

Composition-Explicit Distillation Curves of Waste Lubricant Oils and Resourced Crude Oil: A Diagnostic for Re-Refining and Evaluation

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Abstract: Problem statement: We have recently introduced several important improvements in the measurement of distillation curves for complex fluids. The modifications include a composition-explicit data channel for each distillate fraction and temperature measurements that are true thermodynamic state points that can be modeled with an equation of state. The composition-explicit information is achieved with a sampling approach that allows precise qualitative as well as quantitative analyses of each fraction, on the fly. We have applied the method (called the advanced distillation curve technique) to a variety of fluids, including simple n-alkanes, rocket propellants, gasoline, jet fuels, diesel and biodiesel fuels and crude oils (both petroleum- and bio-derived crude oils). **Approach:** In this study, we present the application of the method to new, recycled and resourced heavy oils. The ultimate purpose of this work is waste reduction and energy utilization, by placing the reprocessing steps on a more fundamental footing. First, we present measurements on four unused automotive crankcase oils and then four samples of used oils: automotive oil, cutting oil, transformer oil and a commingled lubricant waste stream. Using the advanced distillation curve metrology, we can distinguish between the different weights (viscosity ranges) of crankcase oils and compare them to the sample of used crankcase oil. The distillation curves also provide valuable information regarding the presence or absence of low-boiling contaminants in the recycled automotive oil, such as water and gasoline. **Results:** Additionally, we demonstrate the evaluation of all four used lubricant oils. Then, we apply the advanced distillation curve method to a sample of crude oil prepared using a plastic waste stream from an automotive plant. **Conclusion:** Overall, we conclude that the composition-explicit advanced distillation curve metrology is important for understanding the boiling behavior of the various oils streams and is a valuable diagnostic for future re-refining of the used lubricant oils. This information will be essential in the development of models for the thermophysical properties of such fluids.

Key words: Automotive oil, distillate composition, distillation curve, re-refining, used lubricant oil

INTRODUCTION

Lubricant oils: In the United States alone, over two hundred million gallons (approximately 7.6×10^8 L) of used lubrication oil are disposed of improperly each year (American Petroleum Institute, 2009). The oil from one improperly disposed automotive oil change (4-5 L) can contaminate one million gallons of fresh water. It is quite clear, then, that proper collection of used lubricant oils is of great environmental importance. The next question becomes what to do with these used oils once they have been collected.

The majority of used lubricant oil that is generated is automotive crankcase oil (sometimes called drain oil). This oil can be recycled and treated for subsequent use as automotive oil, or used for other applications. The process is called re-refining and is a multi-step, complex and expensive process (OilRe-refining.aspx, 2009). First, the lightweight impurities are removed, then middle-weight impurities (such as components of gasoline) are removed via fuel stripping (Bruno, 1994). Next, vacuum distillation is employed to separate the heaviest impurities. The cleaned oil is then hydrotreated, followed by the addition of an appropriate

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additive package to complete the re-refining process. The totality of these individual steps results in a very energy intensive set of tasks 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 unused crankcase oil in order for the re-refined product to be of value. There are a number of standards and specifications that are used to ensure the quality of lubricating oils; among them is ASTM Method D-4485 (Orbital Engine Company, 2003). In this standard, several other ASTM methods are used and incorporated by reference; these include, for example, flash and fire point (ASTM D-92), corrosivity (ASTM D-130) and foaming tendency (ASTM D-892). 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 (ASTM Standard D2887-02, 2004). The distillation curve is one of the most important properties that can be measured for any complex fluid, since it is the only practical avenue to assess the volatility or the Vapor Liquid Equilibrium (VLE) (Kister, 1988; 1991; Manovyan *et al.*, 1983) Moreover, it can be directly correlated to many engine operating parameters (Cherepitsa *et al.*, 2003; Emel'yanov *et al.*, 1981; 1982; Shin, 1997; Sjogren *et al.*, 1996; Hallett and Ricard, 1992; Karonis *et al.*, 1998; 2003; ASTM Standard D 86-04b, 2004). 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.

Consequently, a method for measuring the distillation curve of automotive oils, lubricant oils and other heavy oils with a much lower uncertainty is critical. Reduced pressure distillations, also known as vacuum distillations, are one possibility; however, the considerable uncertainty in measuring and maintaining the reduced pressures make vacuum distillations unsuitable for measurements required in equation of state development. This makes an atmospheric distillation method desirable for providing temperature and pressure measurements with low uncertainty.

Advanced distillation curve metrology: The most common presentation of an atmospheric pressure distillation curve is a plot of the boiling temperature against volume fraction. The standard test method, ASTM D-86, provides the usual approach to measurement (ASTM Standard D 86-04b, 2004). The data obtained with ASTM D-86 are the initial boiling point, the temperature at predetermined distillate volume fractions and the final boiling point. The ASTM D-86 test suffers from many drawbacks, including large uncertainties in temperature measurements and little theoretical significance. Indeed, the major utility of the method stems from its standardization; everyone does it the same way.

