1	Measuring the distillation curves of non-homogeneous fluids: method and case study of two
2	pyrolysis oils*
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11	

## 12 Abstract

13 Volatility is an important property in fuels research because it can significantly affect performance 14 and because it is highly sensitive to changes in the composition of a mixture. In the laboratory, 15 volatility is measured as a distillation curve. Difficulty arises when the fluid to be measured is non-16 homogeneous; that is, it has more than one liquid phase. Using the advanced distillation curve 17 (ADC) method, we analyzed two such fluids, crude pyrolysis oils containing significant water that 18 formed an aqueous phase separate from the organic phase. In this communication, we present a 19 data analysis method that compensates for non-homogeneity in these samples and enables us to 20 compare the organic phase to the experience base of previously measured petroleum and pyrolysis 21 oils.

22

#### 23 Keywords: distillation; non-homogeneous fluids; pyrolysis oil

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5

#### 6 1. Introduction

7 The distillation curve of a complex fluid is a measurement of the boiling temperature as a 8 function of the volume fraction distilled. This measurement is critical to understanding the 9 volatility of complex fluids and how fuels in particular behave in a refinery or an engine. This 10 measurement of a fluid's volatility is also crucial to the understanding and modeling of fluid 11 mixture thermophysical properties. The advanced distillation curve (ADC) method, developed at 12 NIST, is an improved metrology for distillation curve measurement that provides a 13 thermodynamically significant temperature measurement accompanied by a composition explicit data channel (composition measurement as a function of distillate volume fraction, DVF).<sup>1-4</sup> It is 14 15 an improvement to the traditionally used ASTM International D-86 method.<sup>5</sup>

16 The ADC method was developed at NIST as a robust, data-rich distillation approach that has been described in depth in previous publications.<sup>6-11</sup> The ADC improves on the well-known 17 18 D-86 distillation method in the following ways: (1) a composition-explicit data channel for each 19 distillate fraction (for both qualitative and quantitative analysis), (2) temperature measurements 20 that are true thermodynamic state points that can be modeled with an equation of state, (3) 21 temperature, volume and pressure measurements of low uncertainty suitable for equation of state 22 development, (4) consistency with a century of historical data, (5) an assessment of the energy 23 content of each distillate fraction, and (6) trace chemical analysis of each distillate fraction.

1 Sampling very small volumes of the distillate yields a composition-explicit data channel with 2 nearly instantaneous composition measurements. Chemical analysis of the distillate fractions 3 allows for some understanding of how the composition of the fluid varies with volume fraction 4 and distillation temperature, even for complex fluids. This is critical when the fuel contains 5 additives (such as cetane improvers, oxygenates or stabilizers) or unusual components (such as corrosives and manure sterols).<sup>9, 12-14</sup> The significant advantage offered by the ADC method is the 6 ability to model the distillation curve with an equation of state.<sup>5, 15</sup> The ADC method also features 7 a much lower uncertainty budget than is obtainable by D-86.<sup>1</sup> 8

9 Importantly, this low uncertainty budget usually excludes consideration of sampling 10 uncertainty, that is, how well an aliquot of fluid taken for ADC measurement represents the population material.<sup>16</sup> In previous fuel characterization studies using the ADC method, sampling 11 12 uncertainty has been insignificant because the fluids measured were homogeneous, existing in a 13 single, well mixed liquid phase. This is not always the case; indeed, unrefined pyrolysis fluids pose 14 a particular challenge because the pyrolysis reaction can produce significant amounts of water. We 15 encountered this challenge in the measurement of two crude pyrolysis oils, one made from 16 ponderosa pine shavings and the other from dairy manure.

