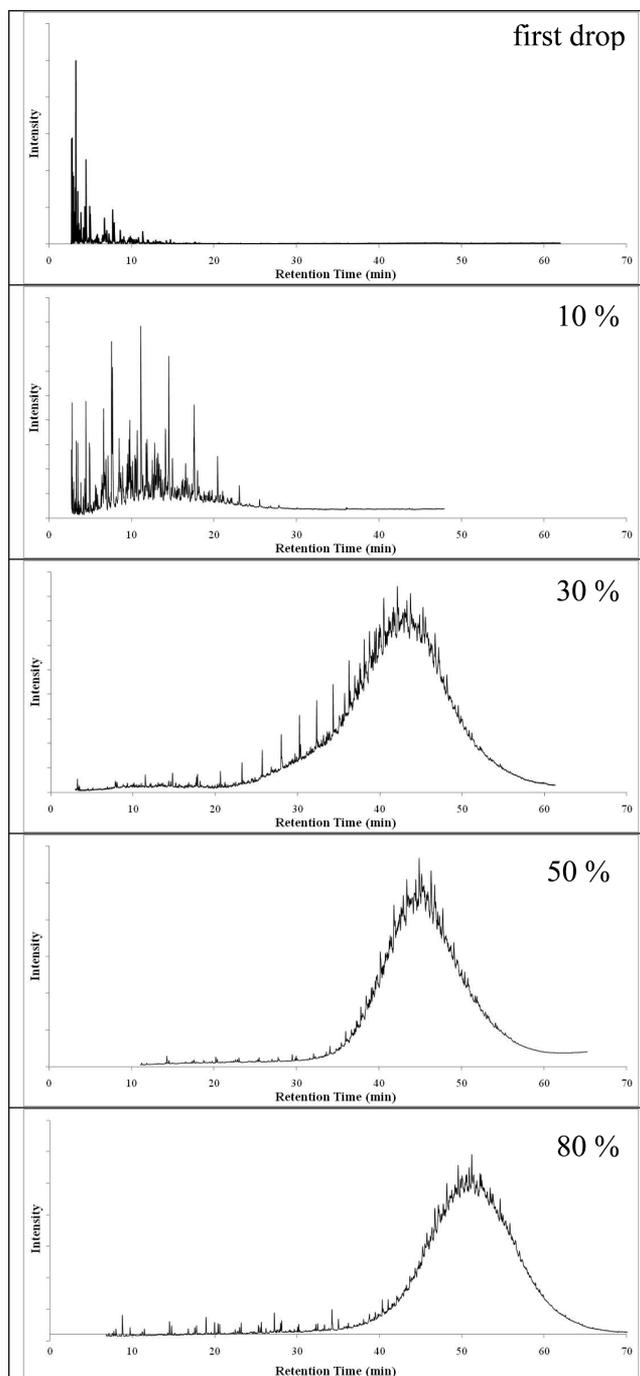
**Figure 7.** Distillate chromatograms for the used transformer oil. Details of the chromatography are discussed in the text.

change in the composition of the sample during distillation. We note only a slight increase in the average retention time with increasing distillate volume fraction, which is consistent with the relatively flat distillation curve observed in Figure 3. On the other hand, the used cutting and commingled oils produced



**Figure 8.** Distillate chromatograms for the used cutting oil. Details of the chromatography are discussed in the text.

very nonlinear distillation curves and showed distinct changes in the distillate composition as seen in Figures 8 and 9. In both of these fluids, the first drop and the 10% volume fraction contain large amounts of lighter/volatile components. This explains the low-temperature boiling behavior in the initial volume fractions for the respective distillation curves, providing an explanation for why the measurements of these fluids were unable to be performed at pressures below 20 kPa. Following the 10% volume fractions, the composition of the cutting oil distillate increases in mass, marked by the increasing retention times of the eluted sample in the distillate chromatograms. For the commingled oil, there is a dramatic change in the distillate



**Figure 9.** Distillate chromatograms for the used commingled oil. Details of the chromatography are discussed in the text.

composition between the 10% and 30% volume fractions. This change in composition profile explains the sharp rise in boiling temperatures indicated by the distillation curve in Figure 4b. Following the 30% volume fraction, the commingled-oil distillate composition undergoes very little change.

## ■ CONCLUSIONS

In this study, a reduced-pressure ADC measurement technique was applied to various waste oil streams, including used cutting, transformer, commingled, and motor oils, as well as unused motor oils of varying viscosity grades. We conclude that the method was able to precisely measure distillation curves at

pressures as low as 1 kPa while providing online sampling of the distillate for a complementary composition analysis. Results were compared to previously performed atmospheric-pressure measurements revealing significant reduction in the overall boiling temperatures but only slight differences in the distillation curve shapes. The only notable difference in the atmospheric and reduced-pressure boiling trends was observed for the high viscosity grade motor oil, 20W-50, which distilled at lower temperatures at atmospheric pressure than expected based on the measurements made at 1 kPa. High-temperature gas chromatography analysis proved to be a highly complementary measurement to the distillation curve, providing a physical meaning for observed boiling behaviors. Because the results from the reduced-pressure ADC represent the true starting fluid, the results of this study are anticipated to aid in subsequent equation-of-state development. It is expected that the application of the technique demonstrated herein will aid in future development, reuse, and refining of virgin and waste oils.

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### Notes

The authors declare no competing financial interest.

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