In an effort to remedy the shortcomings of the standard distillation method described above, we have recently reported in detail an improved distillation method and apparatus. Improvements to the traditional distillation apparatus include (1) a composition-explicit data channel for each distillate fraction (for both qualitative and quantitative analysis), (2) temperature measurements that are true thermodynamic state points that can be modeled with an equation of state, (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, (6) qualitative, quantitative and trace chemical analysis of each distillate fraction, (7) assessment of the corrosivity and stability of each distillate fraction. The new method is called the composition-explicit or advanced distillation curve technique (ADC) (Bruno, 2006a; 2006b; Bruno and Smith, 2006a; 2006b; Ott and Bruno, 2007a; 2007b; Smith and Bruno, 2006; 2007a; 2007b). A schematic diagram of the instrument is presented in Fig. 1. We have applied this method to a wide variety of gasoline, diesel fuel, aviation fuel and rocket propellant mixtures (Bruno and Smith, 2006b; Bruno *et al.*, 2009a; 2009b; 2009c; 2009d; Hadler *et al.*, 2009; Ott *et al.*, 2008a; 2008b; 2008c; 2008d; Ott and Bruno, 2008; Smith and Bruno, 2007c; 2008; Smith *et al.*, 2008a; 2008b; Lovestead and Bruno, 2009a). Moreover, we have used the measurements derived from this method as the basis for the development of thermophysical property models for many of these fluids (Huber *et al.*, 2008a; 2008b; 2009a; 2009b).

Referring to Fig. 1, the stirred distillation flask is placed in an aluminum heating jacket contoured to fit the flask. The jacket is resistively heated, controlled by a model predictive PID controller that applies a precise thermal profile to the fluid. Three observation ports are provided in the insulation to allow penetration with a flexible, illuminated bore scope.

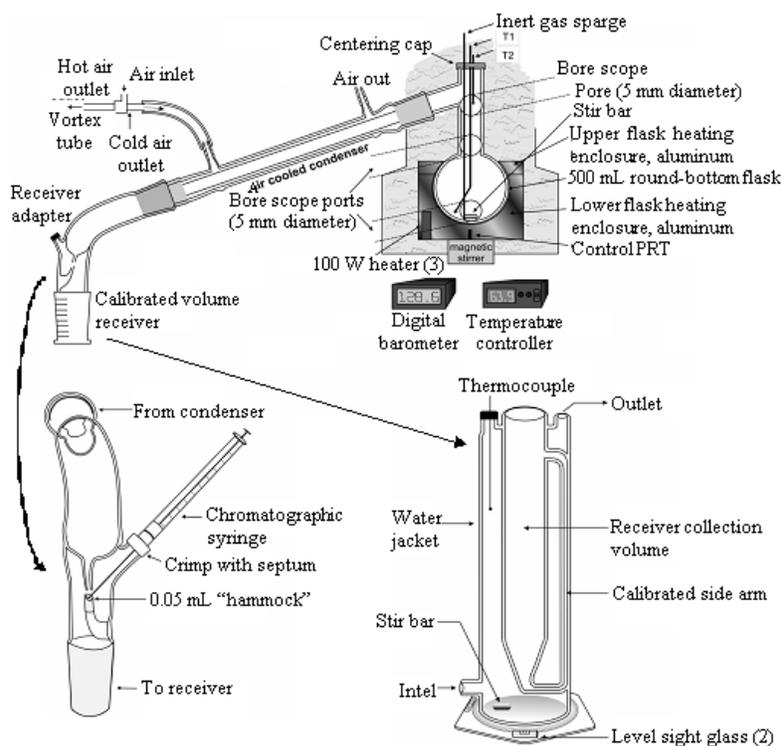


Fig. 1: Schematic diagram of the overall apparatus used for the measurement of distillation curves. Expanded views of the sampling adapter and the stabilized receiver are shown in the lower half of the figure

The ports are placed to observe the fluid in the boiling flask, the top of the boiling flask and the distillation head (at the bottom of the take-off). Above the distillation flask, a centering adapter provides access for two thermally tempered, calibrated thermocouples that enter the distillation head. One thermocouple (T1) is submerged in the fluid and the other (T2) is centered at the low point of distillate take-off. Also in the head is an inert gas blanket for use with thermally-unstable fluids. Distillate is taken off the flask with a distillation head, into a forced-air condenser chilled with a vortex tube. Following the condenser, the distillate enters a new transfer adapter that allows instantaneous sampling (on a "hammock" of known volume) of distillate for analysis. When the sample leaves the adapter, it flows into the calibrated, level-stabilized receiver for a precise volume measurement.

