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Extension of the DSC Method to Measuring Vapor Pressures of Narrow Boiling Range Oil Cuts

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Declaration:
Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology, has not been previously submitted for doctoral or equivalent academic degree.

Carmen Siitsman

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DSC meetodi arendamine õlide kitsaste keemistemperatuuri vahemikega fraktsioonide aururõhu mõõtmiseks

CARMEN SIITSMAN

TTÜ KIRJASTUS

Contents

List of Publications

The present doctoral thesis is based on the following original publications referred to by Roman numerals I-III in the text:

I Siitsman, C., Kamenev, I., Oja, V. (2014). Vapor pressure data of nicotine, anabasine and cotinine using differential scanning calorimetry. – Thermochimica Acta, 595, 35-42.

II Siitsman, C., Oja, V. (2015). Extension of the DSC method to measuring vapor pressures of narrow boiling range oil cuts. – Thermochimica Acta, 622, 31-37.

III Siitsman, C., Oja, V. (2016). Application of a DSC based vapor pressure method for examining the extent of ideality in associating binary mixtures with narrow boiling range oil cuts as a mixture component. – Thermochimica Acta, 637, 24-30.

Author’s Contribution to the Publications

I The author carried out the experimental study, developed experimental procedure and analysed obtained data and wrote of the paper.

II The author carried out the experimental study, developed experimental procedure and analysed experimental results and participated writing of the paper.

III The author carried out the major part of the experiments, participated in the interpretation of the results and writing of the paper.

Introduction

Oil shale, a sedimentary rock rich in organic matter, is a potential source of transportation fuels and chemicals (resources estimated to be equivalent to 4,700 billion barrels of oil (Dyni, 2003)). Since the organic matter in oil shales is mostly in the form of kerogen (crosslinked macromolecular organic matter), in order to commercially produce liquid fuels or chemicals the kerogen must first be broken down to oil in the thermochemical process known as pyrolysis. Industrially this is called retorting, and the retorting process could then be followed by various upgrading processes to produce higher value fuels and chemical products. In these technological steps, and also in product development and handling, reliable thermodynamic data of the narrow boiling point cuts (so-called pseudocomponents) are of importance. Among others, one important type of information is vapor pressure data and related volatility parameters (heats of vaporization, atmospheric boiling points). Vapor pressure data for oil and oil fractions provide information which can be used for calculations related to design, refinery operations, safety, transportation and environmental exposure. Here it should be mentioned that a literature review indicated that there is a lack of thermodynamic data, including vapor pressure data, for shale oils (Oja et al., 2016). For example, some vapor pressure data on wide boiling range fractions of Estonian shale oil can be found in the review published by Kollerov in 1951 (Kollerov, 1951). However, the data are not systematic, from the point of view of modelling, and information concerning the method used for measuring the vapor pressures is deficient.

Although there are a number of methods available in the open literature, both standardized and non-standardized, for measuring vapor pressures of pure compounds and multicomponent solids and liquids, not all of them are suitable or reasonable to use for oil products. In searching for alternative convenient methods to measure the vapor pressures of oil cuts, the capabilities of the standardized method “Standard Test Method for Determining Vapor Pressure by Thermal Analyses (ASTM E 1782)” triggered our interest. This method appears to be one of the widely used and robust methods for measuring the vapor pressures of pure compounds using a small amount of material. In the application of the method a differential scanning calorimetry (DSC), rather than thermogravimetry (TG), is dominantly used. Advantages of the ASTM E 1782 method are the worldwide availability of commercial equipment (DSC instrument) and the very small sample size. This benefit is important, for example, for laboratories where modelling is of interest. There is also no need for degassing, as is usually required in the application of static methods. In addition, the standard test method has broad pressure and temperature ranges, and these ranges may be extended even more when some extra modifications are made.

The basis of the present thesis was a hypothesis that application of the ASTM E 1782 method for measuring the vapor pressures of pure compounds, but also of binary systems (application not standardized), can be extended with some improvements for measuring vapor pressures of oil fractions with narrow boiling ranges. The thesis addresses two related issues (uncommon applications of the DSC based method or the ASTM E1782 approach):

1) to evaluate potential of and to propose ways to improve the DSC based ASTM E 1782 method for application in the area of measuring vapor pressures of narrow boiling shale oil fractions (as pseudocomponents);

2) as a step further to evaluate the potential of the method for measuring the total vapor pressure of binary mixtures where at least one of the mixture components is a narrow boiling range distillation cut.

The oils used in this experimental study were oil shale oils that are rich in phenolic compounds. They were produced from Kukersite oil shale from Estonia. Narrow boiling range fractions were distilled from industrially produced gasoline (atmospheric boiling range from about 50 to 200 ^{o}C) and middle oil (atmospheric boiling range from about 200 to 500 ^{o}C) “straight run” fractions.

Abbreviations

ASTM	American Society for Testing and Materials
ARD	average absolute relative deviation
CAS no	Chemical Abstracts Service Registry number
DSC	differential scanning calorimetry
ERAVAP	name of commercial static vapor pressure tester
FTIR	Fourier-transform infrared spectroscopy
IUPAC	International Union of Pure and Applied Chemistry
MW	molecular weight
RD	relative deviation
TGA	thermogravimetric analysis

Symbols

A, B, C	Antoine constants
k	coverage factor
n	number of measurements
P	pressure (kPa)
$P_{measured}$	pressure measured by DSC
P_R	pressure estimated by Raoult´s law (kPa)
R	ideal gas constant (J mol^{-1} K^{-1})
T_b	boiling temperature (K)
T_b^{DSC}	initial boiling temperature by DSC (K)
T_b^{TGA}	average boiling temperature by TGA (K)
T_c	critical temperature (K)
U(x)	combined standard uncertainty
wt	weight
X	reference value
x	experimental value
ΔH_{vap}	heat of vaporization (J mol^{-1})
ρ	density at 293.2 K (g cm^{-3})
$u(x)$	combined standard uncertainty
$u_a(\bar{x})$	*Type* A uncertainty
u_b	*Type B* uncertainty
Δ_0	absolute error or resolution of the sensor
$\bar{x}$	mean experimental value

1 LITERATURE OVERVIEW

The present PhD thesis is concerned with possibilities for extending application of the DSC based “Standard Test Method for Determining Vapor Pressure by Thermal Analyses (ASTM E 1782)” to measuring the vapor pressures of narrow boiling shale oil fractions and their binary mixtures. Therefore, this chapter is aimed to give insight into current knowledge of shale oil thermodynamic properties, of the vapor pressure determination methods for oils, and of the use of DSC for vapor pressure measurements.

1.1 Kukersite shale oil

Shale oil is an unconventional oil produced from oil shale, a sedimentary rock containing organic matter, mostly in the form of macromolecular kerogen. The oil is produced via the pyrolysis process (retorting process) (Savest et al., 2007; Oja and Suuberg, 2012; Kilk et al., 2010). As the kerogen is insoluble macromolecular organic matter, then thermochemical conversion technologies are currently the only industrial routes to convert the energy from oil shale to more concentrated forms, including the “synthetic crude oil” shale oil (Oja and Suuberg, 2012; Hruljova and Oja, 2015; Hruljova et al., 2014). Oil shale resources in the world have been estimated at about 2.8 to 3.3 trillion barrels of oil. The leading shale oil producers are China (7600 barrels p/day), Estonia (6300 barrels p/day), and Brazil (3800 barrels p/day). (Dyni, 2003) Part of the produced oil can be used directly as a heating fuel; however, for higher value motor fuel or chemical products it should go through an upgrading process.

Shale oil has been produced in Estonia for almost a century using various retorting technologies (Oja, 2006; Oja, 2007). The technologies used industrially have been the Kiviter process (retort generators; in use since 1925), tunnel ovens (1926-1980), Davidson rotating retorts (1931-1961), chamber ovens (1948-1987) and the Galoter process (solid heat carrier retorts; used since 1963). The oil shale used for shale oil production contains high oil yield thermally softening kerogen, i.e. Kukersite oil shale (Savest et al., 2009; Hruljova et al., 2013). The other oil shale found in Estonia, Dictyonema black shale, contains low oil yield thermally non-softening kerogen (Kilk et al., 2010). Dictyonema oil shale is not utilized for shale oil production (Oja, 2007).

Nowadays in Estonia there is a trend towards using the improved and more environmentally friendly Galoter based technologies (Opik et al., 2001; Golubev 2003), such as Enefit (Eesti Energia AS) or Petroter (Viru Keemiagrupp AS).

Depending on the retorting technologies and process conditions used, the properties and composition of the shale oil produced can vary considerably from a thermodynamic property point of view (Qian and Yin, 2010). Therefore, earlier information on the thermodynamic properties from the 1950s and 1960s is not suitable for current design requirements. Moreover, a recent literature review indicated that for thermodynamic properties of Kukersite shale oils only a small amount of data exists in the public literature, and the scattered data, which mostly originates from before the 1960s, is poorly suited for the evaluation of thermodynamic property prediction methods (Oja et al., 2016; Savest and Oja, 2013).

Thermodynamic properties of shale oils

In the design of processes and industrial equipment the physical and thermodynamic properties of shale oil, together with suitable thermodynamic models and property prediction tools, are required. Depending on the property, small errors in calculation (property estimation) can lead to large errors in the construction of industrial processes.

In the estimation of the thermodynamic properties of oils for industrial design purposes the pseudocomponent approach is often used, whether as an independent approach or in some combination with more advanced thermodynamic tools/models. According to this approach oils are presented as consisting of pseudocomponents – narrow boiling range oil fractions that are described with average parameters. For petroleum it has been found that to predict the thermodynamic properties of lighter petroleum fractions (molecular weight less than 300 g/mol and boiling point Tb less than 350 ^{o}C), at least two input parameters (average parameters of pseudocomponents) are needed – one describing molecular size and the other molecular energy (Riazi, 2005). In most cases, average boiling point and specific gravity are used as the two input parameters.

In regard to Kukersite shale oil, the recent review of physical and thermodynamic properties published by Oja et al. (2016) indicated that relatively little systematic experimental data can be found for Kukersite shale oil, even for applying pseudocomponent approach. Moreover, most of the measurements date back to a time period from 1930 to 1960 (Kogerman and Kõll, 1930; Luts, 1944; Kollerov, 1951). In summary, the experimental data for Kukersite shale oils are available as basic physical and thermodynamic properties (such as specific gravity, atmospheric boiling point, molecular weight, enthalpy of vaporization at the boiling point, viscosity, vapor pressure, etc.) and the data are for Kukersite shale oils from the Kiviter, tunnel and chamber oven processes. It is important to notice that the oil fractions studied were characterized using only a limited number of average parameters (i.e. the undefined mixture method) and that no supportive chemical characteristics (elemental composition, amount of functional groups or compound classes) were given for the fractions studied.

It can be brought out here that, other than boiling points, data about vaporization properties, such as vapor pressure and heat of vaporization, are extremely limited and non-systematic. And this is despite the fact that vapor pressure is required in many calculations related to the modelling of oil shale pyrolysis and upgrading processes (Oja et al., 2015), in safety and product handling (Traumann et al., 2014), as well as in design and operation of various units. Some data can be found from the historical book by Kollerov (Kolerov, 1951), and some issues with that data have been addressed in some later publications (Oja, 2005; Oja, 2015).

1.2 Overview of vapor pressure determination methods for oils

When it comes to oil fractions, whether derived from petroleum, coal or oil shale, then in the open literature the published vapor pressure datasets are quite limited. For example, Gray et al. (1983 and 1985) measured vapor pressures of narrow boiling coal liquid fractions using high pressure static and ebulliometric methods; Schwarz et al. (1987) have successfully measured vapor pressures of heavy fossil fuels up to 300 ^{o}C using a simple ebulliometer; Castellanos-Diaz et.al, (2013) measured vapor pressures of heavy oil and bitumen using a high vacuum static apparatus. Also, the nonisothermal Knudsen effusion method has been applied to roughly evaluate the vapor pressure behavior of various pyrolysis tars (coal (Suuberg and Oja, 1997; Oja and Suuberg, 1998), oil shale oil (Oja, 2015), cellulose (Oja and Suuberg, 1997), tobacco (Oja and Hajaligol 2001; Shim et al., 2003) under high vacuum conditions. As can be seen from these examples, in practice there are various methods for measuring the vapor pressure of oil-like and tar substances (Gray et al., 1985; Oja and Suuberg, 1998; Oja et al., 2009; Castellanos-Diaz et al., 2013). However, for well-defined systems such as pure compounds or few component mixtures, there is a larger variety of vapor pressure methods and measurement setups available (Oja et al., 2009). In reviews, these existing vapor pressure measurement methods are often divided into a variety of groups, but their differences can be considered subjective as there are various grouping possibilities. Therefore, in the short overview here the emphasis is not placed on classification, but rather on just briefly presenting methods suitable for oil vapor pressure measurements.

In static methods the vapor pressure is directly measured in a closed vessel (i.e. the sample does not leave the equilibrium cell) at constant temperature using a pressure gauge. In many cases the static vapor pressure apparatus is self-designed and constructed by researchers and engineers. The main advantages of the static vapor pressure method are the high accuracy of the data obtained, good repeatability and temperature stability. One disadvantage is that the partial pressure of the air dissolved in the sample must be taken into account. The accuracy of results depends greatly on the quality of the degassing procedure. There are also ASTM test methods based on static methods that are widely used all over the world. For example, ASTM methods D 323 (Reid method), D 4953 (Dry method), and D 5191 (Mini method) cover procedures for automatic vapor pressure instruments and the determination of the total vapor pressure at only 37.8 ^{o}C. ASTM methods D 6377 and D 6378 are suitable for temperature ranges up to 100 ^{o}C and pressures up to 500 kPa. The limited temperature and pressure ranges of these standard methods are sufficient for the quality control of petroleum products, but are not sufficient for scientists and engineers to evaluate or calculate other thermodynamic properties and to design and operate production processes. For petroleum fractions (gasolines and naphtha), laboratories usually report Reid vapor pressure as the main quality characteristic of the fuel.

Another common group is dynamic methods. The dynamic methods consist of continuous separation of the liquid and vapor phase in a stationary regime. Ebulliometry is one of the standardized (ASTME E1719) dynamic methods which is suitable for vapor pressures of liquids in the range of 1.0 to 101.33 kPa (atmospheric boiling points 10-300 ^{o}C). The accuracy of the data is lower than that obtained by the static method because during experiments a stationary state is obtained instead of the real thermodynamic equilibrium. In addition, an ebulliometer needs a relatively large amount of the sample.

Some more methods can be suitable for vapor pressure measurements of oil fractions, such as gas saturation under ASTM E119 (can also be viewed as a dynamic method), isoteniscope (can be grouped with the static methods) under ASTM D-2879 or the effusion methods (Montemayor, 2008).

In summary, there is no single vapor pressure measurement procedure for the entire range of vapor pressures of industrial interest. For example, dynamic methods (pressure from 1 up to 100 kPa or higher) usually have a more limited pressure range than static methods (from 0.01 kPa up to critical pressures). In addition, each technique has its own advantages and disadvantages related to, for example, coverable temperature region, coverable pressure region, sample size, measurement timescale, expensiveness, complexity, or directness of data analysis (can the pressure be measured directly or is it calculated indirectly from a measured parameter).

1.3 Application of DSC for vapor pressure studies

The search for a robust and easy to use vapor pressure determination/measurement method that is applicable for broad pressure and temperature ranges (as is needed with narrow boiling shale oil cuts), and at the same time allows to use small amounts of sample, led to the idea to test the suitability of the differential scanning calorimetry (DSC) vapor pressure method. This vapor pressure method is standardized for pure compounds (ASTM E1782) has several advantages – it can use very small sample sizes (in total 100-200 µg) and span a broad pressure range (recommended from 5 kPa to 2000 kPa) and temperature range (depends on the specific instrument and sample behavior). In addition, there is no need for degassing the samples and commercial DSC equipment can be used. Moreover, although the standardized procedure is for pure compounds, the method has been extended successfully to binary systems (Falleiro et al., 2010 and Silva et al., 2011-I) and also to multicomponent systems with a single dominating compound (Hazra et al., 2004).

According to the experimental procedure of the DSC method a single vapor pressure datapoint is determined during an experimental run. The datapoint is determined as the onset of the vaporization peak on a DSC thermogram. During a run the sample is heated at a constant rate and the sample evaporates through a pinhole in an otherwise hermetically sealed container at a specified pressure. The vapor pressure curve is obtained by determining a number of boiling points at various pressures in separate experiments.

According to ASTM E1782 "Standard Test Method for Determining Vapor Pressure by Thermal Analyses" the recommended parameters for pure compound vapor pressure measurements is as follows: a heating rate of 5 K/min; sample size of 1-5 mg for solids and 1-5 µl for liquids; a pinhole size smaller than 125 µm; a lower pressure limit of 5 kPa; an upper pressure limit of 2000 kPa.

However, in addition to the advantages named above (wide temperature range, wide pressure range, small sample size, no need for degassing), the method has one major disadvantage – getting a full vapor pressure curve is time-consuming (can take several days). Measuring a single vapor pressure point takes a maximum of about 2 hours (sample preparation, purging, heating, cooling), including a maximum of 1 hour for the sample heating step. Also, it is important to note that ASTM E1782 is considered a less precise method as temperature determination from thermograms is not as accurate as temperature measurements in many other vapor pressure techniques (static methods).

The *Paper II* gives the historical overview of the application of DSC for vapor pressure measurements as of 2014 with a specific focus on the critical evaluation of the potential of the method *(Table 1, Paper II)*. Table 1.1 here, which is an improved version *of Table 1 from Paper II*, presents a summary of the studies on application the DSC technique for vapor pressure measurements as of 2018 (including *Papers I-III* of the current PhD Thesis). The important conclusion from Table 1.1 is that there has been continuous activity towards extending the method's application area outside conditions recommended in ASTM E 1782. Similarly, the present PhD thesis addresses extension of the DSC based method (or the ASTM E1782 approach) towards two uncommon application areas: (1) extension of the DSC method for measuring the vapor pressures of narrow boiling shale oil fractions; (2) extension of the DSC method for measuring the total pressure of binary systems where at least one of the mixture components is a narrow boiling range distillation cut.