Numerous feedstocks are currently in use in pyrolysis reactors and gasifiers, including municipal refuse, various types of plastic, agricultural waste, and other biomass.<sup>17</sup> Indeed, our lab previously performed ADC characterization on a crude oil produced from pyrolysis of swine manure and on two liquid fuels refined from crude polyethylene pyrolysis oil.<sup>9, 18</sup> The appeal of alternative fuels sourced from waste is clear: the widespread use of waste feedstocks like the pine shavings and manure in this case would simultaneously reduce the need for fossil fuels and mitigate the load on landfills and pollution in the environment. For example, in 2006, livestock

in Canada alone produced over 180 million metric tons (1.8e10 kg) of manure.<sup>19</sup> Although the
fluids studied here were produced in a small, lab-scale reactor, a number of industrial scale
plants exist in the United States for fuel production from the pyrolysis of waste.<sup>20</sup>

4

#### 5 2. Material and Methods

6 2.1. Crude pyrolysis oils

7 The crude pyrolysis fluids were produced from ponderosa pine saw-mill residues (< 5 mm) and 8 dairy manure (dried and hammer milled; University of Idaho Dairy Farm) using a pilot scale auger pyrolysis unit (100 mm diameter, 450-500 °C, 20 kg h<sup>-1</sup>) as described by Han et al.<sup>21</sup> The condensed 9 10 fluids were stored frozen and then adjusted to room temperature before measurement. Both fluids 11 were visibly non-homogeneous, having separated into two phases, one primarily aqueous and one 12 organic, and vigorous attempts to adequately mix them were unsuccessful. The pine oil was dark 13 in appearance and smelled like pinene. The manure oil was dark in appearance and had an 14 objectionable odor with notes of cigarette butts and fresh asphalt. In both fluids, we observed phase 15 separation into a light brown aqueous layer and a nearly black, sticky, more viscous organic layer. 16 Both fluids showed a tendency to form a frothy top layer after mixing.

We attempted to mix the fluids by first placing them into one-gallon (nominal) uncoated steel paint cans. We added a handful of clean stainless steel nuts to each can to aid in agitation and mixed each can with a commercial paint shaker. This mixing operation was not effective at homogenizing the fluids.

While we were loath to change the composition of the bulk fluids, we attempted chemical homogenization by adding a surfactant to a small aliquot. We conducted a test combining a small sample of organic phase from the manure oil with 1% (mass/mass) cetyltrimethylammonium bromide (a cationic surfactant) dissolved in a roughly equal volume of water. We found that the surfactant did have a minor effect on promoting mixing; however, even with the application of heat to the oil-water-surfactant mixture, most of the organic material remained in a sticky layer separate from the water phase. Insufficient sample was available for testing additional surfactants or other means of homogenization. This led us to develop a curve offset method that can be applied to ADC measurements.

7

8 2.2. Advanced distillation curve

The ADC protocol has been described in detail in previous publications.<sup>1-4</sup> The result of an ADC 9 10 measurement is a temperature-volume-composition data matrix that includes two temperatures, 11 the kettle temperature  $(T_k)$  and head temperature  $(T_h)$ , and a composition analysis for each DVF. 12  $T_k$  is the thermodynamically consistent value characteristic of the remaining mixture in the kettle 13 as distillation progresses. As in prior work on crude petroleum and pyrolysis oils, the temperatures 14 we report have been adjusted to standard atmospheric pressure (101.325 kPa) using the modified 15 Sydney Young equation in which the constant term was assigned a value of 0.000109 (corresponding to a hydrocarbon chain of 12).<sup>22-25</sup> We acknowledge that the composition of these 16 17 fluids deviated significantly from dodecane, especially in the aqueous region of the distillation 18 curve; however, applying the Sydney Young constant for water (0.000099) results in negligibly 19 different (< 1 °C) corrected temperatures. Applying the Sydney Young constant for phenol 20 (0.000107), sometimes used as a pyrolysis fluid model compound, results in < 0.2 °C differences 21 in corrected temperatures. Taking all of this into consideration, we chose to continue using the 22 constant value 0.000109, as it enables us to most directly compare the results to the distillation curves of relevant previously measured crude oils for which the same constant was used.<sup>24</sup> For 23

each of three replicate distillation curve measurements, a starting volume of 200 mL was measured
 by automatic pipette.

The uncertainty in our pressure measurements was 0.03 kPa, including uncertainty in the calibration with a corrected, fixed cistern mercury barometer. The uncertainty associated with temperature measurements was 1 °C, including uncertainty in calibrations with fixed point cells.<sup>26</sup> The uncertainty in the volume measurements used to determine distillate volume fraction was 0.05 mL.