For each ADC measurement, we can record a data grid consisting of: T_k , the temperature measured in the fluid (with T1), T_h , the temperature in the head (measured with T2), the corresponding fluid volume, the elapsed time and the external (atmospheric) pressure. Along with these data, one withdraws a sample for detailed analysis, which is the most important advantage presented by the ADC. Sampling

very small volumes of the distillate yields a composition-explicit data channel with nearly instantaneous composition measurements. Chemical analysis of the distillate fractions allows us to understand how the composition of the fluid varies with volume fraction and distillation temperature, even for complex fluids. The fraction-by-fraction chemical analysis coupled with the distillation curve (which can be used to approximate vapor-liquid equilibrium of complex mixtures) provides a link between chemical analysis and thermodynamics.

The application of an atmospheric distillation curve measurement to heavy fluids such as lubricant oils requires some discussion. Although atmospheric distillation methods are routinely applied to heavy fluids for many diagnostic or Quality Assurance/Quality Control (QA/QC) applications, a reduced pressure method is sometimes preferred because of the lower temperatures that result. Clearly, at the higher temperatures encountered in atmospheric distillations, it is often not possible to obtain a meaningful final boiling temperature, due to sample decomposition. When approached with the ADC and its composition-explicit data channel, compositions measured from those high temperatures may indeed

reveal such decomposition. The ultimate goal of our work is not QA/QC, but rather the development of reliable fluid models that depend on correlations of experimental measurements. As such, we require pressure control and measurement of very low uncertainty, not generally obtainable with reduced pressure approaches (reduced pressure measurements have temperature uncertainties up to 8°C and pressure uncertainties up to 18%) (Manovyan *et al.*, 1983). For this reason, our measurements of heavy fluids do not generally extend to the final boiling point. Additionally, thermal cracking during the distillation can be probed with any applicable analytical technique (primarily gas chromatography-mass spectrometry, GC-MS) on the distillate fractions. Indeed, GC-MS evaluation of the distillate fractions of petroleum crude oils indicates that these heavy oils do not undergo significant thermal cracking until well above 400°C. Moreover, kinetic determinations of the thermal decomposition of complex fluids lead to a similar conclusion. For example, in studies of the thermal decomposition or cracking of the hydrocarbon fuels Rocket Propellant 1 (RP-1), Rocket propellant 2 (RP-2) and aviation fuel Jet-A, it was found that significant decomposition/cracking of the fluid did not occur until temperatures significantly above 400°C were reached (Lovestead and Bruno, 2009a; 2009b; Huber *et al.*, 2008a; 2008b). Moreover, these measurements were done at a pressure of 35 MPa (approximately 5000 psi). While we recognize the difference between a heterogeneous mixture such as a multi-grade oil with detergents and viscosity improving additives and a finished fuel such as RP-1, there is nonetheless a great deal of similarity in the chemical behavior especially among the nonpolar moieties. Given appropriate constraints and cautions, we find that the ADC is a useful tool for measuring the atmospheric distillation curve (and composition by distillate fraction) of heavier complex fluids such as oils.

Crude oil prepared from waste: The production of heavy fluids similar to crude oil is of interest from two points of view: the minimization and mitigation of waste streams and the production of alternative energy sources. Many different potential feed stocks for alternative crude oils have been explored, including swine manure, poultry parts and assembly line waste. Indeed, we have examined some of these feed stocks with the ADC in the past. Recycling and reclaiming petroleum products for further use are topics under current development in industry. One product that could have further use as a feed stock for a crude oil is plastic produced as a waste stream from automotive factories.

These solid waste plastics would normally be sent to a landfill. This resulting crude oil might then be utilized in a similar manner to traditionally drilled petroleum crude oils. In order to be a useful supplement to the traditional crude oil stream, it is important that the physical and chemical characteristics of resourced oil from waste plastics be evaluated. Thus, evaluating the volatility (as expressed by the ADC) of such a resourced crude oil would be of prime importance. We have chosen to discuss this fluid along with the discussion of the waste oils because many of the same issues of chemical decomposition are encountered.

MATERIALS AND METHODS

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 µm, temperature program from 50-170°C at a heating rate of 5°C min⁻¹) with flame ionization detection and mass spectrometric detection (Huber *et al.*, 2009a). These analyses revealed the purity to be approximately 99% and the fluid was used without further purification.