Table 1.1. Overview of the use of DSC in the literature for vapor-pressure measurements (including Papers I – III of the current PhD Thesis, in bold)

Reference	**Test material**	**Heating rate ($K\ min^{-1}$)**	**Pressure range (kPa)**	**Pinhole size (µm)**	**Notes (N) / Performance (P)**
Morie et al., 1972	hexane, chlorobenzene, ethyl propionate, octyl alcohol, nitrobenzene	10	2.7 – 98	N/A	N: Corborundum powder added as an inert material to reduce overheating and to increase the surface area of the sample. P: Deviation from literature values was 1.2 K. Average relative error of ΔH_v was 8.5%.
Seyler, 1976	water, isopropyl alcohol	10 – 20	0.013 – 1333	≤ 800	N: Recommended optimal parameters for TGA and DSC techniques. Samples of 1-15 µl are advised. Small samples and heating rates that are too slow influence the accuracy of measurements due to vaporization of the sample prior to the boiling point. Sample sizes that are too large results in super-heating and partial self-cooling. P: Relative error of temperatures in terms of literature values was 2.6%.
Tilinski and Puderbach, 1989	toluene, isopalmitic acid, benzoic acid, dibutyl phthalte, fragrances, stearic acid	10 – 20	0.1 – 100	700 + ball 1.6mm	N: A modification using a large pinhole size with a metal ball over the pinhole was suggested. Small sample sizes or low heating rates cause vaporization prior to boiling. A large sample size results in overheating. An inert material such as silicon carbide should be added. A suitable pressure range of 0.1 to 7000 kPa at temperatures from 243 to 873 K was suggested. P: The measuring accuracy was ±1 K.
Wiedemann, 1991	ethanol and benzoic acid	5	100 – 3000	100	N: Exothermal effect at 3 MPa was determined. This effect was described as aluminium oxidation.[a] P: not evaluated

Perrenot et al., 1992	Water	5	100 – 1890	30 or 50	N: See the comment below the table. [a] P: Not evaluated.
Contreras et al., 1993	propylene glycol, isopropyl palmitate, glycerine	5, 10, 15	0.67 – 3.23	400	N: A pinhole of 400 µm is suitable to use with higher heating rates. P: Not evaluated.
Jones and Seyler, 1994	Pure compounds	5 – 10	7 – 2000	25 – 127	N: Recommended practical measurement parameters based on the ASTM task group studies. Pinholes of ≥ 127 µm give acceptable results when the heating rate is sufficient to avoid unnecessary loss of sample. The quality of the pinhole influences the peak shape. Sample size of 2-4 mg.[a] P: Relative error of vapor pressures of water from literature values was 2.4%.
Casserino et al., 1996	decane, dodecane, tetradecane, aromatic compound, 2 brominated aromatic compounds	5	0.67 – 101.3	75	N: Recommended to use a sample size of 2-3 mg below 2.67 kPa to avoid peak broadening.[a] P: Standard error of estimate of 0.1 to 0.3 K.
Butrow and Seyler, 2003	water, DMMP[c], DIMP[c]	5	0.2 – 101.3	50 – 375	N: Extension of the DSC method for wider pressure ranges. An increased pinhole size below or near 5 kPa gives sharper peaks, but also increases vaporization of the sample prior to boiling. It was proposed that the slope of the leading edge of the boiling endotherm be at least -3mW/K to optimize pinhole size as a function of pressure.[b] P: Accuracy of the method for water was ±1 K.
Hazra et al., 2004	multicomponent mixtures (clove and eucalyptus oil)	5	5 – 35	76 – 254	N: The multicomponent mixtures contained one dominant compound. P: Relative error of vapor pressure was 1-3%.
Füglein and Schmölzer, 2009	4 pure compounds (water, cyclohexane, acetic ether, isopropanol)	10	4.5 – 7000	50	P: Not evaluated.

Falleiro et al., 2010	3 binary mixtures (with stearic, palmitic and linoleic acid)	15 and 25	6.67	250	N: The boiling points of mixtures with different compositions were measured at a constant pressure. P: Standard deviation was of 0.20 K. Uncertainties for temperature and pressure are given.
Silva et al., 2011-I	4 binary mixtures (6 fatty acid ethyl esters)	25	3.99; 5.33 and 9.33	250	N: The boiling points of mixtures with different compositions were measured at constant pressures. P: Absolute deviation was of 0.1-1.9 K. Uncertainties for temperature and pressure are given.
Silva et al., 2011-II	6 selected ethyl esters	25	1.33 – 9.33	250	N: The optimal parameters (heating rate, pinhole size) for lower pressures were determined. P: Uncertainty of 0.4 K, relative deviation of boiling temperatures from literature values was less than 3.5 %.[b]
Falleiro, et al., 2012	n-tetradecane, 5 selected fatty acids	25	1.33 – 9.33	800 + ball 1.0 mm	N: Small ball over a larger pinhole was combined with a higher heating rate. P: Standard deviation of 0.4 K; uncertainties for measured pressures are given. Mean abs. deviation from literature values was 0.6-1.5 K and mean abs. deviation of the Antoine equation was 0.3 K.[b]
Brozena, 2013	water, 1-octanol	5	0.2 – 101.4	75, 175, 250, 350	N: Pinholes of 75-350 µm give sharper endotherms and yield accurate results at lower pressures. The slope of the boiling endotherm leading edge is not a suitable criterion for determining the appropriate pinhole size.[b] P: Mean ΔT ±95% confidence level: 0.54 ± 0.33 K (75 µm pinhole); 0.49 ± 0.59 K (175 µm); 0.36 ± 0.24 K (250 µm); 0.42 ± 0.20 K (350 µm).

Damaceno et al., 2014	Monocaprylin, monocaprin, dicaprylin, dicaprin, α-, β-, γ-, δ-tocopherol	25	1.0-13.2	800 + ball 1.0 mm	P: Average absolute deviations and average relative deviations for temperature are given (Clapeyron, Antoine, DIPPR equations). Uncertainties for temperature and pressure are given.
Siitsman et al., 2014*	nicotine, anabasine, cotinine	5	15 – 1000	50	N: Sample size greatly influenced the slope of the boiling endotherm, especially around 15 kPa and over 250 kPa. Incorrect sample size can change the slope and lower the measurement accuracy. P: The mean absolute temperature error was ±0.4 K, accuracy of the measurement pressure was 1.8%. Expanded uncertainties with a 95% confidence level for temperature and pressure were given.
Siitsman and Oja, 2015*	3 narrow boiling shale oil fractions	5	15 – 750	50	N: Sample sizes for narrow boiling shale oil cuts were 3-17 mg. P: The mean absolute temperature error was ±0.4 K, accuracy of the measurement pressure was 1.8%. Expanded uncertainties with a 95% confidence level for temperature and pressure were given.
Cunico et al, 2015	Monocaprylin + palmitic acid; methyl stearate	25	1.20 and 2.50	800 + ball 1.0 mm	N: Non-ideal behavior was observed at both pressures.[b] P: Thermodynamic consistency tests were calculated. Relative deviations were lower than 0.3% compared to Wilson, NRTL and UNIQUAC model data calculations.
Troni et al., 2016	n-hecadecane, glycerol, octanoic acid, monocaprylin, tributyrin, n-octadecane, n-tetradecane, 1-octadecanol	5 – 30	3.47 – 22.39	800 + ball 1.0 mm	N: Nine different combinations of heating rates and samples sizes were used. The effect of heating rate is the most important (in peak sharpness). Large sample size could compensate pre-boiling vaporization at lower heating rates.[b] P: Relative temperature deviations were lower than 0.8%.

Siitsman and Oja, 2016*	Mixtures of two narrow boiling shale oil cuts and mixture of narrow boiling shale oil cut and pure compound	5	10 – 250	50	N: Preliminary study to evaluate deviation from ideality (Raoult´s law). P: The mean absolute temperature error was ±0.4 K, accuracy of the measurement pressure was 1.8%. Pure compounds: nicotine or 2-tert-butylphenol; mixture of toluene and benzene.
Khoshooei et al., 2018	4 binary mixtures (methanol, isopropanol, cyclohexane, toluene, water)	10	101.3	50	N: Sample temperature instead of the heat flow curve was evaluated. Types of mixtures: aqueous, non-aqueous, highly ideal, azeotrope P: Absolute error less than 0.15% for lower and less than 0.6% for higher pressures. Standard uncertainty u(P)=0.2 kPa, combined standard uncertainty includes calibration uncertainty for u(T)=0.07 K.

[a] Studies were carried out before the ASTM E 1782 – 96 standard was approved. However, the main measurement conditions concerning sample size, heating rate, pinhole diameter and pressure range were the same as suggested later by the standard test method;

[b] Studies that extended the ASTM E 1782 standard below 5 kPa with larger pinholes.

[c] DMMP – dimethyl methyl phosphonate; DIMP - diisopropyl methyl phosphonate.

*Paper presents the results of the current PhD study.

2 EXPERIMENTAL STUDY

The aim of the current PhD study was to evaluate a hypothesis that the DSC based vapor pressure measurement technique (ASTM E 1782) can be extended to narrow boiling cuts of oil and binary mixtures containing such cuts. Three major steps of the research were as follows: to evaluate the performance of the DSC based vapor pressure technique (device and method) of our laboratory using reference chemicals (pure chemicals); to investigate the usability of the DSC method for vapor pressure measurements of narrow boiling cuts of oils and to evaluate the reliability of the proposed DSC approach; to evaluate the use of the DSC method with binary mixtures where at least one of the mixture components is a narrow boiling cut.

Consequently, experimental activities of the present thesis are published in three papers. *Paper I*, titled “Vapor pressure data of nicotine, anabasine and cotinine using differential scanning calorimetry”, was written to present the performance of the DSC based vapor pressure technique (device and method) of our laboratory when applied to pure compounds. In this paper toluene and hexadecane were use as the reference chemicals to test the performance of the DSC method. The tobacco alkaloids, which were examined to provide new property information on these compounds for the scientific community, were L-nicotine, (±)-anabasine and (-)-cotinine.

Paper II, titled “Extension of the DSC method to measuring vapor pressures of narrow boiling range oil cuts”, consisted of two topics: the first aim was to give an up-to-date overview of the method, as of 2014, with a specific focus on critical evaluation of the potential of the DSC method for vapor pressure measurements. The second and primary aim was to evaluate the application of the DSC method to measuring vapor pressures of narrow boiling range oil cuts. In this paper benzene and o-xylene were use as the reference chemicals to test the performance of the DSC method as well as the performance of the commercial ERAVAP static vapor pressure tester. The commercial static vapor pressure tester was used to measure comparable vapor pressure data (using the ASTM D 6379 method) to validate the reliability of the proposed DSC approach.

Paper III, titled “Application of a DSC based vapor pressure method for examining the extent of ideality in associating binary mixtures with narrow boiling range oil cuts as a mixture component”, was used to evaluate application of the DSC method to binary systems where at least one of the mixture components is a narrow boiling range distillation cut. The systems under study were either binary mixtures of two narrow boiling range distillation fractions or of a narrow boiling range fraction and a pure compound. In this paper a 50:50 mol% binary mixture of benzene and toluene was used to test the DSC method for binary mixtures, and nicotine and 2-tert-butylphenol were used to prepare binary mixtures with oil fractions. Nicotine was selected because it contains a nitrogen base and 2-tert-butylphenol because it contains a phenolic functional group. The oil fractions (the pure compounds were mixed with) contained large amounts of phenolic and alkyl-aromatic structures. The oil fractions that contained large amounts of phenolic and alkyl-aromatic structures were mixed with the pure compounds.

In the following section the materials and methods used in the experimental study are described.

2.1 Materials

2.1.1 Pure components

A list of all pure chemicals used in the study, together with notes linking each to corresponding papers of this PhD thesis and major information (chemical supplier, CAS number, purity, molecular structure, molecular weight, boiling point), are presented in Table 2.1. All the chemicals were used without further purification.

2.1.2 Kukersite shale oil samples

The shale oil used in this study was produced from Estonian Kukersite oil shale by solid heat carrier retorting (the Galoter process) in Estonian Energy’s Narva Oil Plant. As the crude retort oil has a wide distribution of compounds (Oja, 2005; Oja, 2015; Järvik and Oja, 2017), then in industry the shale oil is divided into “straight run fractions”. In this study gasolines or light shale oil fractions (approximate boiling range of 50 to 200 ^{o}C) and middle oil or fuel oil fractions (approximate boiling range of 200 to 500 ^{o}C) were used.

2.1.2.1 Narrow boiling range cuts from light shale oil

Narrow boiling oil fractions (cuts) given in Table 2.2 were distilled from light shale oil *(Paper II, Section 2.1 Materials)*. In Table 2.2 the following characteristics of the shale oil fractions are presented: cut width by distillation, initial boiling point (T_b^{DSC}) measured by DSC, average molecular weight (MW) and density (ρ).

Table 2.2. Basic properties of shale oil fractions used (Paper II)

Sample ID used in Paper II	Cut width by distillation (K)	T_b^{DSC} (K)	Molecular weight, MW (g mol^{-1})	Density ρ, at 293.2 K (g cm^{-3})
Cut 1_R	10	373.1	99	0.7520
Cut 2_R	5.9	394.8	109	0.7738
Cut 3_S	8.5	407.7	114	0.7993

The cuts were distilled at atmospheric pressure, either in a simple batch distillation (indicated in the Sample ID by subscript S) or in a rectification column (indicated by subscript R). For rectification a laboratory scale rectification column with 4.4 theoretical plates and a reflux ratio of 6 was used.

As each cut is a multicomponent mixture, then Figure 2.1 *(Figure 2, Paper II)* presents indicative atmospheric boiling ranges of these light oil cuts measured using a thermogravimetric technique (Rannaveski et al., 2016).

Table 2.1. Characteristics of pure compounds used in study

Material	**Paper**	**Chemical supplier**	**CAS no**	**Purity**	**IUPAC name**	**Molecular weight**	**T_b, K**
Benzene	II, III	Sigma-Aldrich	71-43-2	≥ 0.998	benzene	78.11	353.2
Toluene	I, III	Sigma-Aldrich	108-88-3	≥ 0.998	methylbenzene	92.14	384
o-xylene	II	Sigma-Aldrich	95-47-6	≥ 0.990	1,2-Dimethylbenzene	106.17	417.5
2-tert-butylphenol	III	Sigma-Aldrich	88-18-6	≥ 0.985	2-(2-Methyl-2-propanyl)phenol	150.22	496.3 (DSC)
Hexadecane	I	Fisher Chemicals	544-76-3	≥ 0.98	hexadecane	226.45	560
L-nicotine	I, III	Acros Organics	54-11-5	≥ 0.99	3-(methylpyrrolidin-2yl)-pyridine	162.23	521.0 (DSC)
(±)-Anabasine	I	Maybridge	13078-04-1	≥ 0.971	3-(2-piperidyl)pyridine	162.23	555.2 (DSC)
(-)-Cotinine	I	abcr GmbH and Co	486-56-6	≥ 0.999	(5S)-1-methyl-5-(3-pyridyl)pyrrolidin-2-one	176.22	619.4 (DSC)

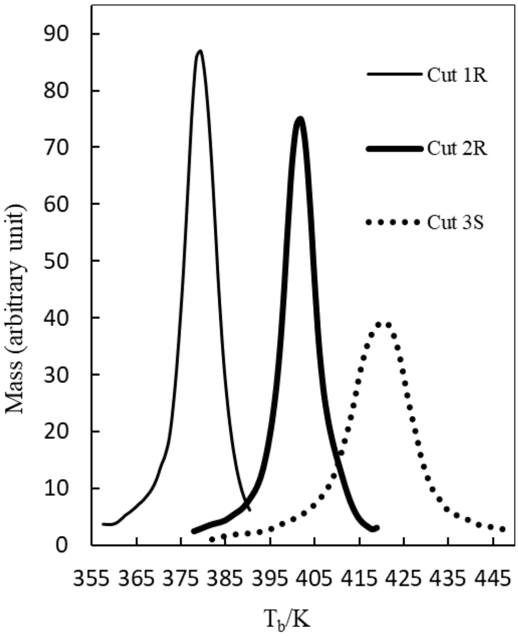

Figure 2.1 Indicative atmospheric pressure boiling point distributions (normalized for the same mass) for rectification and simple distillation cuts, destilled under atmospheric pressure (same as Figure 2, Paper II)

2.1.2.2 Narrow boiling range cuts from middle shale oil

In *Paper III (Section 2.1 Materials)*, cuts distilled from a wide middle shale oil (fuel oil) fraction were used. The cuts were distilled under vacuum conditions (at pressures from 10-1 down to 10-2 Torr) by simple batch distillation. Table 2.3 presents the following characteristics of the oil fractions: cut width by distillation, initial boiling point (T_b^{DSC}) measured by DSC, average boiling point (T_b^{TGA}) measured by TGA, average molecular weight (MW), density (ρ), hydrogen-carbon atomic ratio (H/C), wt% of OH groups and number of OH groups per average molecule.

Table 2.3 Basic properties of shale oil fractions used in Paper III

Sample ID used in Paper III	Cut width (K)	T_b^{DSC} / T_b^{TGA} (K)	Molecular weight MW (g mol^{-1})	Density ρ at 293.2K ρ (g cm^{-3})	H/C ratio	OH wt%	OH per mole-cule
A	14	543/569	191	0.996	1.41	5.9	0.7
B	24	606/626	227	1.056	1.32	7.9	1.1
C	14	648/675	284	1.057	1.27	6.7	1.1

Figure 2.2 (*Figure 1, Paper III* – temperature units are in Celsius) presents the indicative boiling ranges of these middle oil cuts at atmospheric pressure, as measured using the thermogravimetric technique.