8

#### 9 **3. Results and discussion**

#### 10 <u>3.1. Karl Fischer coulombic titrimetry</u>

11 Because we observed an obvious separation between aqueous and organic phases, it was 12 important to determine the water content of both crude pyrolysis oils. Each phase of the composite oils was measured separately, in triplicate, using the Karl Fischer coulometric titration method.<sup>27</sup> 13 14 Samples were introduced by chromatographic syringe (5  $\mu$ L for the aqueous phases and 2  $\mu$ L for 15 the organic phase). The organic fraction of manure oil was too viscous (even at elevated 16 temperature) to introduce reproducibly to the titration cell, so we do not report a moisture value. 17 As we suspected, the aqueous fraction of both oils contained more than 80% water by volume. 18 Table 1 details the results. These measurements are consistent with our later findings using ADC. 19

20 Table 1. Water content (% volume) for each fraction of both crude pyrolysis oil. The manure

21 oil's organic fraction was too viscous to make a measurement. The upper and lower values

22 provided are based on expanded (k = 2) uncertainty.

 Aqueous fraction
 82.1 % ± 1.6 %
 83.1 % ± 1.6 %

 Organic fraction
 12.6 % ± 1.4 %
 83.1 % ± 1.6 %

1

2 3.2. Raw distillation curve results

3 The raw distillation curve data are presented in Figure 1 and Table S1 in Supplementary 4 Information. The fluids boiled near 100 °C (vaporization of the aqueous phase) for a significant 5 portion of the total distillation volume before markedly increasing at the onset of vaporization of 6 the organic constituents, the point we call the water-organic inflection. As the plots show, the 7 amount of water varied significantly among replicates of the same fluid, which indicated that the 8 fluids were not successfully homogenized. Had they been, the DVF of the water-organic inflection 9 would have been repeatable. The high-boiling region after the water-organic inflection is due to 10 the vaporization of the organic fraction.

11 It is important to note that the distillation temperatures of the low-boiling region were not 12 perfectly constant and were also slightly elevated above the boiling temperature of pure water. 13 This could indicate the presence of impurities in the aqueous phase, a phenomenon which we observed in previous analysis of liquors from an ethanol plant.<sup>28</sup> The impurities causing the 14 15 elevated boiling temperatures could be either organic compounds that do mix easily with water 16 (like acetic acid, the pyrolysis byproduct we observed in large quantities in samples from the pine 17 oil's aqueous region) or simply compounds from the organic phase that have similar boiling points 18 to water (like the 2-butenal present in the aqueous region of the pine oil). Indeed, the first drop 19 (0.025 % DVF) of both fluids contained light organic compounds insoluble in water, for example, 20 toluene, ethylbenzene, and propane.

Each replicate distillation was conducted until a solid residue resembling bio char was observed in the boiling flask. At this point, no further distillation could occur. We observed smoke formation in the distillation head at high temperatures during distillations of both fluids, which also signified the end of the distillation and may be evidence of thermal cracking.

5





Figure 1. The raw distillation data (presented in terms of  $T_k$ ) of pine oil (top) and manure oil (bottom) are overlaid to show the variability in the size of the low-boiling region. Data points at 0 % DVF represent the vapor rise or initial boiling temperature (IBT) of each replicate. Uncertainty is discussed in the text. A thermocouple failure during one pine oil distillation caused us to exclude that replicate, and limited sample prevented an additional measurement.

### 8 3.3. Offset procedure

9 Since the data showed that, sample to sample, we were not measuring the same mixture, we have 10 attempted to correct for the water content variability by applying an offset at the water-organic 11 inflection to the replicate distillations. Overlaid curves in Figure 2 show that, once this shift is 12 applied, the characteristic distillation curve shape and boiling range for each fluid becomes 13 apparent. Our method for conducting the offset was to select a water-organic inflection point on 14 each curve such that the largest number of data points remained in the organic region while 15 permitting the best agreement between replicates.