The used lubricant oils were obtained as process streams from a commercial oil re-refining facility. These fluids were dark in color, with the viscosity of typical oils and were all single phase. They were examined by gas chromatography with flame ionization detection and mass spectrometric detection (GC-FID and GC-MS). The samples were analyzed on a 30 m capillary column of 5% phenyl-95%-dimethyl polysiloxane having a thickness of 1 µm. Initially, the temperature was maintained isothermally at 80°C for 2 minutes, followed by an 8°C min⁻¹ ramp to 285°C and held at 285°C for 5 minutes. These analyses revealed the expected cluster of hydrocarbon compounds having the usual Gaussian-like distribution.

The used transformer and cutting oil was also obtained from a commercial oil re-refining facility. This fluid had a deep amber cast but was nevertheless transparent. Like the used lubricant oils, it was a single phase fluid, but was less viscous than the used lubricant oil. The re-sourced crude oil was obtained from a processor of waste or unused automotive plastics. This fluid was a dark gray-brown and was more viscous than the lubricant oil or the transformer oil. It, too, was single phase. A similar survey analysis was done on these fluids as was described above. These analyses revealed the pattern common to highly refined mineral oils, but with some minor polar constituents as well. These included fatty acid esters and ethers in the seven

to eight carbons range. Neither silicones nor fluorinated compounds were found in the sample we examined.

Advanced distillation curves: For each experiment with the lubricant oils, 200 mL of a new or used oil was placed into the boiling flask of the distillation curve apparatus with a 200 mL pipette. 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 take-off position in the distillation head. The uncertainty in the thermocouple measurements was 0.05°C . Enclosure heating was then commenced with a four-step program based upon a previously measured distillation curve. Volume measurements were made in a level-stabilized receiver. For each experiment with the resourced waste plastics oil, an identical procedure was carried out with the exception of the scale of the experiment. For the resourced oil, 50 mL of the oil was distilled from a 100 mL round-bottomed flask. The temperature measurements were carried out in equivalent locations in the smaller apparatus and the uncertainties in the temperature measurements were the same. A smaller apparatus was used in the case of this fluid because of its significantly higher viscosity. In this case, the sample had to be introduced with a 50 mL syringe.

Each of the distillation curves was measured at ambient atmospheric pressure. The pressure was measured with an electronic barometer; the expanded total uncertainty ($k = 2$) in the pressure measurements was 0.003 kPa. Distillation temperature readings were corrected to what should be obtained at standard atmospheric pressure. This was done with the modified Sydney Young equation, in which the constant term was assigned a value of 0.000109 (Huber *et al.*, 2009b; Andersen and Bruno, 2005; Widegren and Bruno, 2008a; 2008b; 2009; Bruno and Svoronos, 2004; 2005; Ott *et al.*, 2008; Young, S., 1902; 1903; 1922; ASTM Standard D 2789-04b, 2005). The magnitude of the correction depends on the extent of departure from standard atmospheric pressure. The location of the laboratory in which the measurements reported herein were performed is approximately 1650 m above sea level (with an average atmospheric pressure of 83 kPa), resulting in a typical temperature correction of 7°C .

To provide the composition channel to accompany the temperature information on the distillation curves, sample aliquots were withdrawn for 10 selected distillate volume fractions. To accomplish this, aliquots of $\sim 7 \mu\text{L}$ of emergent fluid were withdrawn from the sampling hammock in the receiver adapter with a blunt-tipped chromatographic syringe and added to a sealed autosampler vial containing a known mass of n-hexane solvent. A sample was withdrawn at the first drop of

fluid from the condenser and then at each of nine additional predetermined volume fractions of distillate, for ten total sample aliquots.

The oil distillate fractions were evaluated by GC-MS in scanning mode on the same column and with the same temperature program described earlier. Mass spectra were collected in scanning mode for each peak from 15-550 Relative Molecular Mass (RMM) units.

RESULTS AND DISCUSSION

Automotive oils: Three commercially available (unused) automotive crankcase oils were measured with the ADC metrology. These measurements were done to provide a frame of reference for the volatility of lubricating oils and ultimately, used lubricating oils. Each fluid presented here was measured between three and six times. These oils are also called “petroleum” oils because they are produced in petroleum refineries. The distillation curves of the petroleum oils are presented in Fig. 1 as T_k , the temperatures measured in the boiling fluid, plotted against distillate volume fraction. These data are true thermodynamic state points that can be used to model each fluid with an equation of state. In this figure, the estimated uncertainty (with a coverage factor $k = 2$) in the temperatures is 0.3°C . The uncertainty in the volume measurement that is used to obtain the distillate volume fraction is 0.05 mL in each case. Each lubricating oil that we examined was a multi-grade automotive lubricant: petroleum based 5W-30, 10W-40 and 20W-50 and a synthetic 5W-30. Synthetic oils are reported to be advantageous in cold starting situations because they lack the waxes and heavy paraffins found in petroleum based oils. Multi-grade oils have viscosity improvers added to base petroleum oils to increase each oil’s operating temperature range. A trend of higher distillation temperatures with higher viscosity rated oil is observed on Fig. 2. This trend is not surprising, since the higher viscosity oils generally have heavier, less volatile components. The somewhat flatter shape of the petroleum based 5W-30 oil (when compared to the other two petroleum based oils) indicates that this oil has a narrower composition range or contains compounds with similar boiling points.