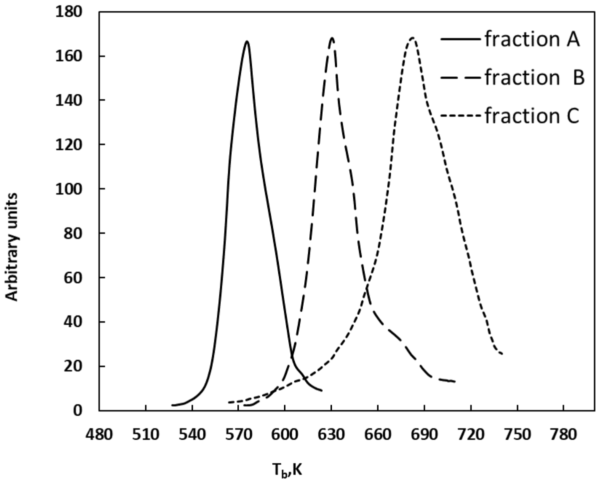

Figure 2.2 Indicative atmospheric boiling distributions (normalized by mass) for middle oil simple distillation cuts distilled under vacuum conditions (Figure 1, Paper III)

2.2 Experimental methods

2.2.1 Differential Scanning Calorimeter (DSC) - equipment

The vapor pressure measurements were carried out using a Netzsch Differential Scanning Calorimeter DSC 204 HP Phoenix with a high pressure DSC cell. The high pressure DSC cell inlet and outlet flow lines were modified by adding cold trap lines to trap the vaporizing samples and an additional pressure sensor connection point (PT) to measure the pressure in the DSC cell. The location of the additional pressure sensor connection point was an estimated 47 cm from the DSC cell, which resulted in a pressure drop of less than 0.003 kPa at atmospheric pressure conditions. The general schematic of the DSC system is shown in Figure 2.3.

For measurements at elevated pressure, the commercial pressure-flow control system was modified with a pressure controller (4) (Brooks Instrument Model 5866) with the operating range of 100 to 1000 kPa to improve stability of the pressure control between 200-500 kPa. To improve pressure recording accuracy, a factory calibrated pressure sensor (Omegadune Inc., model PX409-150AUSB) was added to the system (to the pressure sensor connection point PT, approximately 47 cm from the DSC cell). The pressure sensor PX409-150AUSB had a specified full-scale error of 0.008%.

For measurements in a vacuum a control-measurement system, consisting of a Vacuum-brand PC 3001 Vario membrane vacuum pump with a variable motor-speed controller CVC 3000, a MKS Baratron Type 626B vacuum sensor (approximately 47 cm from the DSC cell) and a 2 litre ballast tank, was constructed. The MKS Baratron vacuum sensor was factory calibrated with an accuracy of 0.25% of the reading.

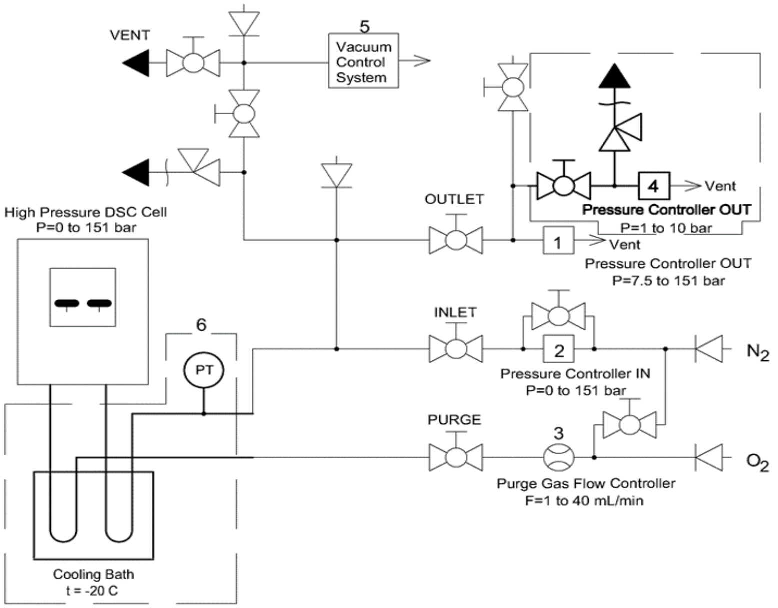

Figure 2.3. The scheme of the modified DSC equipment

Temperature calibration was carried out with indium, tin, bismuth and zinc standards. The operating conditions (heating rate, inert gas, type of crucible) for calibration and sample measurements were the same. Calibrations were carried out at atmospheric pressure, 500 kPa, 1000 kPa and in a vacuum at 15 and 50 kPa. The melting temperatures of the metals were determined as onset temperatures where the tangent to the baseline intersects the tangent to the melting peak.

2.2.2 Differential Scanning Calorimeter (DSC) - experimental procedure to measure vapor pressures

The experimental procedure applied mainly followed the recommendations of the "Standard Test Method for Determing Vapor Pressure by Thermal Analyses" (ASTM E 1782): a heating rate of 5 K/min; sample pans that were hermetically sealable aluminium crucibles (40µl of volume) with 50 µm laser-drilled pinholes in the lid; the purge gas (inert carrier gas) was nitrogen (purity 99.999%) with a flow rate of 40 ml/min. The DSC cell was purged for about 20-30 minutes at atmospheric pressure before vacuum experiments or at the given pressure before elevated pressure measurements. The boiling temperature was determined as the onset temperature where the tangent to the baseline intersects the tangent to the boiling endotherm.

The sample was weighted with an accuracy on the order of ten micrograms on a Mettler M3/TG microbalance. For each data point, at least two DSC measurements were performed with somewhat different sample amounts. If the measured boiling points differed more than 0.2 K additional measurements were carried out.

Although ASTM E 1782 recommends using a sample size of 1-5 µl in order to get reproducible results (temperatures that fall in the 0.2 K range), the influence of sample size had to take into account in this research. The best data were obtained for endothermic peaks with a suitable shape, sharpness and height. The selection of optimal sample sizes was described in detail in *Paper I* for pure compounds and in *Paper II* for oil cuts.

2.2.3 DSC - determination of the optimal sample mass

Although ASTM E 1782 recommends a sample size of 1-5 µl for liquids and 1-5 mg for solids, our study (*Paper I*) indicated that sample size has a considerable influence on the onset of the boiling endotherm. Particularly, measurements over the whole pressure range (from 5 to 1000 kPa) with toluene and hexadecane showed that too much of a sample causes overheating whereas too little of a sample results in preboiling. The optimal sample size was determined as follows. Firstly, sharp endothermic peaks at atmospheric pressure were obtained with sample sizes of about 5 µl. Secondly, all other endotherms over the measured pressure range were compared with the atmospheric pressure endotherm (Figure 2.4, *same as Figure 3, Paper I*). Endotherms were eliminated if they were too low (peak height less than 50 µV or 5 µV/mg), very flat and wide or in another way distorted. It was found that the sample amount is important at pressures below 50 kPa (especially around 15 kPa) and over 250 kPa.

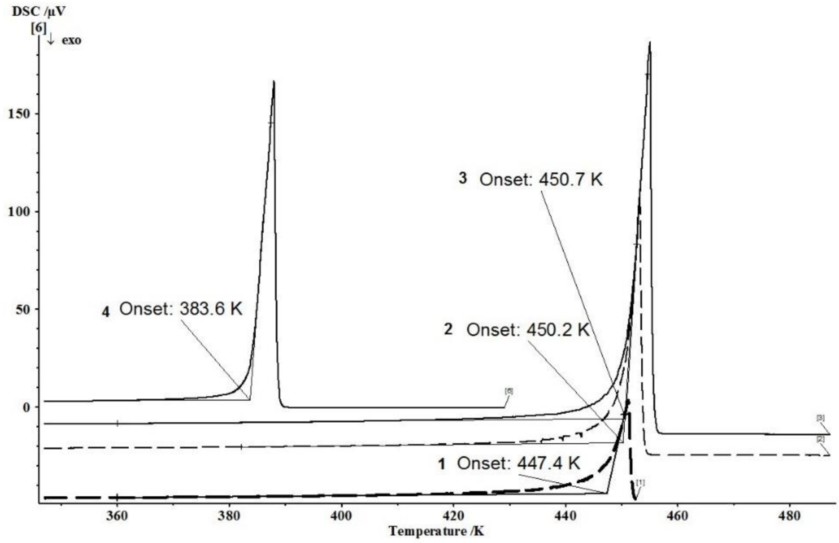

Figure 2.4 Boiling endotherms of toluene at around 101 kPa and at 500 kPa using different sample amounts (same as Figure 3, Paper I)

In Figure 1 of Paper II the normalized DSC endotherms are presented for light shale oil cuts. As the shale oil cut is a multicomponent continuous mixture, then more broadening and shortening of the DSC endotherm occurs than with a single compound DSC endotherm. Therefore, a larger sample size is needed to achieve an endotherm with a height comparable to a pure compound endotherm.

The shape, sharpness and signal strength of the endotherm depend on the chemical properties (enthalpy of vaporization) of the materials, and therefore, cannot be described unambiguously. Consequently, optimal sample size should be estimated for each compound.

2.2.4 Data fitting

Experimental data were correlated (data points were fitted) either using the integrated form of the Clausius-Clapeyron equation or the Antoine equation. The integrated form of the Clausius-Clapeyron equation has the following form

$$ln\,P = \frac{B}{T} + C = \frac{-\Delta H_{vap}}{RT} + C \tag{2.1}$$

where P is the vapor pressure (kPa), T is the temperature (K), ΔH_{vap} is the heat of vaporization (J mol^{-1}), C is a constant and R is the ideal gas constant (J mol^{-1} K^{-1}). The constants B (or $-\Delta H/R$) and C were found directly from a linear regression equation on a lnP versus 1/T plot. This type of correlation was used for pure compounds over a narrow temperature range, where samples followed a linear trend on a lnP versus 1/T plot, and also for oil cuts.

The Antoine equation, used when pure compound vapor pressure data did not follow a linear trend on a lnP versus 1/T plot because it covered a wider temperature range, has the following form:

$$\log_{10} P = A + \frac{B}{T+C} \tag{2.2}$$

where P is the vapor pressure (kPa), T is the temperature (K) and A, B, C are the Antoine constants. The constants were calculated using multilinear least squares regression:

$$\log_{10} P = A + \frac{AC-B}{T} - C\,\frac{\log_{10} P}{T} \tag{2.3}$$

2.2.5 Data analysis

The accuracy of the DSC method (the closeness of the measured value to the reference value) was evaluated either as an absolute deviation, relative deviation or average absolute relative deviation:

absolute deviation	$\Delta = x - X$
relative deviation	$RD\% = 100\,\frac{x-X}{X}$
average absolute relative deviation	$ARD\% = 100\,\frac{1}{N}\sum\left\lvert\frac{x-X}{X}\right\rvert$

where x is the experimental value and X is the reference value.

Similarly, for binary mixtures the deviation from ideality, or Raoult's law, *(Paper III)* was evaluated using the relative deviation (RD) and average absolute relative deviation (ARD) between the measured pressure ($P_{measured}$) and the pressure estimated by Raoult's law (P_R):

$$RD\% = 100\,\frac{P_{measured}-P_R}{P_R} \tag{2.4}$$

$$ARD\% = 100\,\frac{1}{N}\sum\left\lvert\frac{P_{measured}-P_R}{P_R}\right\rvert \tag{2.5}$$

A negative RD corresponds to negative deviation from Raoult's law and a positive RD corresponds to positive deviation from Raoult's law.

2.2.6 Error analysis

Expanded uncertainties with 95% confidence level were calculated both for temperature and pressure measurements. The uncertainties were calculated as described in *Paper I, section 2.5.*

In short, *Type A* uncertainty is calculated as follows:

$$u_A = \sqrt{\frac{\sum_{i=1}^{n}(x_i-\bar{x})^2}{n(n-1)}} \tag{2.6}$$

where n is number of measurements, $\bar{x}$ is the mean experimental value.

Type B uncertainty was calculated using uniform distribution as

$$u_B = \frac{\Delta_0}{\sqrt{3}} \tag{2.7}$$

where Δ_0 is the absolute error or resolution of the sensor.

The overall value of uncertainty or combined standard uncertainty, that takes into account the uncertainty components evaluated by *Type A* and *Type B* methods, was calculated as following:

$$u_c = \sqrt{u_A^2 + u_B^2} \tag{2.8}$$

The combined standard uncertainty was calculated as

$$U = k \times u_c \tag{2.9}$$

where k is a coverage factor.

The expanded uncertainties for pressure measurements were calculated for two sensors used. For measurement above atmospheric pressure (Omegadune Inc., model PX409-150AUSB), the calculated *Type B* uncertainty was 0.76 kPa, which was calculated from the sensor´s full scale error of 0.008%. For vacuum measurement (MKS Baratron type 626B) the calculated *Type B* uncertainty was 0.25% of the reading. *Type A* uncertainty was negligible for both sensor´s. The expanded uncertainties accompany data presented in *Papers I, II and III.*

The expanded uncertainties for temperature measurements are given in the Result and Discussion section, as these values depend on whether pure compounds or oil cuts are used. As the shale oil cut is a multicomponent continuous mixture then broadening and shortening of the DSC endotherm occurs relative to a single compound DSC endotherm resulting in somewhat poorer temperature determination accuracy from the DSC endotherm.

2.2.7 Vapor pressure measurements using a static vapor pressure tester (ERAVAP)

A commercial vapor pressure tester ERAVAP from Eralytics GmbH with measuring temperature range of 273 to 393 K and pressure range of 0-1000 kPa was used to verify data obtained by DSC in Article II. The measurements with ERAVAP were run according to the Standard Test Method for Determination of Vapor Pressure (VP_x) of Petroleum Products, Hydrocarbons, and Hydrocarbon-Oxygenate Mixtures (Triple Expansion Method) ASTM D 6378 i.e. the single point static vapor pressure method with a vapor-oil ratio of 4:1 was used.

The volume of the injected sample was approximately 1 ml. The repeatability of ERAVAP was 0.3 and reproducibility 0.7 kPa. The accuracy of vapor pressure of benzene was approximately 2% in the range of 15 to 300 kPa and above 40 kPa better than 5% for toluene and o-xylene. Based on large number of measurements, it could be stated that reliable results with ERAVAP were obtained with samples having vapor pressure between 15 and 300 kPa at 37.8 ^{o}C. More detailed preview of ERAVAP tester is given in *Paper II, section 2.2.2.*

2.2.8 Characterization of oil cuts

Other characteristics of the narrow boiling range oil cuts, aimed to support data analysis, were measured using the following analytical equipment:

- Densities were measured with an Anton Paar DMA 5000M, which had an accuracy of ±0.00001 g cm^{-3} at 293.15 K.
- Average boiling points were measured using recently developed thermogravimetry based new method (Rannaveski et al., 2016).

The thermogravimetric analyzer used was a DuPont 951 thermogravimetric analyzer (TGA), which had accuracy of ±2 K.

- Average molecular weight was measured using a cryoscopic method using benzene as solvent. Method had accuracy of ±5 g mol^{-1}.
- Elemental composition was measured using an Exeter Analytical model CE440 elemental analyzer, which had an accuracy of ±0.15 wt% C and ±0.05 wt% H).

3 RESULTS AND DISCUSSION

To achieve the main aim of the present PhD work – the extension of the DSC method for vapor pressure measurements of narrow boiling point cuts of oils – the following experimental studies were carried out. First, the performance of DSC in measuring the vapor pressures of pure compounds was evaluated and the accuracy of the method was estimated. Then, the DSC method was evaluated for measuring vapor pressures of narrow boiling range cuts and binary mixtures where at least one of the mixture components is a narrow boiling range distillation cut. The DSC method was also applied for evaluation of the nonideality of binary mixtures of narrow boiling range oil cuts. In the present chapter, the results of the experimental study are presented and discussed.

3.1 Evaluation of performance of DSC using vapor pressure measurements of pure compounds

The performance of the DSC technique (the experimental setup and method of our laboratory) was assessed on the basis of measured vapor pressures of pure compounds. In Table 3.1 the average absolute relative deviation (ARD) between the measured vapor pressures and those from references are given for 6 pure compound, along with several reliable references to vapor pressures given in the literature.

Table 3.1 indicates that DSC based vapor pressure data are comparable to those from widely accepted vapor pressure measurement techniques. The average absolute relative deviation (ARD) falls in the range from 0.5 to 2.2%. There is only one exception seen in the case of nicotine, with an ARD value of 6.6% (Young and Nelson, 1929). Also, the R^2 coefficients for the pure compound vapor pressure data, which are higher than 0.9997 *(see Papers I, II, III),* indicate that the Clausius-Clapeyron or Antoine equations (regressions) fit the data points to a level comparable to other accepted vapor pressure measurement techniques.

In order to get reproducible results and the good linearity mentioned above it was important to take into account the influence of sample size *(Paper I, Section 2.3.).* The sample size range had a considerable influence on precise determination of the onset temperature of the boiling endotherm – it influenced the shape and sharpness of the endotherms. To establish the correctness of the temperature measurements it was assured that in the suitable sample size range (shape and sharpness range of the endotherm) the temperature values of repeatable experiments with somewhat different sample amounts fell within 0.2 K of each other, or at least within 0.3 K (±0.1 K, or at least ±0.15 K, around the midpoint). Therefore, for pure compounds the expanded uncertainty at the 95% level of confidence for temperature measurements was evaluated to be ±0.2 K in the range from 15 to 101 kPa and ±0.4 K at higher pressures. In *Paper I* (based on tobacco alkaloids) it was estimated that the optimal sample sizes for pure compounds were 2-3 mg at pressures below 50 kPa, 3-5 mg between 50 and 80 kPa, 6-7 mg at around atmospheric pressure, 10-12 mg at pressures between 200-250 kPa, 15-16 mg between 400 and 500 kPa, and up to 18-23 mg at higher pressures.

In summary, Table 3.1 revealed that DSC based vapor pressure data and curves, when the experiments are carefully performed, are comparable to those from widely accepted vapor pressure measurement techniques.