1 This manipulation imposes limitations on the analysis of the data; however, by applying 2 the same procedure to previously measured ADC data, we are able to draw comparisons to another pyrolysis oil, made from swine manure, that also contained some water.<sup>9, 18</sup> Contrary to the present 3 4 samples, the swine manure oil either existed as a single phase or as a stable emulsion, despite 5 significant water content. As is typical for pyrolysis fluids made from biomass, the swine manure 6 oil was composed of nitrogenated and oxygenated species as well as paraffins in the organic phase. 7 In Table S3, it can be seen that the organic phase of the pine and manure oils had similar 8 composition. Both fluids measured here were reasonably similar in boiling range to the swine 9 manure pyrolysis oil. The offset pine and manure oil curves were also comparable in boiling range 10 to previously measured two crude petroleum oils, one extracted from oil sands in Canada ( $T_k$  = 100-476 °C) and one North American crude oil from a Wyoming refinery ( $T_k = 74-392$  °C).<sup>24, 29</sup> 11 12 It is important to note that while the boiling ranges and component molecular weights of these oils 13 are similar, the chemical composition of the pyrolysis fluids (Table S3) was significantly different 14 from petroleum crude oils, which are overwhelmingly composed of hydrocarbons. The pyrolysis 15 fluids we report on would require extensive processing to resemble these petroleum crude oils in 16 other respects important to their use as petroleum replacements or blend stocks.



2

3 Figure 2. An offset has been applied to the horizontal axis of the distillation curves (the distillate

• Replicate 1 (30%) Replicate 2 (60%)

 $\land$  Replicate 3 (40%)

40

Volume after water departure, mL

• Swine manure pyrolysis oil (Ott et al. 2008)

60

80

4 volume) for pine oil (top) and manure oil (bottom) to account for the variability in the initial

200

150

100

0

amount of water included in each replicate aliquot. The percentage in parentheses next to each
legend entry represents the % DVF from the original measurements where the curves have now
been offset to begin. We have compared the results to a previously-measured crude pyrolysis oil
made from swine manure.<sup>9</sup> Uncertainty is discussed in the text.

5

#### 6 3.4. Challenges and opportunities

7 Several difficulties arose during our data analysis, and we have considered ways to improve the 8 procedure for measuring the distillation curves of non-homogeneous fluids in the future. First, the 9 resolution on the horizontal (distillate volume) axis of the distillation curve was not fine enough 10 to precisely pinpoint the starting temperature for the offset curves. In this context, resolution refers 11 to the granularity or fineness of the temperature data grid (the number of and separation between 12 temperature-volume pairs). Because the last of the water boiled off between recorded data points, 13 there was a limit to the effectiveness of the offset procedure; for example, even after shifting there 14 remained considerable difference among the replicates of manure oil at the 10 mL volume (Figure 15 2). The offset procedure could be made more precise by taking temperature measurements at 1 % 16 DVF increments, especially in the transition zone between the low and high boiling regions. These 17 additional data would make the distillation curve more continuous and allow for a more precise 18 location of the water-organic inflection. Insufficient sample remained after these measurements 19 were done to allow testing of this approach.

Second, in the future, the composition-explicit data channel provided by the ADC method could also be utilized to identify the correct offset. If samples were collected during every replicate distillation, an appropriate offset in composition space could be determined by requiring the composition, including water content, of each DVF to be comparable among all the replicates

within a given uncertainty. Importantly, the ADC is the only method that offers this ability to fix 1 2 the distillation curve of a non-homogeneous mixture in the composition dimension.

3

Finally, a solution that might avoid the need for an offset at all is to use a membrane 4 separation to remove the water prior to distillation without materially changing the composition of 5 the organic fraction. Again, sample availability prohibited a test of this method.