We note that the petroleum based 5W-30 and the synthetic 5W-30 have similar distillation curves, but the distillation temperature of the synthetic oil leads the petroleum oil slightly. The maximum difference is 5°C at the 0.05 distillate volume fraction, gradually decreasing to less than 2°C at the 0.80 volume fraction. This indicates that the compounds used to formulate the synthetic 5W-30 are slightly less volatile than the compounds found in the petroleum 5W-30.

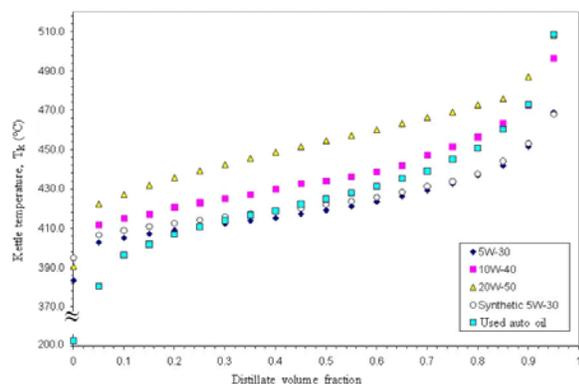


Fig. 2: Distillation curves of three weights of virgin (unused) petroleum crankcase oil and a virgin synthetic crankcase oil. Also shown is the distillation curve for a stream of used crankcase oil. The error bars on the measurements are smaller than the symbols used

The distillation temperatures of each of the petroleum automotive oils are all well above the upper temperature specification of 310°C for an atmospheric pressure distillation recommended by ASTM D-2892 to avoid “significant cracking”. It is unlikely that the onset of severe cracking actually occurs until significantly higher temperatures, however, as discussed earlier. Hence, the application of an atmospheric distillation method at temperatures higher than 310°C is suitable with the ADC provided one uses the composition-explicit data channel to monitor cracking. Moreover, the excellent repeatability (0.3°C) and the clear trends observed among the distillation curves of the petroleum derived lubricants suggest that an atmospheric distillation curve method can be a source of useful diagnostic information for such heavy fluids.

Also shown in Fig. 2 is the distillation curve of a sample of used automotive crankcase oils. The used automotive oil sample shown has not been treated or altered in any way; it is simply a composite sample presented to a re-refiner from multiple used oil collection centers. The first drop of the used automotive oil begins to distill at 207.7°C, which is more than 160°C lower than that of the unused oils. This suggests some gasoline contamination in the used oil. We did not find appreciable water in this sample (indeed, collection centers refuse to accept oil contaminated with a separate liquid water phase). The temperature profile of the used oil rapidly approaches that of the typical lubricating oil profile after this initial low temperature point. The early part of the distillation curve is near the curve for 5W-30. It then approaches the curve for 10W-40 oil in the middle range, where it remains almost to

the last fraction distilled. At the very end of the distillation curve, we note that the used oil curve climbs and merges with the distillation temperature of the 20W-50 oil at the end of the curve. This suggests that the used oil is made up of a mix of all three of these common oil weights, with a clear preponderance for the (most commonly used) 10W-40, although there is a small amount of residual fuel that distills early. This observation is consistent with expectations from a sample in an oil collection facility.

The composition-explicit data channel of the advanced distillation curve method can be used to probe the used automotive oil sample via GC-MS. Although a peak by peak analysis of these complex mixtures is possible and even desirable under some circumstances, some survey analyses can be performed to provide important information. For example, it is possible to evaluate the hydrocarbon moiety composition of each distillate fraction by use of a mass spectrometric classification method. For this we use a modification of the procedure suggested in ASTM Method D-2789 (ASTM Standard D 2789-04b, 2005). In this method, one uses mass spectrometry (or GC-MS) to characterize hydrocarbon samples into six types; it is convenient to think of D-2789 as presenting a hydrocarbon-type analysis of each distillate fraction. The six types or families are paraffins, monocycloparaffins, dicycloparaffins, alkylbenzenes (arenes or aromatics), indanes and tetralins (grouped as one classification) and naphthalenes. Although the method is specified only for application to low olefinic gasolines and it has significant limitations, it is of practical relevance to many complex fluid analyses and is often applied to gas turbine fuels, diesel fuels, rocket propellants and missile fuels. The uncertainty and the potential pitfalls of this method were treated earlier (Smith and Bruno, 2007a). Additionally, it is possible that not all of the components of the higher boiling fractions of distillate are sufficiently volatile to permit analysis by GC. In the present study, these higher boiling compounds are likely the heavy, greasy, hydrocarbons that comprise lubricant oils. Even in the absence of these heavy hydrocarbons, we would still be able to detect the families of lower boiling compounds that would be a primary concern for re-refining.