Table 3.1 Accuracies of the vapor pressures measured using the DSC method in terms of average absolute relative deviation from reference values

Compound	Paper	Measurement range used both in papers and reference studies, kPa	ARD, %	Method used in reference	Reference
Toluene	I, III	14.9 – 101.6	0.8	dynamic method	Willingham et al., 1945
		498.30 – 1009.33	1.0	Dynamic method	Ambrose et al., 1967
		29.65 – 101.6	1.1	Dynamic method	Forziati et al., 1949
		29.65 – 247.5	0.5	Static method	Lee and Holder, 1993
		29.65 – 101.6	0.8	Static device	Mokbel et al., 1998
Hexadecane	I	14.78 – 101.35	0.8	Dynamic method	Camin et al., 1954
		14.78 – 101.35	0.8	Hoover-John-Melien semimicro ebulliometer	Mills and Fenton, 1987
		14.78 – 101.35	1.0	Static method	Morgan and Kobayashi, 1994
Benzene	II	247.52 – 750.14	2.2	Static device	Bender et al., 1952
		49.45 – 247.52	1.1	isoteniscopic method	Eon et al., 1971
		39.52 – 750.14	0.5	dynamic method	Willingham et al., 1945
o-xylene	II	14.75 – 102.78	1.0	dynamic method	Willingham et al., 1945
		14.75 – 102.78	0.7	dynamic method	Forziati et al., 1949
L-nicotine	I	14.96 – 79.61	1.8	manostat	Gorbachev, 1934
		14.96 – 99.84	6.1	air saturation method up to 373K, above that static method	Young and Nelson, 1929
2-tert-butylphenol	III	9.9 – 64.61	1.1	Dynamic boiling point method	McDonald et al., 1959
		9.9 – 64.61	1.2	Swietoslawski´s ebulliometry	Tsvetkov et al., 1986, Nesterova et al., 1990

3.2 Evaluation of the DSC method for measuring vapor pressures of narrow boiling range oil cuts

Performance of the DSC method, when applied to narrow boiling range cuts, was evaluated using cuts distilled from light shale oil (the characterization of the cuts is presented in Table 2.2). Experiments were carried out in the temperature range from 318 to 484 K and at pressures from 15 to 750 kPa. *(Paper II).* Comparative vapor pressures were obtained for these fractions using the ERAVAP, and were measured at temperatures from 333 to 393 K in the pressure range of 7 to 184 kPa (ASTM 6378; vapor-liquid ratio of 4:1).

Figure 3.1 *(Figure 4, Paper II)* shows experimental vapor pressure curves obtained using DSC and ERAVAP in the linearized form of the Clausius-Clapeyron equation for oil cuts and also for reference chemicals - benzene and o-xylene.

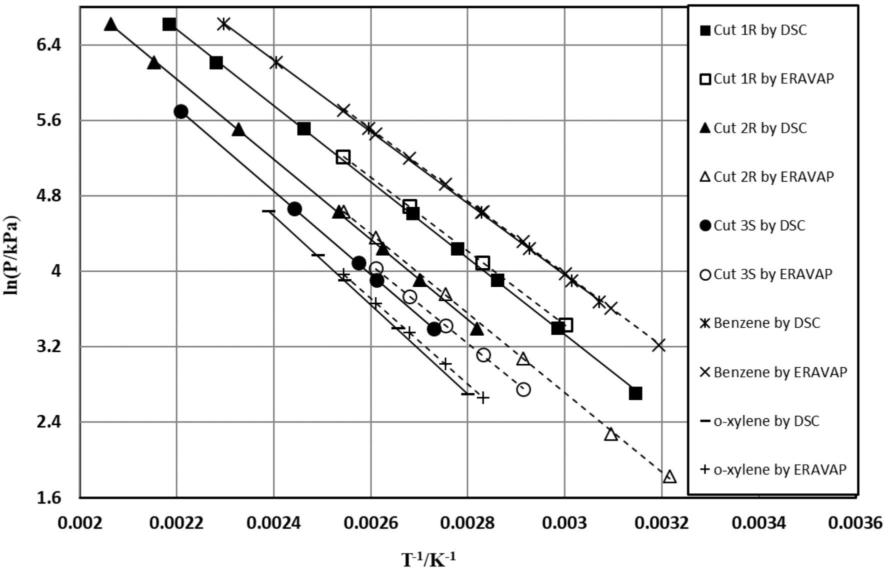

Figure 3.1 Vapor pressure data using DSC and ERAVAP. Solid lines present trendlines for DSC measurements and dashed lines for ERAVAP (same as Figure 4, Paper II)

First, it can be seen from Figure 3.1 that narrow boiling shale oil cuts have a good linearity. In terms of R^2 the linearity was found to be 0.9998 or better. This is comparable to vapor pressure measurements of pure compounds indicating that the vaporization behavior of narrow boiling fractions (viewed as pseudocomponents) through a pinhole is close to that of pure compounds. Therefore, compositional changes of the narrow boiling point cuts when the sample was vaporized through a pinhole did not significantly influence the accuracy of boiling temperature determination from the onset of the endotherm and did not cause increased scatter around the integrated Clausius-Clapeyron equation fit to the data.

In Figure 1 of Paper II the normalized DSC endotherms are presented for light shale oil cuts. In contrast to pure compounds, as the shale oil cut is a multicomponent continuous mixture, then broadening and shortening of the DSC endotherm occurs relative to a DSC endotherm of a single compound. Therefore, a larger sample size is needed to achieve an endotherm with a height comparable to a pure compound endotherm. The following optimal sample sizes were found suitable for light oil cuts: (1) the sample size for narrow boiling fractions obtained by rectification were 3-6 mg at 15-50 kPa and 7-15 mg around atmospheric and higher pressures; (2) the sample sizes for fractions from simple batch distillation were 6-13 mg at 30-70 kPa and up to 17 mg at atmospheric and higher pressures *(Paper II, Section 2.2.1 and Section 3)*.

Second, the DSC vapor pressure curves show close similarity to the curves measured using the ERAVAP. The ERAVAP measurements were performed with a vapor-to-liquid ratio of 4:1, as specified by the ASTM 6378 standard. With a static method the vapor-to-liquid ratio (vapor volume to liquid volume or small sample vaporization to vapor space of the system), which causes some deviation from the true vapor pressure, can be specified precisely. By contrast, with the DSC method the effect of vaporization of some lighter part of a sample cannot be precisely specified. The effect of so called “pre-boiling” before the main endothermic peak depends on the shape of the boiling point distribution, which can vary from sample to sample.

In this study the DSC vapor pressure method was also applied for narrow boiling range oil cuts distilled from middle shale oil using a simple distillation technique. These cuts have broader boiling cut ranges than the light shale oil cuts used above. The characterization of the cuts is presented in Table 2.3 and in Figure 2.2. The results are presented and discussed in detail in *Paper III*. The vapor pressure curves (lnP=f (1/T)) for middle oil cuts are presented in *Figures 4-8 of Paper III.* It can be seen that although there is also a good linearity in terms of R^2 (better than 0.996), the linearity is slightly poorer than in the case of pure compounds or light oil cuts. Also, the temperature values of repeat experiments with somewhat different sample amounts fell within 0.3 K (±0.15 K around the midpoint), which is slightly wider than the 0.2 K repeatability of pure compounds and light oil cuts. Comparative vapor pressure curves for middle oil cuts could not be measured with the ERAVAP technique because it was not suitable for these higher boiling materials.

To find the estimated range of applicability for narrow boiling Kukersite shale oil fractions the following empirical equation was derived (average relative deviation of +/- 27% in terms of pressure):

$$ln\,P = (0.0128T_b + 10.545) - \frac{(19.633T_b - 3513.3)}{T} \qquad (3.1)$$

where T is the temperature (K), P is the pressure (kPa) and T_b is the initial boiling point determined using the DSC method (K).

The equation was found using additional experimental data for narrow boiling range fractions obtained from light oil (rectification) and middle oil (Engler) (some of the data has not yet been published in articles). The Figure 3.2 shows the tentative temperature range of the DSC method, as calculated using the equation, depending on the boiling point of the fraction. For light oil fractions it is possible to use the DSC method in the range from 5 to 1700 kPa, determined by the standard and by calculation (3.1) respectively. For this the upper temperature limit (T_{max}) for light oil fractions is estimated using the experience-based relation. The relation relates the critical temperature (T_c) of alkanes with corresponding boiling points of fractions as

$$T_{max} = T_b + (T_c - T_b)\frac{4}{5} \qquad (3.2)$$

For comparison, the results for toluene as measured by the DSC were P = 3000 kPa and T_b^{DSC}= 287.7 ^oC.

The lower measurement limit can be determined by extrapolating the region in the figure down to a boiling point of 40 ^oC (313 K). For lower boiling temperatures (below 60 ^oC, or 333 K) cooling is used during experiments (the light grey region in the Figure 3.2) so that the starting point for the measurement would be at least 30 K lower than the expected boiling point. The upper temperature limit for fractions from middle oil is 365 ^oC (638 K, T_b=667 K) because based on experiments the fractions can start to decompose at this point. Therefore, the upper portion in the figure can likewise be extrapolated to a boiling point of 460 ^oC (733 K), above which it is no longer possible to get a 5-point vapor pressure curve that has a temperature range of 50 ^oC (minimum of 30 ^oC).

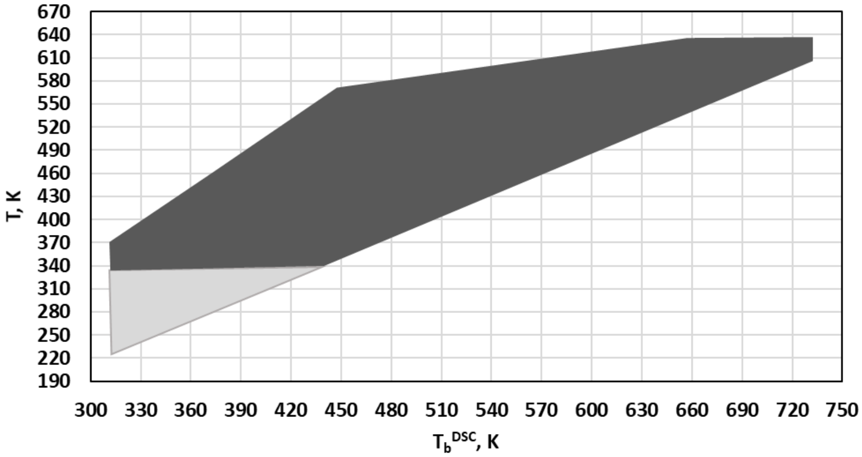

Figure 3.2 Tentative temperature ranges of the DSC method. Light grey triangle indicates temperature region were cooling is needed.

In summary, the DSC based vapor pressure method could be suggested as an alternative method for determining the vapor pressures of narrow boiling oil fractions. The experimental procedure applied mainly followed the recommendations of ASTM E 1782, i.e. there was no need to modify the method for narrow boiling shale oil fractions. Sample size was the only parameter that was optimized for precise determination of the onset temperatures. As with pure compounds, the sample size has a noticeable effect on the shape of the boiling endotherm. The major deviation from the true vapor pressure comes from the uncertainty in the amount of “pre-boiling” of lighter compounds before the main endothermic peak. This makes the method suitable for rough determination of the true vapor pressure of oil cuts, with benefits such as a small sample size (100 mg), no need for degassing and a wide pressure-temperature range.

3.3 Evaluation of the DSC method for measuring vapor pressures of binary mixtures of narrow boiling range oil cuts

In the previous chapter (3.2) it was shown that the DSC based vapor pressure method can be applied as an alternative method for determining the vapor pressure of narrow boiling oil fractions. As a second aim, the goal of the research was to evaluate extension of the DSC based vapor pressure method to binary mixtures containing narrow boiling range oil cuts. A related target was the preliminary screening of the ideality/nonideality of those binary mixtures. Two types of "binary systems" were examined: (1) a narrow boiling range oil fraction (or distillation cut) mixed with a pure compound (2-tert-butylphenol or nicotine); (2) a mixture of two narrow boiling range oil fractions.

The results of the study are presented in detail in *Paper III*. First, the vapor pressure curves for both types of binary mixture showed quite good linearity on an lnP versus 1/T plot (R^2 of 0.996 or better, *Figures 4-8 of Paper III*). This is comparable to results from middle oil cuts, but slightly poorer than those of light oil fractions or pure compounds. Also, the temperature values of repeatable experiments with somewhat different sample amounts fell within 0.3 K (±0.15 K around the midpoint) which is comparable to results with middle oil cuts, but slightly wider than the 0.2 K repeatability of pure compounds and light oil cuts.

Second, the behavior of binary mixtures showed logical nonideality/ideality trends, which could be expected due to the structures of substances and observations given in the literature. For example, it can be seen from Figure 3.3 *(Figures 7, 8, Paper III)* that when the difference between the average boiling points of fractions is about 50 K the behavior of the mixture is close to that predicted by Raoult´s law (Fractions B and C, blue line and markers in Figure 3.3).

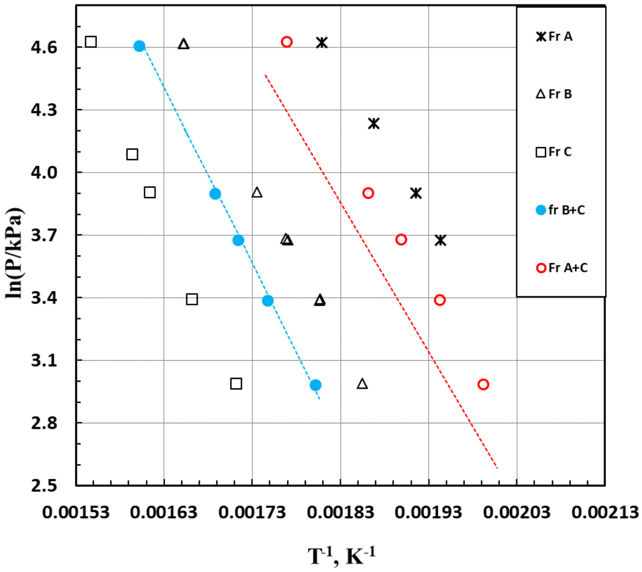

Figure 3.3 Vapor pressure behavior of binary mixtures (50:50mol%). Red lines and markers indicate considerable deviation from Raoult´s law (nonideal behavior). Blue line and markers indicate ideal vapor pressure behavior (close to Raoult´s law)

When the difference between the average boiling points of the fractions is about 100 K considerable deviation from Raoult´s law, i.e. considerable nonideal behavior, is seen (Fractions A and C, red lines and markers in Figure 3.3). To evaluate the extent of nonideality/ideality, the measured total vapor pressure curves of mixtures were compared to those calculated from Raoult´s law as

$$P = \sum^{N}_{i} x_i P_i = x_1 P_1 + x_2 P_2 \tag{3.3}$$

where x_i is the mole fraction of the component (or distillation cut's) and P_i is the vapor pressure of the component (or distillation cut). The mole fraction x_i of a cut (considered a pseudocomponent) was calculated using the average molecular weight of the cut, whereas the vapor pressure of the cut P_i, measured in this study using DSC, corresponds to the cut's initial boiling point (not to the average boiling point).

In summary, the DSC based vapor pressure method could be used to measure the vapor pressures of binary mixtures containing narrow boiling range oil cuts and could be applied for preliminary screening of the ideality/non-ideality of mixtures of narrow boiling oil fractions. Only note that there are concentration limits to be kept in mind when using standard crucibles with a 40 µl of volume. If the components mixed have different volatilites that are clearly separable on the DSC thermogram, then in order to achieve an acceptable sharpness of the endothermic peak a suggested lower concentration limit of 10 mol% of the component *(see Figure 6, Paper III)* giving DSC peak should be kept in mind.

4 CONCLUSIONS

The basis of the present thesis was a hypothesis that the DSC based vapor pressure measurement technique (ASTM E 1782 method) could be extended, with some improvements/modifications, to measuring the vapor pressures of narrow boiling range oil fractions (distillation cuts) and their binary mixtures.

The thesis showed that the DSC based vapor pressure method can be used with narrow boiling cuts without modification of the standard ASTM E 1782 method. Only optimization of the sample size was found to be important, due to its considerable effect on the onset and shape of the boiling endotherm. The experiments showed that the vapor pressure curves of narrow boiling fractions distilled from light oil had good linearity, as assessed by the R^2 coefficient. This means that the accuracy and consistency of determining the onset from a DSC thermogram (vaporization peak) is comparable to that of pure compounds. When comparing these vapor pressures from DSC measurements to those measured using a static method (ASTM D 6378, vapor-liquid ratio 4:1) quite similar behavior was observed, indicating that the DSC based method can be recommended as an alternative method for determining the vapor pressures of narrow cuts. The major deviation of the DSC measured vapor pressure from the true vapor pressure comes from the uncertainty of the amount of “pre-boiling” of lighter compounds before the main endothermic peak (could be viewed as something similar to the vapor-liquid ratio of static methods, which of course is well defined in static methods). This makes the method suitable for rough determination of the true vapor pressure of oil cuts, with benefits such as a small sample size (100 mg), no need for degassing and broad pressure and temperature ranges.

The study showed that the DSC based vapor pressure method (ASTM E 1782) is also suitable for measuring the vapor pressures of binary mixtures containing narrow boiling range oil cuts and can be used for preliminary screening of the ideality/non-ideality of such mixtures. Two types of “binary systems” were examined: a narrow boiling range oil fraction mixed with a pure compound (2-tert-butylphenol or nicotine) and a mixture of two narrow boiling range oil fractions. In both cases vapor pressure curves, in the form of the integrated Clausius-Clapeyron equation, exhibited good linearity, in terms of R^2. The mixtures also had logical ideality/nonideality behavior that matched the expectations based on their structure.