6

#### 7 3.5. Fluid composition

8 In addition to the ADC measurement, we analyzed the composite (undistilled) organic 9 fractions by gas chromatography coupled to mass spectrometry (GC-MS) for insight into their bulk 10 composition. The GC-MS methods used are given in Table S2. Table S3 summarizes the major 11 components of the composite organic fractions, both of which were complex mixtures. Over 70 12 compounds were identified in the pine oil, and several of them were indicative of the feedstock, 13 ponderosa pine shavings, used to make the oil. Substituted phenols such as creosol, catechol, and 14 vanillin were abundant; the literature suggests that these represent the decomposition of lignin, the heterogeneous biopolymer that primarily composes plant material.<sup>30</sup> We also found a sugar 15 16 derivative, levoglucosan, which may have formed from the depolymerization of cellulose and hemicellulose.<sup>31</sup> A heavier component consistent with the feedstock, dehydroabietic acid, was also 17 18 present in the composite oil. Like the pine oil, the main peaks detected in the manure oil also 19 included phenols. Notably, the organic fraction of the manure oil also contained long-chain nitriles, 20 long-chain fatty acids, fatty acid methyl esters and thiols. The presence of oxygen and other 21 heteroatoms in these fluids is typical for biomass pyrolysis, and removal of these species by upgrading is an active area of research.<sup>32</sup> 22

1 3.6. Conclusion

2	The replicate distillation curves of two non-homogeneous crude pyrolysis fluids, made
3	from pine shavings and dairy manure, were complicated by variable water content in each aliquot.
4	We devised an approach to the data analysis to correct for the variability among the samples and
5	elucidate a coherent distillation curve that can be compared to the experience base of previously
6	measured crude oils. The water-organic inflection is the crucial data point driving the distillation
7	curve offset procedure. The high-boiling regions of the distillation curves were comparable in
8	temperature range and curve shape to a previously measured homogeneous crude pyrolysis oil.
9	Finally, the composition of each fluid was determined; some components were indicative of the
10	feedstock used in their production.
11	

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1			
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2	Table S1. Distillation curve data for (a) the manure oil and (b) the pine oil. Due to problems
3	achieving sample homogeneity, these distillation curves have not been averaged, as is typical;
4	instead, temperatures from all replicates are given in series, separated by commas. Asterisks (*)
5	indicate that for the given replicate, the distillation ended prior to the given DVF. The
6	uncertainties associated with temperature and pressure are discussed in the text. These
7	temperatures have been adjusted to 101.325 kPa (1 atm) with the modified Sydney Young
8	equation; the constant term was assigned a value of 0.000109. The experimental atmospheric
9	pressures are provided to allow recovery of the actual measured temperatures.

	(a) Manure oil essure (kPa) 83.87, 83.99, 83.45	
Pressure (kPa)		
DVF (%)	T <sub>k</sub> (°C)	$T_h$ (°C)
5	106.2, 102.3, 107.1	101.7, 99.7, 100.3
10	106.7, 102.9, 108.0	100.7, 100.1, 100.6
15	107.8, 103.3, 110.2	103.5, 100.3, 101.5
20	109.5, 103.9, 109.2	103.7, 100.8, 102.0
25	117.1, 104.1, 109.9	105.0, 101.0, 102.6
30	238.7, 104.5, 113.0	152.1, 101.2, 103.4
35	297.7, 105.4, 118.2	221.3, 101.4, 104.6
40	326.4, 105.6, 171.5	230.8, 101.9, 118.1

45	362.6, 106.7, 275.2	265.5, 102.4, 201.1
50	387.0, 108.7, 325.6	265.8, 103.5, 258.8
55	409.6, 117.8, 355.8	265.3, 106.8, 279.2
60	447.9, 176.8, *	260.3, 139.5, *
65	*, 271.7, *	*, 197.5, *
70	*, 341.6, *	*, 251.7, *
75	*, 396.3, *	*, 254.1, *

	(b) Pine oil	
Pressure (kPa)	82.99, 83.30	
DVF (%)	T <sub>k</sub> (°C)	$T_{h}(^{\circ}C)$
5	102.2, 101.3	99.8, 99.7
10	102.9, 101.4	100.1, 100.0
15	103.4, 101.5	100.2, 100.2
20	103.4, 101.6	100.4, 100.4
25	104.1, 101.8	100.8, 100.5
30	104.7, 101.9	101.1, 100.6
35	105.9, 101.9	101.2, 100.7
40	109.2, 102.1	103.2, 101.0