The solutions were prepared from 7 μL samples of distillate fraction that were dissolved in a known mass of solvent (n-hexane). This solvent was chosen because it causes no chromatographic interference with the sample constituents. For the hydrocarbon type analysis of the distillate fraction samples, 1 μL injections of the distillate diluted in hexane solvent were made into the GC-MS. Because of this consistent injection volume between samples, no corrections were needed for volume.

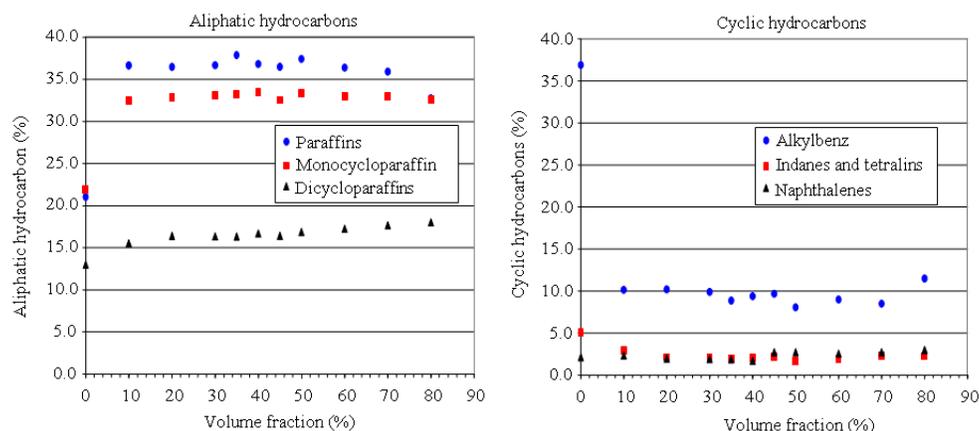


Fig. 3: Hydrocarbon type survey analysis on the used automotive oil distillate fractions

The results of the hydrocarbon type analysis are presented in Fig. 3. This Fig. 3 shows that the first drop of the used automotive oil distillate has significantly different chemical characteristics than those of the remaining 10 distillate fractions evaluated. Consistent with a separate, explicit investigation of the GC-MS peaks (discussed below), the first drop of distillate has a very high proportion of alkylbenzenes, containing nearly 37% (vol/vol), while the rest of the distillate fractions contain between 8 and 10% (vol/vol). Due to this high percentage of alkylbenzenes in the first fraction, the total percentage of paraffinic hydrocarbons in the first drop is significantly lower (approximately 22% for both paraffins and monocycloparaffins) than in the remaining distillate fractions. The dicycloparaffinic compounds are relatively unaffected; these percentages rise gently from 13-18% during the course of the distillation. The indanes/tetralins and naphthalenes are consistently low, with the indanes/tetralins showing a slightly higher percentage in the first drop. These major differences in the composition of the first drop of the used automotive oil are the cause of the very different distillation temperature of this drop compared to the rest of the distillation curve. We note that the results of this analysis are consistent with the suspicion of contamination of the used oil with residual fuel. The composition profile beyond the first drop is consistent with a lubrication oil, with a high content of paraffinics and monocyclic paraffinics and relatively low content of aromatics.

After this moiety-by-moiety characterization, which gives us a survey profile of each distillate fraction's composition, we can use the composition-explicit data channel to explicitly investigate the composition of the first drop of the used automotive oil. We focus on this fraction explicitly for additional

analysis: (1) because it is a departure from the remainder of the composition profile and (2) to confirm our preliminary conclusion or suspicion regarding its cause. For this analysis, we applied GC-MS, with a method developed and optimized for a light component in a heavier hydrocarbon liquid matrix (30 m capillary column of 5% phenyl-95%-dimethyl polysiloxane having a thickness of 1 μm , temperature was maintained isothermally at 50°C for 2 minutes, followed by a 8°C min^{-1} ramp to 285°C and held at 285°C for 5 min).

The results of this analysis show that the first drop of the used automotive oil does not contain a Gaussian-like "envelope" of peaks characteristic of a heavy hydrocarbon mixture, but instead contains several common components of gasoline (Smith and Bruno, 2007a), including shorter hydrocarbons, cyclic paraffins such as naphthalenes and indanes and some aromatics (primarily alkyl-substituted benzenes). While these data indicate that further treatment of this specific sample of used oil will be required before it is suitable for re-use, it also shows that for this particular sample of used oil, the residual fuel will only affect the very earliest distillate fractions.