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Lühikokkuvõte

DSC meetodi arendamine õlide kitsaste keemistemperatuuri vahemikega fraktsioonide aururõhu mõõtmiseks

Eesti põlevkivikeemiatööstuse üks olulisemaid saadusi on põlevkiviõli. Põlevkiviõli (ja ka teiste õlide) tootmisprotsesside, sealhulgas destillatsiooni, optimeerimisel, transpordil ja ladustamisel ning keskkonnamõju hindamisel on oluliseks informatsioon õli aururõhu kohta. Eesti põlevkiviõlide mõningad aururõhu andmed pärinevad enam kui 60 aasta tagusest ajast. Seega on käesoleval ajal vajadus põlevkiviõlide aururõhu andmete ja nende arvutuslike määramismeetodite järele. Õlide aururõhu mõõtmiseks on enim kasutusel staatilised ja ebulliomeetrilised meetodid, mis üldiselt on mõeldud õlide kvaliteedikontrolliks. Puhaste ainete ja mitmekomponentsete segude aururõhkude mõõtmiseks on kasutusel mitmeid metoodikaid, millel on erinevad eelised ja puudused (erinevad rõhu ja temperatuuri piirkonnad, vajaliku proovi koguse suurus, degaseerimine jm). Käesoleva töö aluseks oli hüpotees, et üheks alternatiivseks meetodiks kitsaste keemispiiridega õlifraktsioonide aururõhu mõõtmiseks võib olla puhastele ainetele mõeldud kõrgsurve diferentsiaalsel kalorimeetrial (DSC-l) põhinev ASTM standardmeetod “Standard Test Method for Determining Vapor Pressure by Thermal Analyses (ASTM E 1782)” edasiarendus. Nimetatud meetodit kasutatakse laialdaselt puhaste ainete auruõhu mõõtmiseks; meetodi eelisteks on täpsus, metoodika lihtsus, väike proovi kogus, lai rõhu ja temperatuuri piirkond ja kommertsseadmete laialdane kättesaadavus. Samuti puudub vajadus proovi degaseerimiseks, mis on nõutav aururõhkude mõõtmisel staatiliste meetoditega.

Käesoleva töö peamine eesmärk oli laiendada kõrgrõhu DSC-l põhinevat standardmeetodit ASTM E 1782 kitsaste keemispiiridega (keemistemperatuuride vahemik kuni 10 K) põlevkiviõli fraktsioonide aururõhkude mõõtmiseks. Samuti oli eesmärgiks uurida, kas nimetatud metoodikat on võimalik rakendada kahekomponentsete segude, mille vähemalt üks komponent on õlifraktsioon, aururõhkude mõõtmiseks, et hinnata nende segude ideaalsust või mitteideaalsust.

Käesoleva töö esmased uuringud näitasid, et eelpool nimetatud DSC standardmetoodika on kitsaste keemispiiridega õlifraktsioonide aururõhu mõõtmisel rakendatav ilma täiendusteta ning järgnevates uuringutes teostati auruõhu mõõtmised selle järgi. Töös kasutati kõrgsurve diferentsiaalset skaneerivat kalorimeetrit Netzsch DSC 204HP Phoenix. Mõõtetäpsuse tõstmiseks täiendati DSC seadet – lisati rõhukontroller, täpsemad rõhuandurid ja täiendav süsteem mõõtmiseks vaakumis. Mõõtmistel kasutati vastavalt standardmetoodikale hermeetilist tüüpi suletavaid tiigleid (50 µm avaga kaanes), kuumutuskiiruseks oli 5 K/min. Kuna eelkatsetes selgus, et proovi kogus mõjutab proovi aurustumisel saadava endotermilise piigi kuju ja ka alguspunkti määramise täpsust, optimeeriti mõõtmistulemuste täpsuse tõstmiseks edasiste uuringute käigus proovi koguseid. Uuringutes kasutati nii puhtaid aineid (seadme täpsuse hindamisel) kui ka põlevkivi kerg- ja keskõli fraktsioone. Metoodika rakendamise võimalikkust uuriti võrdlusmõõtmistel staatilise seadmega ERAVAP (meetod ASTM D 6378).

Eksperimentaalsed uuringud teostati kolmes etapis. Esiteks, määrati kasutatava DSC seadme ja meetodi täpsus, nendes mõõtmistes kasutati standardaineid (puhtaid aineid). Mõõtmiste tulemused näitasid, et kasutatud DSC-l põhineva mõõtmismetoodika täpsus on võrreldav üldiselt aktsepteeritavate aururõhu määramise meetodite täpsusega.

Doktoritöö käigus määrati ka mõnede puhaste ainete (alkaloidide nikotiini, anabasiini ja kotiniini) aururõhu temperatuurisõltuvused.

Järgmises etapis uuriti DSC meetodi rakendatavust ja usaldusväärsust kitsaste keemispiiridega põlevkiviõli (nii kerg- kui ka keskõli) fraktsioonide aururõhkude mõõtmisel ning seejärel uuriti segude ideaalsuse ja mitte-ideaalsuse hindamist kasutades kahte tüüpi segusid – esiteks, kitsaste keemispiiridega õlifraktsioonide segusid puhaste ainetega (2-tert-butüülfenooli või nikotiiniga) ning teiseks, kahe kitsa keemispiiriga õlifraktsiooni segu.

Doktoritöös teostatud eksperimentaalsete uuringute tulemused näitasid, et DSC põhinev aururõhu määramise meetod on kitsaste keemispiiridega õlifraktsioonide aururõhu mõõtmisel kasutatav ilma standardmeetodi ASTM E 1782 modifikatsioonideta. Töö tulemuste põhjal selgus, et meetodi rakendamisel on siiski tähtis optimaalse proovi koguse määramine, kuna see avaldab olulist mõju endotermilise piigi alguspunktile ja kujule, mis omakorda mõjutavad mõõtmistäpsust.

Eksperimendid näitasid, et kitsaste keemispiiridega kergõli fraktsioonide aururõhu temperatuurisõltuvustel (Clausius-Clapeyron võrrandi lineaarsel kujul) on kõrged korrelatsioonikordajad R^2, millest järeldub, et kasutatud metoodika võimaldab mõõta õlifraktsioonide aururõhkusid samaväärselt puhaste ainete aururõhkudega. DSC meetodil määratud õlifraktsioonide aururõhkude temperatuurisõltuvuste võrdlemisel käesoleval ajal tunnustatud staatilise meetodiga s.o ERAVAP-iga (ASTM D 6378, aur-vedelik suhtega 4:1) saadud sõltuvustega selgus, et need on sarnased, mis näitab, et DSC põhinevat meetodit võib soovitada kui alternatiivset meetodit õlifraktsioonide aururõhkude mõõtmiseks. DSC meetodiga mõõdetud aururõhu hälve tegelikust aururõhust on tingitud õlifraktsiooni koostises olevate kergemini lenduvate komponentide aurustumisest nn „eel-keemisel“ enne endotermilise piigi tekkimist. Seega võib DSC meetodit kasutada õlifraktsioonide tegeliku aururõhu hindamiseks, meetodi eeliseks on proovi väike mass (väiksem kui 100 mg), degaseerimise vajaduse puudumine ning lai temperatuuri ja rõhu piirkond.

Doktoritöös teostatud uuringud näitasid ka, et DSC põhineva aururõhu määramise meetodiga (ASTM E 1782) on võimalik mõõta selliste binaarsete segude aururõhkusid, mis koosnevad õlifraktsioonidest ning nende mõõtmiste alusel anda eelhinnang segude ideaalsuse või mitteideaalsuse kohta. Eksperimentides kasutatud segude – nii kitsaste keemispiiridega õlifraktsioonide ja puhta aine segude kui ka kahe õlifraktsiooni segude-aururõhkude temperatuursõltuvustel Clausius-Clapeyroni võrrandi lineaarsel kujul olid kõrged korrelatsioonikordajad. Tehti kindlaks, et uuritud segude ideaalsus/mitteideaalsus on loogiline ja vastab nende segude komponentide struktuuri põhjal ennustatule.

Abstract

Extension of the DSC Method to Measuring Vapor Pressures of Narrow Boiling Range Oil Cuts

The basis of the present thesis was a hypothesis that the differential scanning calorimeter (DSC) vapor pressure measurement technique (ASTM E 1782 method) can be used, with some improvements/modifications, for measuring vapor pressures of narrow boiling range oil fractions (distillation cuts with a width of 10 K). The potential of the method for measuring total vapor pressures of binary mixtures to evaluate the ideality/non-ideality behavior of those mixtures was also investigated.

Although there are a number of methods available in the open literature for measuring the vapor pressures of pure compounds and multicomponent solids and liquids, not all of them are suitable or reasonable to use with oil products. In searching for alternative convenient methods to measure the vapor pressures of oil cuts, the capabilities of the standardized method "Standard Test Method for Determining Vapor Pressure by Thermal Analyses (ASTM E 1782)" triggered our interest. This method is a widely used and robust methods for measuring the vapor pressures of pure compounds. Advantages of the ASTM E 1782 method are the worldwide availability of commercial equipment (DSC instrument) and the very small sample size. There is also no need for degassing, as is usually required in the application of static methods. In addition, the standard test method has broad pressure and temperature ranges, and these ranges may be extended even more when some extra modifications are made. Our experiments showed that DSC vapor pressure data and curves for pure compounds, when the experiments are carefully performed, are comparable to those from other widely accepted vapor pressure measurement techniques. As a first step in this thesis new vapor pressure data for three tobacco alkaloids (nicotine, anabasine, cotinine) were determined and published using the DSC method.

For oil distillation cuts the DSC measurements were carried out according to the standard test method (ASTM E 1782), as it was found that the method was suitable without further modifications for measuring vapor pressures of narrow boiling fractions. The main recommendations of the standard method were usage of hermetically sealable pans with a 50 µm pinhole in the lid and a heating rate of 5 K/min. It was shown that determination of the optimal sample size is important to precisely obtain the onset temperature of the boiling endotherm. Sample size has a considerable influence on the shape, and therefore also on the onset, of the boiling endotherm. Under these conditions the vapor pressure curves of narrow boiling fractions, in linearized Clausius-Clapeyron form, showed good linearity, as assessed by the R^2 coefficient. However, while light oil cuts had repeatabilities comparable to pure compound measurements, middle oil cuts, which have wider boiling point distributions, showed slightly poorer values than the former. Comparative vapor pressure measurements of narrow boiling range cuts (distilled from light shale oil) were performed using a static method (ERAVAP vapor pressure tester, ASTM D 6378). Comparing these results to those from the DSC indicated that the DSC based method can reliably be used for determining the vapor pressures of cuts. Comparative measurements for higher boiling middle oil cuts were not made because of the limited temperature and pressure ranges of the static device (ERAVAP).

For evaluation of mixture ideality, the DSC vapor pressure method was used with binary mixtures containing narrow boiling range oil cuts. Two types of “binary systems” were examined: (1) a narrow boiling range oil fraction (or distillation cut) mixed with a pure compound (2-tert-butylphenol or nicotine); (2) a mixture of two narrow boiling range oil fractions. The qualitative study showed that the DSC method could be used as a preliminary screening tool for evaluating the ideality/non-ideality of mixtures of narrow boiling oil fractions. Vapor pressure curves for both types of binary mixture showed good linearity on an lnP versus 1/T plot.

Appendix

Paper I

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Vapor pressure data of nicotine, anabasine and cotinine using differential scanning calorimetry

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ABSTRACT

The aim of the present study was to determine the vapor pressures of three tobacco alkaloids using the high pressure differential scanning calorimeter based technique, in accordance with a standard test method ASTM E 1782. The measurements were conducted in the pressure range from 15 to 1000 kPa. Temperature ranges for (L)-nicotine were from 447.7 to 617.8 K, for (±)-anabasine from 478 to 644.3 K and for (−)-cotinine from 537.7 to 669.7 K. Hermetic-type sealable pans with a pierced lid (pinhole diameter 50 μm) and a heating rate of 5 K/min were used. The experimental vapor pressure data were fitted to the Antoine equation. Enthalpies of vaporization and the normal boiling temperatures of the compounds were estimated from the measured data. Comparisons are made with published literature data. In addition, a review of the vapor pressure studies of nicotine and anabasine is given.

1. Introduction

Tobacco use by smoking (either by water pipe, cigarette, or pipe smoking) is a thermochemical conversion of tobacco with the major processes being pyrolysis and combustion. The tobacco smoke produced is a complex mixture estimated to contain more than 7000 chemical compounds from many different classes [1]. From the chemical engineering point of view, the thermochemical conversion of tobacco is a complex interplay between different type of processes such as chemical, heat-transfer and mass- transfer processes. Therefore, chemical engineering modelling and analysis need wide-variation physicochemical and transport properties. One important physicochemical property is the vapor pressure of both tobacco semi-volatile constituents (occurring naturally in tobacco or added to tobacco as flavors) and tobacco thermal decomposition products, condensable at room temperature [2]. This vapor pressure information is important for describing tobacco devolatilization in thermochemical conversion processes (smoke generation) and smoking devices constructions. In the past two decades there have been several vapor pressure studies in this regard, both on tobacco tar [3,4] and on low volatile compounds generated from tobacco devolatilization [5,6]. Vapor pressure information can also be used to determine the fate and transport of materials released during tobacco smoking in the environment (as second- and third-hand smoke in an indoor environment) or in the human respiratory system, and additionally in developing safety measures to avoid human exposure. Thus, a large number of tobacco smoke constituents could potentially be of practical interest as target compounds for specific applications, from design to environmental and safety purposes. These constituents can have very different volatilities (very different vapor pressures at specified temperatures) and different thermal stabilities. In addition, being biomass thermochemical conversion products, the majority of these are oxygen and nitrogen hetero-atomic compounds with complex structures (heterocyclic for example) and likely have capability of forming hydrogen bonds.

Therefore, an application of different experimental methods for the determination of vapor pressure curves is of interest in tobacco research and related fields. One of the simplest techniques for experimentally determining vapor pressure curves of volatile organic compounds is the differential scanning calorimetry (DSC) based technique. In this technique, the vapor pressure curve is established by determining, via separate experiments, several boiling points at different pressures, from vacuum to elevated pressures. Each boiling temperature is determined from the onset of a heat effect when the sample is evaporated through a pinhole from a hermetically sealed container at a specified pressure under what is called an “isothermal boiling condition” [7]. The advantage of the technique is that only a very small amount of sample (in total 250 mg or less) can be used to obtain a vapor pressure curve with at least 5 replicated points.

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The experimental conditions for DSC based vapor pressure measurements were standardized in 1996 as The Standard Test Method for Determining Vapor Pressure by Thermal Analyses (ASTM E 1782) [8]. The ASTM task group [8] suggested a heating rate of 5 K/min, sample size of 1–5 mg for solids and 1–5 μl for liquids and a pinhole size smaller than 125 μm. Generally, at these conditions the lower pressure limit is 5 kPa. The upper pressure limit is 2000 kPa, but it depends on the apparatus used and the thermal stability of the materials [8].

The present study focuses on the experimental determination of the vapor pressures of three tobacco alkaloids: (L)-nicotine, (±)-anabasine and (−)-cotinine, using differential scanning calorimetry (standard test method ASTM E 1782). There is no reported experimental data for nicotine above the atmospheric boiling point. There is a lack of consistent vapor pressure data for anabasine and only some boiling ranges (at low vapor pressures) were found for cotinine.

2. Experimental

2.1. Chemicals

The tobacco alkaloids examined in this research were L-nicotine, (±)-anabasine and (−)-cotinine. The structures of these tobacco alkaloids are presented in Fig. 1.

L-nicotine (CAS No. 54-11-5; systematic IUPAC name: 3-(methylpyrrolidin-2-yl)-pyridine; $C_{10}H_{14}N_2$) with a purity of 99% +, was obtained from Acros Organics. The refractive index of l-nicotine was n_d^{20} 1.5255–1.5285, the optical rotation was $[\alpha]_D^{20}$ −140° to −152° (given by the supplier). The melting point is presumed to be lower than −79 °C [9].

(±)-Anabasine (CAS No. 13,078-04-1; systematic IUPAC name: 3-(2-piperidyl) pyridine; $C_{10}H_{14}N_2$), with a purity of 97.1%, was purchased from Maybridge (part of Thermo Fisher Scientific, Inc.). The sample had a refractive index of n_d^{20} 1.544 (given by the supplier). The literature melting point is 9 °C [10].

(−)-Cotinine (CAS No. 486-56-6; systematic IUPAC name: (5S)-1- methyl-5-(3-pyridyl) pyrrolidin-2-one; $C_{10}H_{12}N_2O$) with purity of 98% (99.9% with GC) was supplied by abcr GmbH and Co., KG. The optical rotation of $[\alpha]_D^{20}$ −19.6° and n_d^{20} 1.5560 were given by the supplier. The literature melting point is approximately 41 °C [11].

According to literature the nicotine is thermally stable in an inert atmosphere up to 600 °C [12,13]. No thermal stability information was found for the other two tobacco alkaloids; however, the DSC measurements performed did not indicate thermal instabilities in the measured temperature regions.

The reference chemicals used to test the DSC method were toluene and hexadecane. Toluene (CAS No. 108-88-3, anhydrous, purity of 99.8%) was obtained from Sigma-Aldrich and hexadecane (CAS No. 544 -76-3, with purity of 98%) was produced by Fisher Chemicals.

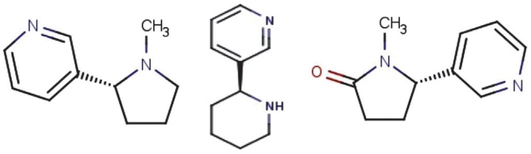

Fig. 1. Structures of L-nicotine, (±)-anabasine and (−)-cotinine (from left to right).

2.2. Apparatus

The high pressure differential scanning calorimeter used was a Netzsch DSC 204HP Phoenix with accompanying DSC cell and pressure-flow control system. To improve the pressure control stability and pressure measurement accuracy in the pressure region from 100 to 1000 kPa an additional pressure controller (Brooks Instrument Model 5866) and pressure sensor (Omegadune Inc., model PX409- 150AUSB) were added to the system. The pressure sensor was manufacturer calibrated with a full scale error of 0.008%.

For vapor pressure experiments in a vacuum an extra vacuum control and measurement system was designed. The system consisted of a membrane vacuum-pump (vacuum-brand PC 3001 Vario) with a variable motor-speed controller CVC 3000, a vacuum sensor MKS Baratron (type 626B) and a ballast tank (2 l in volume). The operating range of the vacuum sensor was 0.0133–130 kPa. The sensor was calibrated by the manufacturer and the accuracy was specified to be 0.25% of the reading.

The distance between the sensors (both pressure and vacuum) and DSC cell was approximately 47 cm and the pressure drop less than 0.003 kPa at atmospheric conditions.