45	172.9, 102.4	106.0, 101.1
50	270.2, 102.6	101.2, 101.2
55	*, 102.6	*, 101.8
60	*, 102.9	*, 102.3
65	*, 103.5	*, 103.3
70	*, 104.3	*, 103.7
75	*, 105.4	*, 104.4
80	*, 110.1	*, 105.0
85	*, 148.7	*, 121.3
90	*, 260.7	*, 155.2

1 Table S2. Summary of GC-MS methods used to characterize the fuels.

Fuel	Method	
Manure oil	30 m, 5 % phenyl polydimethylsiloxane column with a coating thickness of 0.1 $\mu$ m;	
	50:1 split, manual injection, temperature of injector = 275 °C at 55 kPa (8 psi) head	
	pressure, injection volume = 0.2 $\mu$ L, column temperature of 35 °C for 1 min,	
	followed by temperature program at 7 °C/min to 250 °C; hold for 2.5 min; scan m/z	
	from 29 to 1000	
Pine oil	30 m, 5 % phenyl polydimethylsiloxane column with a coating thickness of 0.1 $\mu$ m;	
	100:1 split, manual injection, temperature of injector = 325 °C at 55 kPa (8 psi)	
	head pressure, injection volume = 0.2 $\mu$ L, column temperature of 35 °C for 2 min,	
	followed by temperature program at 5 °C/min to 285 °C; hold for 5 min; scan m/z	
	from 29 to 1000	

Table S3. Summary of the major components in the composite organic fractions. Components found
 in the organic fractions of the manure oil (a) and pine oil (b) are ordered by retention time (RT) in minutes.
 The instrument response to each compound was not calibrated, and percentage abundance presented below

4 is based on raw area counts only.

(a) Manure oil			
RT	Peak Identity	Area (%)	
12.16	phenol	4.9	
12.35	acetaldehyde, methyl(2-propynyl)hydrazone	3.4	
13.57	cyclohexanone, 3-methyl-	1.2	
13.76	2-cyclopenten-1-one, 2,3-dimethyl-	3.8	
14.63	phenol, 3-methyl-	4.9	
15.41	cresol	3.3	
15.47	phenol, 2-methoxy-	19.9	
16.19	phenol, 2,3-dimethyl-	2.5	
17.49	1H-indene, 3-methyl-	3.3	
17.68	phenol, 3,4-dimethyl-	3.2	
18.32	phenol, 4-ethyl	3.9	
18.84	creosol	4.6	
20.38	2,3-dimethylanisole	4.0	
21.41	phenol, 4-ethyl-2-methoxy-	6.7	
21.98	tridecane	2.3	
22.43	2-methoxy-4-vinylphenol	4.9	
23.63	eugenol	2.7	
23.92	phenol, 2-methoxy-4-propyl-	1.5	
24.51	tetradecene	2.3	

24.72	tetradecane	1.2
26.11	isoeugenol	3.4
27.12	pentadecene	1.5
29.59	hexadecene	1.2
32.79	1-dodecanol, 3,7,11-trimethyl-	1.1
37.74	hexadecanoic acid	4.2
41.58	octadecanoic acid	4.0

# (b) Pine oil

RT	Peak Identity	Area (%)
0.72	propane	2.1
0.76	methanol	0.9
0.87	acetone	1.8
1.12	acetaldehyde, hydroxy	7.9
1.20	acetic acid	5.7
1.33	acetic acid	11.1
1.59	2-propanone, 1-hydroxy	15.1
2.71	propanoic acid	22.3
2.94	1-hydroxy-2-butanone	0.7
3.17	succindialdehyde	4.9
4.21	furfural	0.2
4.32	3-methyl furan	1.0
8.72	phenol	2.9
9.99	1,2-cyclopentanedione, 3-methyl	1.6
11.28	octanol	7.9
11.80	phenol, 2-methoxy	2.8

14.98	creosol	1.5
15.57	catechol	3.6
17.52	phenol, 4-ethyl-2-methoxy	0.9
21.03	vanillin	1.5
22.19	phenol 2-methoxy-5-(1-propenyl)	1.0
23.27	levoglucosan	1.9
42.31	dehydroabietic acid	0.6
44.62	dioctyl ester hexanedioic acid	0.2