Used and resourced heavy oils: Although used automotive oil is the most abundant oil in the total oil waste stream of industrialized countries, there are also several other significant contributors. To include some of the other sources of used lubricant oil waste streams, we examined used cutting oil from machine shop operations, used transformer oil and a sample of commingled waste lubricant oils collected by a reprocessor in a nationwide facility. The latter sample of commingled oil typically contains a significant quantity of cutting fluid and coolant oil from large scale

automated machine shop operations in industry, as well as smaller amounts of unclassified oils from smaller facilities. Additionally, we present the distillation curve of a resourced heavy crude oil, prepared from waste plastics from an automotive factory. Representative distillation curves, again presented as T_k and with the same uncertainties as given earlier, are presented in Fig. 4. As before, each curve was measured between 4 and 6 times.

Both the used commingled oil and cutting oil begin distilling at approximately 100°C, suggestive of the presence of dissolved or dispersed water in these samples. Indeed, the collected distillate in the receiver for the used cutting oil was clearly composed of two phase layers: the first 10 mL (which corresponds to 5 volume%) of the distillate was light yellow and transparent, which we have found to be characteristic of a primarily aqueous phase distilled from a mixed waste fluid stream (Ott *et al.*, 2008a). A dramatic rise in temperature was then observed and an abrupt change to a dark brown immiscible phase was observed to accumulate in the receiver. The presence of oil hydrocarbons in this phase was confirmed by GC-MS. These curves provide a valuable evaluation of these two oils, indicating that lower-boiling components would require re-refinement before these oils might be re-used.

The used commingled oil also began to distill around 100°C; unlike the cutting oil (which distilled around 100°C for only the first 5%, vol/vol), the first 25 volume percent of the distillate continues to boil at a

much lower temperature (less than 203°C). Then, a temperature increase of 185°C occurs before the next 5 volume% distills. These characteristics of the distillation curve indicate that the used commingled oil has a wider composition distribution with a relatively high proportion of low-boiling components when compared to that of the other used lubricant oils.

The used transformer oil has a much flatter distillation curve than those of the other three used oils, with a total temperature change of only 85°C. Unlike the used automotive oil, which shows a temperature increase of greater than 125°C between the first drop of distillate and the 5 volume% fraction, the first boiling drop of the used transformer oil is within 2°C of the 5 volume% fraction. This indicates that the transformer oil does not contain lower boiling components from light contaminants, unlike the other two oils previously discussed. It follows that the used transformer oil likely needs less re-refinement than the other used oils before it might be suitable for re-use.

The difference in the three distillation curves discussed above can be probed with the composition-explicit data channel and again by employing the moiety-by-moiety analysis method described above for the automotive lubricants. As an example, the results of this analysis for the used transformer oil are shown in Fig 5. Consistent with the relatively flat distillation curve for this fluid, indicative of a narrow composition range, the moiety-by-moiety analysis presented in Fig. 5 shows that each distillate fraction has a similar composition.

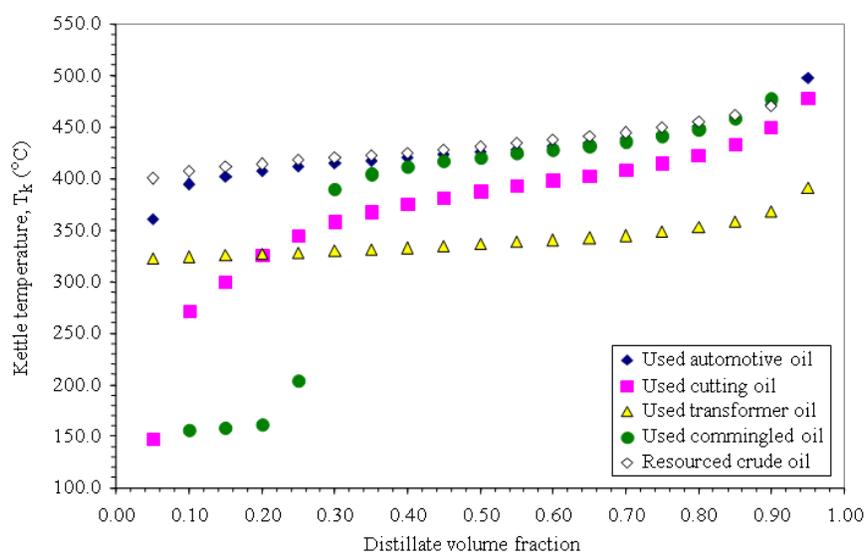


Fig. 4: Distillation curves of the four used lubricant oils and the re-sourced crude oil. Each single curve shown for a given sample is representative of data collected for 3-6 distillation curves. The error bars on the temperature measurement are smaller than the symbols used