2.3. Experimental procedure

The experimental procedure used was selected in accordance with the “Standard Test Method for Determining Vapor Pressure by Thermal Analyses (ASTM E 1782)”. Vapor pressure measurements were performed in the pressure range between 5 kPa and 1000 kPa. The heating rate applied was 5 K/min. Hermetic type sealable pans (40 μl) with laser-drilled pinholes of 50 μm in the lid were used. The liquid samples were injected with a micro- syringe into an aluminum crucible. Then the crucible was mechanically sealed with a lid. Samples were weighed on a micro-analytical balance (Mettler M3/TG). For each sample point, the DSC experiments were repeated with somewhat different sample amounts at least two times or three times if the measured boiling point difference was more than 0.3 K.

Nitrogen was used as a purge gas (purity 99.999%) with a flow rate of 40 ml/min. The DSC cell (i.e., the sample and reference pans) was stabilized in the nitrogen flow at room temperature at the given pressure for about 20–30 min before measurements were started. Inert gas purging for about 20–30 min at atmospheric pressure was also used before the vacuum measurements to avoid oxidation of the samples.

Temperature calibration was carried out with indium, tin, bismuth and zinc standards at 15, 50, 100 (atmospheric pressure),

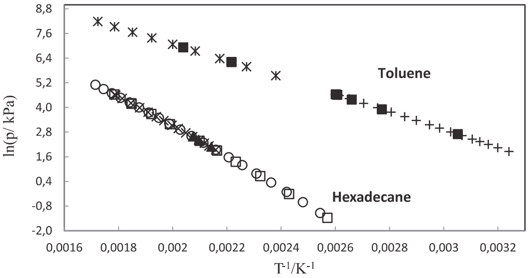

Fig. 2. Comparison of the experimental vapor pressure data with the literature values. Hexadecane: (◆) present study; (x) Camin et al. [14]; (□) Mills and Fenton [15]; (○) Morgan and Kobayashi [16]; (▲) Abdi and Meisen [17]. Toluene: (■) present study; (+) Willingham et al. [18]; (*) Ambrose et al. [19].

500 and 1000 kPa. The calibration and the subsequent measurements were performed at the same conditions (heating rate, inert gas, type of crucible).

The performance of the DSC technique and experimental method was tested using toluene and hexadecane (data is presented in Appendix 1 of Supplementary data). The test results showed that the mean absolute error of the temperature was ±0.4 K and the accuracy of the measurement of the pressure in the range of 15–1000 kPa was better than 1.8%. Fig. 2 shows a good agreement between measured and literature values of vapor pressure values of hexadecane [14–17] and toluene [18,19].

Although ASTM E 1782 recommends a sample size of 1–5 μl for liquids and 1–5 mg for solids, the present study indicated that sample size had considerable influence on precise determination of the onset temperature of the boiling endotherm at the tenth of a degree level. For endotherms that were distorted, especially those that were too low (peak height less than 50 μV or 5 μV/mg), very flat and wide, the extrapolated onset temperature taken had a lower accuracy. The shape, sharpness and signal strength of the endotherm depend on the sample size, chemical properties (enthalpy of vaporization) of the materials and the applied pressure. In Fig. 3, the endothermic peaks of toluene at around 101 kPa (4) and 500 kPa (1–3) are presented. Measurement with a sample size of 5 μl (3.88 mg) at 500 kPa (endotherm 1) produced a lower endotherm than that obtained at atmospheric pressure (endotherm 4) with a sample size of 6 μl (4.833 mg). For the endotherms at a pressure of 500 kPa, obtained using different sample sizes of 5 μl (3.88 mg), 8 μl (6.42 mg) and 12 μl (9.67 mg), the onset temperatures increased with sample size and were respectively 3.2, 0.4 and 0.2 K lower than the temperatures measured by Ambrose [19]. This indicates that although the hole diameter is very small (50 μm) part of the sample evaporates through the hole of the pan before the boiling point which causes determination of onset temperature to have lower accuracy for small sample sizes. Consequently, optimal sample size had to be estimated for each compound. It was found that the sample amount is important at pressures below 50 kPa (especially around 15 kPa) and over 250 kPa.

2.4. Determination of the optimal sample mass for alkaloids

The optimal sample size for alkaloids was determined as follows. Firstly, sharp endothermic peaks at atmospheric pressure were obtained with sample sizes near 5 μl. Secondly, all other endotherms over the measured pressure range were compared with the atmospheric pressure endotherm. Therefore, the sample size used for tobacco alkaloids was 2–3 mg for pressures below 50 kPa, 3–5 mg at 50–80 kPa, 6–7 mg at around 101.3 kPa, 10–12 mg at 200–250 kPa, 15–16 mg at 400–500 kPa, and up to 18–23 mg (max 25 μl) at higher pressures (note: the densities of L-nicotine and (±)-anabasine were approximately 1.01 g/cm^3 and 1.05 g/cm^3, respectively). Note that the importance of sample size has been also emphasized by other researchers. Another option to determine best sample size is from a leading edge slope (a slope of at least −3 mW/mg) as reported by Butrow and Seyler [20]. However, Brozena [21] has recently specified that this is not an ideal characteristic for finding the best pinhole size for lower pressure ranges.

2.5. Error and uncertainty analysis

The accuracy of the DSC method was estimated from the experimental vapor pressure data of the reference compounds, toluene and hexadecane. The accuracy was defined as the closeness of the measurement value (x) to its true or acceptable value (X) and was expressed as mean absolute error ($x - X$) or relative error:

$$\Delta = \frac{|x - X|}{X} \times 100\% \tag{1}$$

where x is the experimental value and X is the reference value.

Precision is usually defined as the agreement among several results measured in the same way. There are several ways to express the precision. In this study a *Type A* uncertainty was estimated by the statistical calculation of the repeated pressure and temperature measurements. *Type A* uncertainty was calculated as follows:

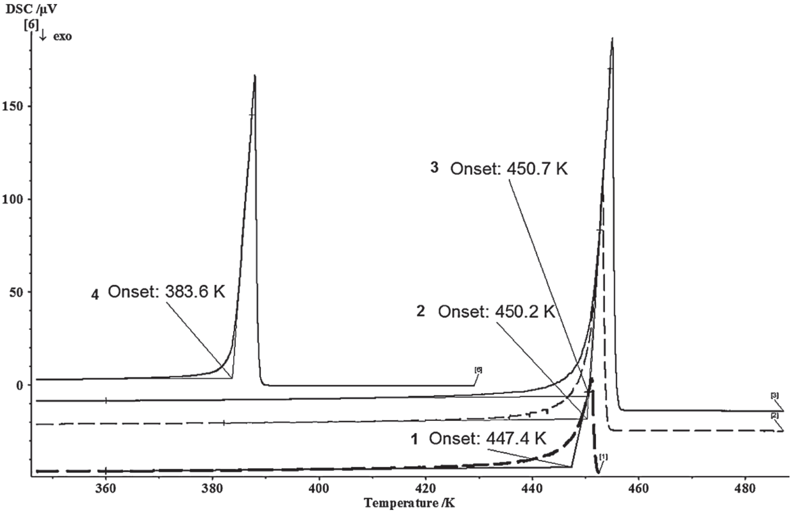

Fig. 3. Boiling endotherms of toluene at around 101 kPa (4) and at 500 kPa (1–3) using different sample amounts. (Note: the baseline is shifted to clarify the onset temperatures of different endotherms 1–3) (1) sample amount of 5 μl (3.875 mg) at 500 kPa; (2) sample amount of 8 μl (6.420 mg) at 500 kPa; (3) sample amount of 12 μl (9.670 mg) at 500 kPa; (4) sample amount of 6 μl (4.833 mg) at 101 kPa.

Table 1
Experimental values of vapor pressure of tobacco alkaloids and comparison with values calculated from equations given in the literature. In this study, expanded uncertainties with a 95% confidence level for temperature and pressure were calculated.

Nicotine

T (K)	p (kPa)				
Measured	Measured	Gorbachev (1934)	Δp^a (%)	Young and Nelson (1929)	Δp^b (%)
447.7 ± 0.2	14.96 ± 0.04	15.51	3.5	15.74	4.9
457.2 ± 0.2	19.93 ± 0.5	20.46	2.6	20.97	5.0
471.1 ± 0.2	29.87 ± 0.7	30.21	1.1	31.35	4.7
490.6 ± 0.2	49.83 ± 0.10	50.27	0.9	52.97	5.9
510.1 ± 0.2	79.61 ± 0.20	80.52	1.1	85.92	7.3
520.4 ± 0.2	99.84 ± 0.76			109.24	8.6
566.4 ± 0.4	247.84 ± 0.76				
594.8 ± 0.4	397.81 ± 0.76				
609.3 ± 0.4	500.02 ± 0.76				
617.8 ± 0.4	568.97 ± 0.76				

Anabasine

T (K)	p (kPa)				
Measured	Measured	Nelson (1934)	Δp^c (%)	Gorbachev (1934)	Δp^a(%)
478.0 ± 0.2	14.95 ± 0.04	20.53	27.2	15.42	3.1
488.0 ± 0.2	19.90 ± 0.05	26.05	23.6	20.31	2
502.9 ± 0.2	29.84 ± 0.07	36.52	18.3	30.04	0.7
523.0 ± 0.2	49.73 ± 0.10	55.85	11	49.24	1
543.5 ± 0.2	79.59 ± 0.20	83.44	4.6		
555.1 ± 0.2	99.57 ± 0.76	103.45	3.7		
602.5 ± 0.4	248.35 ± 0.76				
631.3 ± 0.4	398.33 ± 0.76				
640.7 ± 0.4	468.91 ± 0.76				
644.3 ± 0.4	498.63 ± 0.76				

Cotinine

T (K) Measured	p (kPa) Measured
537.7 ± 0.2	14.95 ± 0.04
548.4 ± 0.2	19.90 ± 0.05
564.2 ± 0.2	29.82 ± 0.07
585.6 ± 0.2	49.74 ± 0.10
601.3 ± 0.2	69.56 ± 0.17
607.4 ± 0.2	79.50 ± 0.20
619.2 ± 0.2	101.32 ± 0.76
655.4 ± 0.4	197.04 ± 0.76
669.7 ± 0.4	247.52 ± 0.76

$$u(x_i) = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n(n-1)}} \qquad (2),$$

where n is number of measurements, $x$is the mean experimental value. A *Type B* uncertainty can be evaluated by means other than the statistical analysis of series of observations [22]. Here, the manufacturers' specifications have been taken into account and uniform distribution was used to calculate *Type B* uncertainty.

The combined standard uncertainty takes into account the uncertainty components evaluated by *Type A* and *Type B* methods:

$$u_c(y) = \sqrt{u_a{}^2(y) + u_b{}^2(y)} \qquad (3)$$

To meet the needs of industrial, commercial, or other applications, it is usually required to convert the combined standard uncertainty to an expanded uncertainty:

$$U = k \times u_c(y) \qquad (4),$$

where k is a coverage factor [22].

In this study, expanded uncertainties with a 95% confidence level for temperature and pressure were calculated. First, the expanded uncertainty for temperatures at each pressure were evaluated, assuming triangular distribution in the case of two repeated measurements ($k = 1.902$) and assuming uniform distribution in the case of three temperature measurements ($k = 2$). The expanded uncertainty was found to be ±0.2 K in the range from 15 to 101.325 kPa and ±0.4 K above atmospheric pressure. It should be mentioned that the sample temperature resolution was 0.01 °C, and therefore, assuming a uniform distribution *Type B* uncertainty was negligible.

Next, the expanded uncertainties for pressures were determined for the two sensors. For measurements above atmospheric pressure the *Type B* uncertainty was 0.76 kPa, which was calculated from the sensor's full scale error of 0.008%. For vacuum measurements the calculated *Type B* uncertainty was 0.25% of the reading. *Type A* uncertainty was negligible for both pressure sensors and therefore the *Type B* uncertainty was dominant. All expanded uncertainties are shown in Table 1.

3. Results and discussion

The experimental vapor pressure data for (L)-nicotine, (±)-anabasine and (−)-cotinine are summarized in Table 1 and re-plotted as ln (p) versus $1/T$ in Fig. 4 for nicotine and in Fig. 5 for anabasine and cotinine.

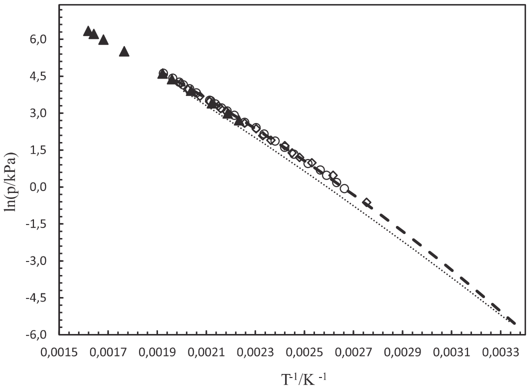

Fig. 4. Comparison of the experimental vapor pressure data for nicotine with the values and correlations in the literature. (▲) Present study ($R^2 = 0.9998$); (○) Young and Nelson [25]; (◇) Gorbachev [26]. (– – –) Lencka et al. [28]; (. . . . .) Lipkind et al. [32].

To present vapor pressure curve equations (data fitting equations), the experimental data were correlated in accordance with the Antoine equation in the following form (in accordance with ASTM E 1782):

$$\log_{10}p = A + \frac{B}{T+C} \qquad (5)$$

where p is the vapor pressure (kPa), T is the temperature (K) and A, B, C are the Antoine constants. This equation was linearized and the constants were calculated using a multilinear least-square regression:

$$\log_{10}p = A + \frac{AC-B}{T} - C\frac{\log_{10}p}{T} \qquad (6)$$

Table 2 summarizes basic parameters derived from vapor pressure data: normal boiling points, enthalpies of vaporization at normal boiling points and Antoine equation constants. The boiling points at 101.325 kPa were calculated using Eq. (5) and derived Antoine constants. Note that the normal boiling points of all three substances are situated roughly in the middle of the corresponding experimental temperature regions studied. Therefore, the heat of vaporization values at the normal boiling points were calculated using two common approaches. Firstly, vaporization enthalpies were derived as an average over the measured pressure range – determined with a 95% confidence level from the slope of the integrated Clausius–Clapeyron equation fitted through all experimental data. Secondly, using the following equation:

$$\Delta_l^g H(T_m) = 2.303RB\left[\frac{T_m}{T_m + C}\right]^2 \qquad (7),$$

where ΔH_l^g is the enthalpy of vaporization (kJ/mol), T_m is the mean temperature of measurement (K) and B, C are the Antoine constants. The equation is derived from the Clausius–Clapeyron equation and the Antoine equation.

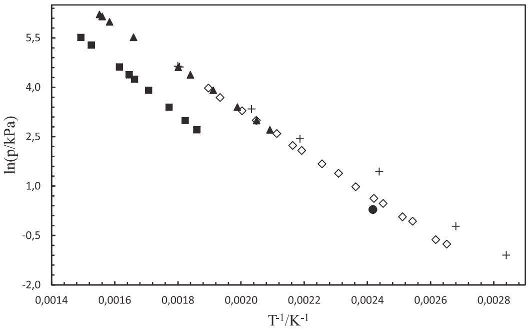

Fig. 5. Experimental vapor pressure data of anabasine and cotinine and comparison with the values in the literature. (▲) Anabasine in the present study ($R^2 = 0.9999$); (◇) Gorbachev [26]; (+) Nelson [33]; Babak et al. [34]. (■) Cotinine in the present study ($R^2 = 0.9997$).

Table 3 presents vapor pressure and heat of vaporization values extrapolated down to 298.15 K for liquid nicotine and anabasine. The vaporization enthalpies at 298.15 K were found using the Kirchhoff's Law:

$$\Delta_l^g H(298.15) = \Delta H_l^g(T_m) + \Delta C_p(T_m - 298.15) \qquad (8),$$

where ΔC_p is the difference in heat capacities of the liquid and gas phases. Values of ΔC_p were calculated using the group contribution method of Acree and Chickos [23]. Vapor pressures at 298.15 K were extrapolated directly from the Antoine equation. Comparison with corresponding literature based values in Table 3 shows that there is a fair agreement between the values of this study and those from references.

In total ten nicotine vapor pressure data-points were measured in the temperature range from 447.7 to 617.8 K, which corresponds to the pressure range of 15–570 kPa. The normal boiling point of L-nicotine in the present study was found to be 521.0 K. There are number of publically available publications that present comparative vapor pressure information, both original experimental data and vapor pressure curve fittings, on nicotine. These cover vapor pressure range from room temperature (298 K) to normal boiling point. Overview of publicly available nicotine vapor pressure information is summarized in Tables 4 and 5.

Table 4 presents a summary of publications with the originally measured vapor pressure data and fitting equations proposed by the authors. Most of measurements date back to a time period from 1928 to 1940 (Harland and Hixon [24]; Young and Nelson [25]; Gorbachev [26]; Norton et al. [27]). Among the available data, the most reliable vapor pressure temperature dependences appear to be those based on the data of Young and Nelson [25] and Gorbachev [25]. Young and Nelson [27] reported vapor pressures in the range of 334–519 K. They used the air saturation method up to 373 K and a static apparatus with an isoteniscope for higher temperatures. Gorbachev [26] measured vapor pressures in the range of 363–501 K using a manostat. Table 5 shows publications with vapor pressure fitting equations derived by others from data from publications given in Table 4. Examination indicates that the first three equations in Table 5 (references [28–30]) are derived only from the data of Young and Nelson [25]. Here, it is worth mentioning that our evaluation of the Wagner equation constants presented in reference [30] indicate that the Wagner and modified Redlich–Kwong–Soave equation constants could have been switched at the time of publication. In Table 5 the correct constants for the correlation of Basarova et al. [30] are shown in accordance with our observation. The two equations from reference [31] are derived from the combined data of Young and Nelson [25], Gorbachev [26], and Norton et al. [27].

In Table 1, the measured vapor pressure data of nicotine from this study are compared with data (derived from equations proposed by authors) of Gorbachev [26] and Young and Nelson [25] in the overlapping temperature ranges. As it can be seen from the table, the experimental data agree satisfactorily with the previous results. The comparison with all other data (experimental data and curve fittings) is presented graphically in Fig. 4. It can be seen that

Table 2
Heat of vaporization and Antoine constants for tobacco alkaloids.