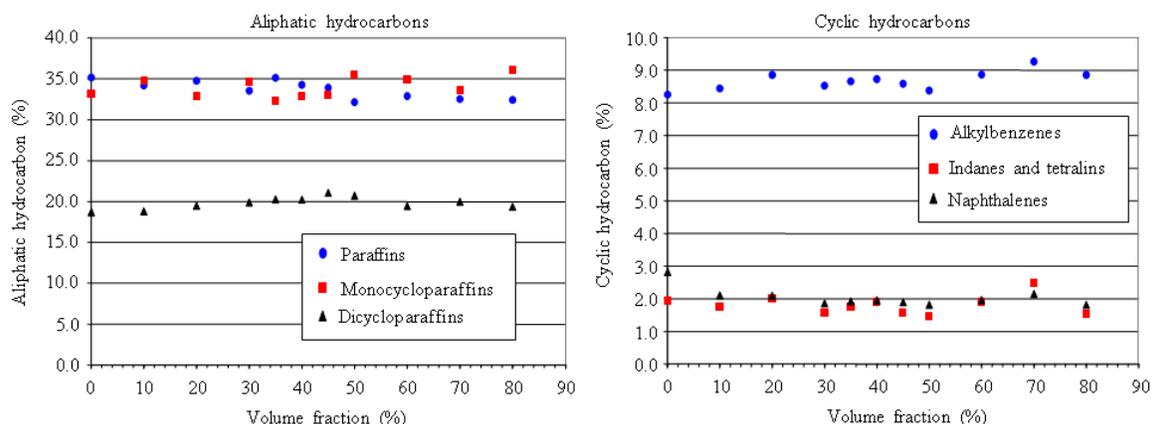


Fig. 5: The hydrocarbon type survey analysis for the used transformer oil distillate fractions

Paraffins and monocycloparaffins are the primary constituents of each distillate fraction, each moiety type being responsible for between 30 and 35% of the total composition. The dicycloparaffins are also a relatively large proportion of the total composition, varying between 19 and 21% throughout the course of the distillation. Each of the cyclic hydrocarbon moieties has a significantly smaller total percentage. Of the cyclic hydrocarbons, the alkylbenzenes have the highest overall percentages, between 8 and 10%. The indanes/tetralins and naphthalenes are consistently between 1 and 3% of the total composition. This narrow composition range is what would be expected for a highly refined fluid such as transformer oil. Additionally, the composition profile throughout the course of the distillation confirms the absence of the low-boiling species found in the other used lubricant oils.

Finally, we discuss the distillation curve of a sample of crude oil prepared from re-sourcing waste plastic from an automotive plant. This oil is intended to divert plastics from the landfill stream and to supplement petroleum crude oil reserves. Examination of the distillation curve of this resourced oil shows that the distillation curve has a relatively flat shape, indicative of a narrow compositional profile. No low-boiling components are indicated, as was found in some of the used oils. GC-MS investigation of the resourced oil before distillation showed that it was primarily composed of long-chain aliphatic hydrocarbon compounds, with naphthalenes and alkylbenzenes present as minor components. Examination of the composition of each distillate fraction shows the expected envelope of heavy hydrocarbon peaks, with the hydrocarbon envelope progressing to longer retention times as the distillation proceeds. However,

each fraction also contains some peaks indicative of shorter, likely thermally cracked, hydrocarbons. Even with the observed cracking, the distillation curve is still useful because it determines that there are no low-boiling components in the resourced heavy crude oil.

CONCLUSION

The advanced distillation curve metrology was used to examine four unused automotive crankcase oils and four used lubricant oils, including a used automotive crankcase oil. The distillation curves of the three unused petroleum crankcase oils followed the expected trends based on the stated weights of the oils. A synthetic automotive crankcase oil was slightly less volatile than the petroleum oil of the same viscosity rating. Three out of the four used lubricant oils had distillation curves that indicated initial boiling at much lower temperatures than the remainder of the distillation curves, indicating that these three used oils contained lower boiling components that would require re-refining of the oil if the oil were to be re-used. The composition-explicit data channel was used to probe the composition of a low-boiling distillate fraction of the used automotive oil; several components of automotive gasoline were present. Moiety-by moiety analysis by a mass spectral method similar to ASTM D-2789 gave good insight into the composition of the oils as a function of distillate fraction. The resourced crude oil shows a relatively flat distillation curve, indicating the lack of low-boiling compounds. We conclude from this work that the advanced distillation curve metrology is a valuable diagnostic for new, used and resourced heavy oils. This method can be used to develop thermodynamic models for such complex fluids as mixed waste oils. These models are needed for the

design and optimization of separation processes used in re-refining and reprocessing. Moreover, the method can be used as a QA/QC tool, since the chemical composition can be related to the thermal information that is measured.

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