Tobacco alkaloid	Temp. range (K)	Antoine constants			Normal boiling point	Heat of vaporizationat at T_b
		A	B	C	T_b (K)	Δ_l^gH (T_b) (kJ/mol)
Nicotine	447.7–617.8	6.158 ± 0.025	1827.400 ± 18.880	−80.977 ± 2.761	521.0	48.9 ± 0.6 (slope) 49.1 ± 0.5 (Eq. (7))
Anabasine	478–644.3	6.539 ± 0.142	2261.812 ± 113.366	−56.298 ± 15.610	555.2	53.7 ± 0.5 (slope) 53.6 ± 2.7 (Eq. (7))
Cotinine	537.7–669.7	6.325 ± 0.101	2184.923 ± 80.140	−113.630 ± 10.722	619.4	63.9 ± 0.9 (slope) 62.7 ± 2.3 (Eq. (7))

Table 3
Vaporization enthalpies and vapor pressures at 298.15 K.

Tobacco alkaloid	Δ_l^gH (kJ/mol)	$\Delta_l^gH_{lit}$ (kJ/mol)	p (kPa)	p_{lit} (kPa)
Nicotine	68.5	65.7 ± 2.7 [25][a] 67.4 ± 0.3 [28][a] 64.5 [29][a] 61.77 [30] 62.3 [31] 65.7 [31] 63.9 ± 2.1 [32]	0.6×10^{-2}	0.27×10^{-2} [24][b] 1.6×10^{-2} [25][b] 2.3×10^{-2} [26][b] 0.57×10^{-2} [27] 0.36×10^{-2} [32][c]
Anabasine	75.2		0.2×10^{-2}	0.5×10^{-2} [26][c] $1.8 * 10^{-2}$ [33][c]

[a] Calculated by Lipkind et al. [32] .
[b] Calculated by Norton et al. [27] .
[c] Calculated from equations presented in Tables 4 and 6.

Table 4
Literature based experimental vapor pressure data and each author's vapor pressure equations for nicotine.

Temp. range (K)	No of points	Correlation or value	Purity	Method	Reference
298–313	4	Concentration units (vapor pressures may be approximately calculated from these data)	Nosp	Air saturation	Harlan and Hixon [24]
334–373	4	$\log (p/\text{mmHg}) = 8.0935 - (2695.5)/T_{abs}/\text{K}$	Nosp	Air saturation	Young and Nelson [25]
375–519	23			Static	
293–518					
363–503	17	$\log (p/\text{atm}^{a}) = \log (T/\text{K}) - (2408.4/\text{T/K}) + 1.9135$	Nosp	Gas saturation	Gorbachev [26]
298.15	1	0.0425 ± 0.0003 mmH (0.0057 kPa at 25 °C)	$[\alpha]_D^{20} = -168.90^\circ$	Gas saturation	Norton et al. [27]
298–500	10 K intervals[b]	$\ln(p/p_o) = 69850065.0(T/\text{K})^{-3} - 1{,}084{,}705.54(T/\text{K})^{-2} - 2782.671(T/\text{K})^{-1} + 8.667$ $p_0 = 101.325$ kPa	≥98%[c]	Gas chromatography	Lipkind et al. [32]

Nosp: not specified.
[a] Unit not specified in the primary source, atm evaluated by author of the present study.
[b] Only vapor pressure correlation in the range of 298.15–500 K was given.
[c] Specified as (−)-nicotine.

Table 5
Vapor pressure correlations for nicotine in the literature.

Temp. range (K)	Correlation	Notes	Reference
298–523	$\ln (p/\text{kPa}) = (13.284947 \pm 0.092598) - (3552.865 \pm 63.670)/(T/\text{K} - 109.292 \pm 3.057)$[a] Antoine equation	$T_b = 519.24$ K (calculated); standard deviation 0.207 K and 0.014 kPa	Lencka et al. [28]
406–520	$\log (p/\text{kPa}) = 5.91387 - 1650.347/(T/\text{K} - 96.779)$[b] Antoine equation	(±)-nicotine	Stephenson and Malanowski [29]
300–520	$\ln (p_r) = (1/T_r)[-8.83376(1 - T_r) + 3.40331(1 - T_r)^{1.5} - 5.13787(1 - T_r)^3 - 6.91787(1 - T_r)^6]$[c] Wagner equation	$T_r = T/T_c$; $p_r = p/p_c$ $p_c = 3059$ kPa; $T_c = 756.3$ K	Bašarova et al. [30]
298–393	$\log (p/\text{mmHg}) = 9.541 - (3259/T/\text{K})$[d] 5.5% mean relative error in vapor pressure	ΔH at 298.15 K was calculated to be 14.9 kcal/mol (62.3 kJ/mol)	Corrod [31]
298–523	$\log (p/\text{mmHg}) = 43.745 - (4929/T/\text{K}) - 11.561 \log (T/\text{K})$[d] Standard error of estimate 0.025; mean relative error in pressure 4.1%	ΔH at 298.15 K was calculated to be 15.7 kcal/mol (65.7 kJ/mol)	

[a] Recalculated data and calculated vapor pressure equation from Young and Nelsons [25] data.
[b] The primary source was not specified.
[c] The reference of vapor pressure was Lencka et al. [28] and the data was made available in form of the Wagner equation.
[d] These equations are derived on the basis of the data published by Young and Nelson [25], Gorbachev [26], Norton et al. [27].

Table 6
Vapor pressure literature data and correlations for anabasine.

Temp. range (K)	No of points	Correlation or value	Purity	Method	Reference
377–527	8	log (p/mmHg) = 7.2423 – (2416.14/T/K) Accuracy 5% up to 100 °C and better than 0.1% for higher temperatures	$[\alpha]_D^{20} = -59.66^\circ$; specificgravity ${}^{20}_{20}$1.0481; $[n]_D^{20} = 0.5443$	Static	Nelson [33]
363–523	16	log (p/atm) = log (T/K) – (2586.6/T/K) + 1.9143	Nosp	Gas saturation	Gorbachev [26]
413.65	1	1.333 kPa	Nosp	Nosp	Babak et al. [34]

Table 7
Vapor pressure values for cotinine in the literature.

Temp. range (K)	Vapor pressure value	Note	Reference
483.15–484.15	6 mmHg (0.8 kPa)	From distillation data	Frankenburg and Vaitekunas [35]
443.15–448.15	Under approx. 1 mmHg (0.13 kPa)	From distillation data	Lamberts and Byerrum [36]
418.15–423.15	0.7 mmHg (0.09 kPa)	From distillation data	McKennis et al. [37]

the most recent data by Lipkind et al. [32], derived by correlation gas chromatography, are somewhat lower than other available data. For example, Lipkind et al. [32] reported the normal boiling point of 528.8 K for (−)-nicotine. Thus, the value given by Lipkind et al. [32] differs from value found in present study by 7.8 K, from Corrods [31] by 7.1 K and from Young and Nelsons [25] by 11.6 K.

The vapor pressure of anabasine was measured in the temperature range from 478 to 644.3 K and pressure range from 15 to 500 kPa. Only two articles were found that present vapor pressure curves for anabasine. Nelson [33] and Gorbachev [26] determined vapor pressures of anabasine in the temperature ranges of 352–556 K and 377–527 K, respectively. The comparison with these data in the overlapping temperature region is shown in Table 1. Values obtained in present study corroborate with data measured by Gorbachev [26]; however, there is a noticeable difference from Nelsons [33] experimental data. Fig. 5 presents a comparison with all data found. Vapor pressure literature data of anabasine is listed in Table 6. The data of this study show consistency with the vapor pressure curve measured by Gorbachev [26] and with the one data point of Babak et al. [34]. This indicates that the data of Nelson [33] are less reliable. The enthalpy of vaporization from this study is (53.7 ± 0.5) kJ/mol and from Gorbachevs [26] and Nelsons [33] experimental data, which were (52.3 ± 0.6) and (45.4 ± 2.3) kJ/mol, respectively. These values were calculated from the slopes in Fig. 5. The data of Gorbachev [26] and Nelson [33] converge around the boiling point, giving similar values of 555.2 K and 554.1 K, respectively. In the present study, the boiling point of (±)-anabasine was found to be 555.2 K.

The vapor pressure of cotinine was measured in the temperature range 537.7–669.7 K and pressure range 15–250 kPa. Experimental data are tabulated in Table 1 and plotted in Fig. 5. There is no reference data available for the vapor pressure range measured in the present study. Some indicative data of low vapor pressure values found in three different literature sources [35–37] are shown in Table 7. These literature values are boiling ranges, not boiling points of cotinine, and therefore, are not presented in Fig. 5. The reported boiling ranges were 483.15–484.15 K (at 0.8 kPa), 443.15–448.15 K (under about 0.13 kPa) and 418.15–423.15 K (at 0.09 kPa). Corresponding extrapolated temperatures from the Antoine equation obtained in this study were 453.8 K, 417.1 K and 410.7 K, respectively. The atmospheric boiling point for (−)-cotinine was found to be 619.4 K.

4. Conclusions

The paper presents new sets of vapor pressure data for three tobacco alkaloids: L-nicotine, (±)-anabasine, (−)-cotinine. New data expands the measured pressure range of nicotine, improves the current values for anabasine and gives the first vapor pressure curve for cotinine. Good precision and small total amount of samples were the main advantages to use DSC standard method measuring vapor pressures of selected alkaloids.

To improve the precision and accuracy of the measurements at higher temperatures, the influence of the parameters affecting the determination of the vapor pressure were analyzed and experimentally studied. It was shown that the amount of the sample had a noticeable effect on the shape of the boiling endotherm.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tca.2014.08.033.

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Paper II

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Extension of the DSC method to measuring vapor pressures of narrow boiling range oil cuts

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A B S T R A C T

An application of the standard test method for determining vapor pressure of pure compounds by thermal analyses (ASTM E 1782) was extended to vapor pressure measurements of narrow boiling range oil cuts by differential scanning calorimetry (DSC). The reliability of this application was examined by measuring comparable vapor pressure curves of selected narrow boiling oil cuts via a DSC based method and a static method. The oil cuts were distilled from a gasoline fraction (boiling range from about 363 to 453 K) from oil shale retorting oil, which was produced from Estonian kukersite oil shale by the Galoter process. The representative DSC measurements presented cover the temperature range from 318 to 484 K and pressure range from 15 to 750 kPa. Based on the results of the study, the DSC based method (ASTM E 1782) can be suggested as an alternative approach for determining vapor pressures of narrow boiling range oil cuts, with advantages such as a small sample size, use of commercial equipment and no need for sample degassing.

1. Introduction

When dealing with production and storage of oil products, the volatility characteristics, such as distillation behavior and vapor pressure, are important [1]. Vapor pressure measurements of oil and oil fractions provide information which can be used for design, refinery operations, safety, transportation, environmental exposure estimation, etc. There are numerous methods available for measuring vapor pressures of products (or compounds) derived from petroleum or alternative fuels [2–5]. For oil fractions not all these methods are suitable or reasonable. The use of direct methods, such as static methods [6–9] and ebulliometric methods [10,11], for narrow boiling range oil fractions or cuts can be widely found in the literature. With static methods the vapor pressure at a specific constant temperature is measured directly in a closed vessel (i.e., the sample does not leave the equilibrium cell) with a pressure gauge. The ebulliometric techniques are based on measuring boiling points at various specified pressures. Applications of additional methods to oil and oil fractions can also be found. For example, the flow method [6–8] or a continuous version of the knudsen effusion method [12].

We were looking for a simple, robust and convenient method to measure vapor pressures of narrow boiling range oil cuts. We needed a method that could be used for very small sample sizes (up to 100 mg per vapor pressure curve) over broad pressure and temperature ranges. This led us to the idea to test the suitability of the differential scanning calorimetric technique. In this DSC technique, the vapor pressure curve is determined by measuring, via separate experiments, a number of boiling points at various specified pressures. Advantages of the technique are the worldwide availability of commercial equipment and the very small sample size required. Small sample size is important, for example, for laboratories which are interested in measuring vapor pressures of alternative oils, which are often produced in small amounts by laboratory scale equipment. Another advantage is that no degassing is needed.

In 1967, the DSC manufacturer PerkinElmer suggested using hermetically sealed sample pans with pinholes in the lids [13]. This innovation became the basis for vapor pressure measurements by differential thermal analyses, including DSC. In this approach, the test specimen is placed in a sealed crucible, which has a pinhole in the lid, and the sample is heated at a constant rate to temperatures higher than the boiling point for the given pressure. The boiling temperature is determined as the extrapolated onset temperature where the tangent to the baseline intersects the tangent to the boiling endotherm. Excellent analysis of the parameters affecting the DSC measurement of vapor pressure of pure compounds can be found in earlier summaries [14,15]. Different factors, such as heating rates, sample sizes, pressure ranges, etc., were examined in these reviews. The first was written in 1976 and described the

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parameters influencing the results measured by differential thermal analyses (DTA) and DSC methods in the pressure range of 0.0133–1333 kPa. The second review [15] was published in 1994 and presented the results of the informational study conducted by an ASTM task group. The method was standardized in 1996 as the standard test method for determining vapor pressure by thermal analyses (ASTM E 1782) [16]. The standard is a recommended procedure for vapor pressure measurements of pure liquids and solids. The ASTM task group [16] suggested a pressure range of 5–2000 kPa, a heating rate of 5 K min^{-1}, sample size of 1–5 mg for solids and 1–5 μl for liquids and a pinhole size smaller than 125 μm. It is worth mentioning that an alternative to the expensive laser drilled or pinched pinholes is a small metal ball over a larger hole [17,18], although this approach does usually require higher heating rates. This adaptation was first used by Farritor and Tao [19].

Table 1 presents a summary of studies [14,15,17,18,20–32] which have used the DSC technique for vapor pressure measurements. It contains a list of compounds studied, measurement conditions used (such as the heating rate, pinhole size and pressure range) and also major problems, notes and requirements selected from the original publications. The information compiled in Table 1 reveals that there has been continuous emphasis on developing the method. Before the method was standardized, studies were directed toward determining the best operating conditions for obtaining reliable results; after standardization, the studies focus on extension of the method to wider applications, and thus, the requirements recommended by the standardized method have seldom been fully applied. From Table 1 the following can be mentioned: although the DSC method is standardized, it is useful to optimize parameters, such as the diameter of the pinhole, heating rate, sample size and pressure range, to achieve results of the highest accuracy. Although the standard test method already has a broad pressure and temperature range, it may be extended when some extra modifications are made. Some authors have successfully measured vapor pressures below 5 kPa using larger pinhole sizes [25,31] or larger pinholes with higher heating rates [23,30]. Although DSC has generally been used to measure the vapor pressures of pure compounds, its application can be extended to vapor pressure determination of multicomponent systems that contain a single dominant compound [26] or of binary systems [28,29].

The present work aims to evaluate the possibility of extending the DSC based vapor pressure technique to determine vapor pressure curves of narrow boiling range oil fractions, also called cuts. These narrow boiling range cuts are generally taken from a distillation temperature range that is about 10–50 K wide [33]. A narrow boiling oil cut can also be defined as a fraction whose ASTM 10–90% distillation curve has a slope of less than 0.8 K/%, but this definition may vary from one source to another [33].

2. Experimental

2.1. Materials

Narrow boiling oil range cuts were distilled from the light oil fraction (also called a gasoline fraction) of an oil shale oil, which is an alternative synthetic crude oil. The crude oil shale oil was manufactured from Estonian kukersite oil shale by the Galoter process [34]. Oil shale is a sedimentary rock with organic matter being mostly in the form of kerogen. Kerogen is a highly cross-linked macromolecular organic material [35]. To produce synthetic crude oil from oil shale, the kerogen is broken down by heat in a process called retorting. This involves heating oil shale to about 773 K in an inert environment [36,37].

The light shale oil fraction used in the present study was provided by the Estonian Energy Narva Oil Plant. The fraction had a refractive index of $n^{20}{}_{d}$ 1.444 and a density of 0.790 g cm^{-3}. The light shale oil was further distilled into narrow boiling range cuts under atmospheric pressure (which was between 96 and 99 kPa depending on the day) by using a laboratory scale rectification column (4.4 theoretical plates and a reflux ratio of 6) and also by using a simple batch distillation system. For the present study, two cuts from the rectification (with suffix “R” for rectification) and one cut from the simple distillation (with suffix “S” for simple distillation) were selected to verify the reliability of the application in this paper. Basic characterization data for these cuts are listed in Table 2. Average molecular weights were determined using the cryoscopic method with benzene as the solvent, which had an accuracy of ±5 g mol^{-1}. Densities were measured to ±0.00001 g cm^{-3} at 293.15 K with an Anton Paar DMA 5000 M.

The pure reference chemicals used to test the vapor pressure measurements of the DSC apparatus and the ERAVAP tester (static method) were benzene and *o*-xylene. Benzene (CAS No. 71-43-2, assay of 99.96%) was supplied by Lach-Ner s.r.o. *o*-Xylene (CAS No. 95-47-6, purity of ≥99.0% by GC) was produced by Sigma–Aldrich. The chemicals were used without further purification.

2.2. Apparatus and procedure

2.2.1. Differential scanning calorimeter for vapor pressure measurements

DSC based vapor pressure measurements were conducted using a high pressure differential scanning calorimeter, model Netzsch DSC 204HP Phoenix, equipped with a standard DSC cell and a pressure and flow control system. The technical data of the apparatus, procedure for performance tests with reference materials and temperature calibration were described in detail previously [32]. In short, a sample was placed into a hermetically sealed 40 μl aluminum crucible, which had a pinhole in the lid. The diameter of the pinhole was 50 μm, the heating rate was 5 K min^{-1} and the purge gas (nitrogen) had a flow rate of 40 ml min^{-1}. The sample size used for narrow boiling fractions obtained by rectification was 3–6 mg at 15–50 kPa and 7–15 mg around atmospheric and higher pressures. The sample size used for fractions obtained by simple batch distillation was 6–13 mg at 30–70 kPa and up to 17 mg at atmospheric and higher pressures. These experimental parameters were selected on the basis of the previous study [32] and the ASTM standard (ASTM E 1782) [16]. Performance tests with benzene and *o*-xylene are presented in Table 3 and plotted also in Fig. 4. These results compare reliably with literature values [38–42].

2.2.2. Vapor pressure measurements by a static vapor pressure tester

An ERAVAP commercial static vapor pressure tester from Eralytics GmbH was used to verify the reliability of the vapor pressure curves obtained by the DSC method. The instrument has a temperature range of 273–393 K and a pressure range from a few kPa to 1000 kPa. Static instruments of this type are widely used all over the world, in the aforementioned temperature and pressure ranges, to obtain data for quality control and storage of petroleum products. The measurements with the ERAVAP were run according to the standard test method for determination of vapor pressure (VP$_x$) of petroleum products, hydrocarbons, and hydrocarbon–oxygenate mixtures (Triple Expansion Method) ASTM D 6378 [43]. The single point approach with a vapor–oil ratio of 4:1 was used. This test method is best suited for samples with vapor pressures between 7 and 150 kPa at 310.95 K.

Performance tests with benzene and *o*-xylene are presented in Table 4 and also plotted in Fig. 4. These results are compared with reliable literature values [38–42]. It can be seen that the

Table 1
Overview of the use of DSC in the literature for vapor-pressure measurements. The method was standardized in 1996.

Year/ Ref.	Test material	Heating rate (K min^{-1})	Pressure range (kPa)	Pinhole size (μm)	Notes (N)/performance (P)
1972/ [20]	5 Pure compounds (hexane, chlorobenzene, ethyl propionate, octyl alcohol, nitrobenzene)	10	2.7–98	N/A	N: Corborundum powder added as an inert material to reduce overheating and to increase the surface area of the sample. P: Deviation from literature was 1.2 K. Average relative error of ΔH_v was 8.5%.
1976/ [14]	2 Pure compounds (water, isopropyl alcohol)	10–20	0.013–1333	≤800	N: Recommended optimal parameters for TGA and DSC techniques. Samples of 1–15 μl are advised. Small samples and heating rates that are too slow influence the accuracy of measurements due to vaporization of the sample prior to the boiling point. Sample sizes that are too large results in super-heating and partial self-cooling. P: Relative error of temperatures from literature values was 2.6%.
1989/ [17]	7 Pure compounds (toluene, isopalmitic acid, benzoic acid, dibutyl phthalte, fragrances, stearic acid)	10–20	−0.1	700 + ball 1.6mm	N: A modification using a large pinhole size with a metal ball over the pinhole was suggested. Small sample sizes or low heating rates cause vaporization prior to boiling. A large sample size results in overheating. An inert material such as silicon carbide should be added. A suitable pressure range of 0.1–7000 kPa at temperatures between 243 and 873 K was suggested. P: The measuring accuracy was ±1 K.
1991/ [21]	2 Pure compounds (ethanol and benzoic acid)	5	100–3000	100	N: Exothermal effect at 3 MPa was determined. This effect was described as aluminum oxidation.[a] P: not evaluated
1992/ [22]	Water	5	100–1890	30 or 50	N: See the comment below the table. [a] P: Not evaluated.
1993/ [23]	3 Pure compounds (propylene glycol, isopropyl palmitate, glycerine)	5, 10, 15	0.67–3.23	400	N: A pinhole of 400 μm is suitable to use with higher heating rates. P: Not evaluated.
1994/ [15]	Pure compounds	5–10	7–2000	25–127	N: Recommended practical measurement parameters based on the ASTM task group studies. Pinholes of ≥127 μm give acceptable results when the heating rate is sufficient to avoid unnecessary loss of sample. The quality of the pinhole influences the peak shape. Sample size of 2–4 mg.[a] P: Relative error of vapor pressures of water from literature values was 2.4%.
1996/ [24]	6 Pure compounds (decane, dodecane, tetradecane, aromatic compound, 2 brominated aromatic compounds)	5	0.67–101.3	75	N: It was recommended to use a sample size of 2–3 mg below 2.67 kPa to avoid peak broadening.[a] P: Standard error of estimate of 0.1–0.3 K.
2003/ [25]	3 Pure compounds (water, DMMP, DIMP)[c]	5	0.2–101.3	50–375	N: Extension of the DSC method for wider pressure ranges. An increased pinhole size below or near 5 kPa gives sharper peaks, but also increases vaporization of the sample prior to boiling. It was proposed that the slope of the leading edge of the boiling endotherm be at least −3 mW/K to optimize pinhole size as a function of pressure.[b] P: Accuracy of the method for water was ±1 K.
2004/ [26]	2 Multicomponent mixtures (clove and eucalyptus oil)	5	5–35	76–254	N: The multicomponent mixtures contained one dominant compound. P: Relative error of vapor pressure was 1–3%.
2009/ [27]	4 Pure compounds (water, cyclohexane, acetic ether, isopropanol)	10	4.5–7000	50	P: Not evaluated.
2010/ [28]	3 Binary mixtures (with stearic, palmitic and linoleic acid)	15 and 25	6.67	250	N: The boiling points of mixtures with different compositions were measured at a constant pressure. P: Standard deviation of 0.20 K. Uncertainties for temperature and pressure are given.
2011/ [29]	4 Binary mixtures (6 fatty acid ethyl esters)	25	3.99; 5.33 and 9.33	250	N: The boiling points of mixtures with different compositions were measured at constant pressures. P: Abs. deviation of 0.1–1.9 K. Uncertainties for temperature and pressure are given.
2011/ [30]	6 Pure compounds (selected ethyl esters)	25	1.33–9.33	250	N: The optimal parameters (heating rate, pinhole size) for lower pressures were determined. P: Uncertainty of 0.4 K, relative deviation of boiling temperatures from literature values was less than 3.5%.[b]
2012/ [18]	6 Pure compounds (*n*-tetradecane, 5 selected fatty acids)	25	1.33–9.33	800 + ball 1.0 mm	N: Small ball over a larger pinhole was combined with a higher heating rate. P: Standard deviation of 0.4 K; uncertainties for measured pressures are given. Mean abs. deviation from literature values was 0.6–1.5 K and mean abs. deviation of the Antoine equation was 0.3 K.[b]
2013/ [31]	2 Pure materials (water, 1-octanol)	5	0.2–101.4	75, 175, 250, 350	N: Pinholes of 75–350 μm give sharper endotherms and yield accurate results at lower pressures. The authors rebutted the earlier article [25] – the slope of the boiling endotherm leading edge is not a suitable criterion for determining the appropriate pinhole size.[b] P: Mean $\Delta T \pm$ 95% confidence level: 0.54 ± 0.33 K (75 μm pinhole); 0.49 ± 0.59 K (175 μm); 0.36 ± 0.24 K (250 μm); 0.42 ± 0.20 K (350 μm).
2014/ [32]	3 Pure materials (nicotine, anabasine, cotinine)	5	15–1000	50	N: Sample size greatly influenced the slope of the boiling endotherm, especially around 15 kPa and over 250 kPa. Incorrect sample size can change the slope and lower the measurement accuracy. P: The mean absolute temperature error was ±0.4 K, accuracy of the measurement pressure was 1.8%. Expanded uncertainties with a 95% confidence level for temperature and pressure were given.

[a] Studies were carried out before the ASTM E 1782–96 standard was approved. However, the main measurement conditions concerning sample size, heating rate, pinhole diameter and pressure range were the same as suggested later by the standard test method.

[b] Studies that extended the ASTM E 1782 standard below 5 kPa with larger pinholes.

[c] DMMP – dimethyl methyl phosphonate; DIMP – diisopropyl methyl phosphonate.

Table 2
Basic properties of shale oil fractions used in this study.

Sample	Cut width by distillation (K)	T_b by DSC[a] (K)	Molecular weight MW (g mol^{-1})	Density ρ at 293.2 K (g cm^{-3})
Cut 1_R	10	373.1	99	0.7520
Cut 2_R	5.9	394.8	109	0.7738
Cut 3_S	8.5	407.7	114	0.7993

[a] Calculated from linear regression of vapor pressure data obtained by DSC at 101.33 kPa.

Table 3
Vapor pressures of benzene and *o*-xylene by DSC and comparison to literature values.

Material	T (K)[a]	p (kPa)[b]	p (kPa) Ref. [38]	Δp (%)	p (kPa) Ref. [39]	Δp (%)	p (kPa) Ref. [40]	Δp (%)
Benzene	325.6	39.52	39.73	0.5			40.12[c]	1.5
	331.7	49.45	49.65	0.4			49.88	0.9
	341.7	69.20	69.87	1.0	73.25[c]	5.5	69.87	1.0
	353.6	101.60	102.57	0.9	104.97[c]	3.2	102.47	0.8
	385.3	247.52	247.45[c]	0.0	244.98	1.0	251.17[c]	1.5
	415.8	499.10	498.24[c]	0.2	487.04	2.5	518.19[c]	3.7
	435.4	750.14			726.67	3.2		
Material	**T (K)[a]**	**p (kPa)[b]**	**p (kPa) Ref. [38]**	**Δp (%)**	**p (kPa) Ref. [41]**	**Δp (%)**	**p (kPa) Ref. [42]**	**Δp (%)**
o-Xylene	357.3	14.75	14.90	1.0	14.75	0.0	14.39	2.5
	376.7	29.61	29.82	0.7	29.45	0.5	28.96	2.2
	392.7	49.44	50.02	1.1	49.47	0.1	48.95	1.0
	401.5	64.27	64.81	0.8	64.65	0.6	64.17	0.2
	418.6	102.78	104.27	1.4	105.32	2.4	105.13	2.2

$\Delta p = \left(\frac{|(p_{DSC} - p_{Ref})|}{p_{Ref}}\right) \times 100\%$.

[a] Expanded uncertainties (0.95 level of confidence) of 0.2 K (from 15 to 101 kPa) and 0.4 K (>101 kPa).

[b] Expanded uncertainties (0.95 level of confidence) of 0.76 kPa for pressures $\geq$101 kPa, calculated from the sensor's full scale error of 0.008%; type B uncertainties of 0.25% of the reading for pressures $\leq$101 kPa (level of confidence = 0.95, k = 1.645).

[c] Extrapolated outside of the measured temperature range by the author of the present study.

performance of the instrument used is better for benzene (vapor pressure of 22.9 kPa at 310.95 K; boiling point of 353.3 K) than for *o*-xylene (vapor pressure of 2.5 kPa at 310.95 K; boiling point of 416.9 K). In general, the specific instrument used here showed a slight decrease in performance (a decrease in heats of vaporization and increase in vapor pressure) as the boiling point of the substance increased.

Table 4
Vapor pressures of benzene and *o*-xylene by ERAVAP and comparison to literature values.

Material	T (K)	p (kPa)[a]	p (kPa) Ref. [38]	Δp (%)	p (kPa) Ref. [39]	Δp (%)	p (kPa) Ref. [40]	Δp (%)
Benzene	313.2	25.0	24.36	2.6			25.0[b]	0.0
	323.2	36.9	36.16	2.0			36.60[b]	0.8
	333.2	53.2	52.19	1.9			52.38	1.6
	343.2	74.7	73.43	1.7			73.40	1.8
	353.2	102.8	101.01	1.8	104.97[b]	2.1	100.90	1.9
	363.2	137.8	136.10[b]	1.3	139.47[b]	1.2	136.29	1.1
	373.2	181.0	179.97[b]	0.6	182.50	0.8	181.12	0.1
	383.2	234.2	234.06[b]	0.1	235.48	0.5	237.15[b]	1.2
	393.2	300.2	299.68[b]	0.2	299.23	0.1	306.27[b]	2.0
Material	**T (K)**	**p (kPa)[a]**	**p (kPa) Ref. [38]**	**Δp (%)**	**p (kPa) Ref. [41]**	**Δp (%)**	**p (kPa) Ref. [42]**	**Δp (%)**
o-Xylene	353.2	14.3	12.66	13.0	12.62	13.3	12.29	16.3
	363.2	20.4	18.53	10.1	18.35	11.2	17.95	13.7
	373.2	28.5	26.46	7.7	26.13	9.1	25.67	11.0
	383.2	38.8	36.97	4.9	36.55	6.2	36.04	7.7
	393.2	52.8	50.63	4.3	50.24	5.1	49.72	6.2

$\Delta p = \left(\frac{|(p_{ERAVAP} - p_{Ref})|}{p_{Ref}}\right) \times 100\%$.

[a] Expanded uncertainties (level of confidence = 0.95) of 1.8 kPa.

[b] Extrapolated outside of the measured temperature range by the author of the present study[a].

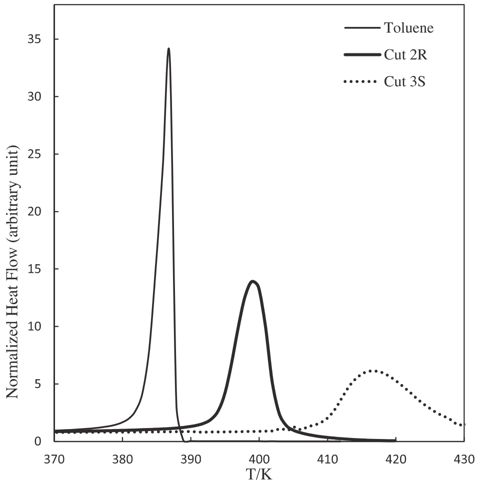

Fig. 1. Normalized DSC endotherms at atmospheric pressure for toluene, rectification cut 2_R and a simple distillation cut 3_S.

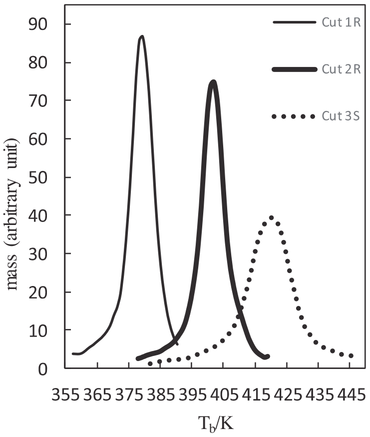

Fig. 2. Boiling point (T_b) distributions for rectification (1_R; 2_R) and simple distillation (3_S) cuts.

3. Results and discussion

Fig. 1 shows a comparison of select DSC endotherms at atmospheric pressure (which was between 96 and 99 kPa depending on the day) for a pure compound with a boiling point of 383 K (toluene), a rectification cut with a boiling point of 395 K (cut 2_R) and a simple distillation cut with a boiling point of 408 K (cut 3_S). For comparative purposes, the endotherms are normalized by sample amount and heat of vaporization. The heats of vaporization of the cuts were taken from Tables 3 and 5, where these were estimated from the slope of the integrated Clausius–Clapeyron equation. Fig. 1 shows that in comparison to the pure compound signal (a sharp, narrow and high signal) the signals from cuts are broader and shorter, with the endotherm from the simple distillation fraction being broader and shorter than that from rectification. This indicates that for narrow cuts more sample is needed to achieve an endotherm with a size comparable to that of an endotherm of a pure compound. It was shown in reference [16] that there is a substance specific optimal sample size below which determination of the onset temperature of the boiling endotherm could be of lower accuracy. One of the major reasons for the broadening and shortening of the DSC endotherm is that a cut is not a single compound. The cut contains a distribution of

Table 5
Experimental results from DSC and ERAVAP, calculated enthaplies of vaporization.

	DSC					ΔH (kJ mol^{-1}) at T_b	
Sample	T (K)[a]	p (kPa)[b]	p_{Eravap}[c] (kPa)	Δp (kPa)	Δp[d] (%)	DSC[e]	ERAVAP[f]
Cut 1_R	318.0	14.95	17.60	−2.6	17.7	33.6	32.4
	335.1	29.92	32.92	−3.0	10.0		
	349.6	49.69	53.35	−3.7	7.4		
	360.0	69.48	73.65	−4.2	6.0		
	372.4	101.30	105.67	−4.4	4.3		
	406.2	247.43					
	438.4	498.43					
	458.1	749.32					
Cut 2_R	354.9	29.78	32.34	−2.6	8.6	35.4	35.1
	370.4	49.65	53.20	−3.5	7.1		
	381.1	69.49	73.25	−3.8	5.4		
	394.7	102.71	107.29	−4.6	4.5		
	429.8	246.87					
	464.4	498.26					
	484.4	749.33					
Cut 3_S	366.3	29.82	33.94	−4.1	12.2	36.7	34.7
	382.9	49.72	55.61	−5.9	10.6		
	388.4	59.67	64.88	−5.2	8.0		
	409.6	106.27					
	452.8	297.74					

[a] Expanded uncertainties (0.95 level of confidence) of 0.2 K (from 15 to 101 kPa) and 0.4 K (>101 kPa).

[b] Expanded uncertainties (0.95 level of confidence) of 0.76 kPa for pressures $\geq$101 kPa, calculated from the sensor's full scale error of 0.008%; type B uncertainties of 0.25% of the reading for pressures $\leq$101 kPa (level of confidence = 0.95, $k = 1.645$).

[c] Calculated from linear regression of vapor pressure data obtained by ERAVAP.

[d] $\Delta p = \left(\frac{|(p_{DSC} - p_{ERAVAP})|}{p_{DSC}}\right) \times 100\%$.

[e] Expanded uncertainties (level of confidence = 0.95) of 0.5 kJ mol^{-1}.

[f] Expanded uncertainties (level of confidence = 0.95) of 1.8 kJ mol^{-1}.

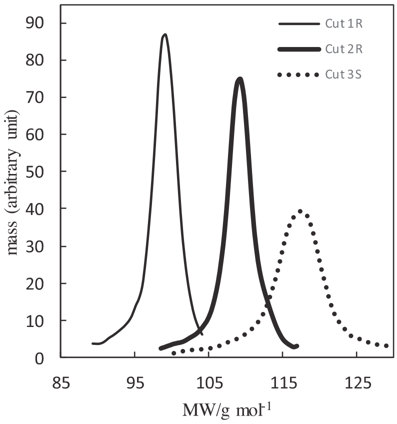

Fig. 3. Molecular weight (MW) distributions for rectification (1_R; 2_R) and simple distillation (3_S) cuts.

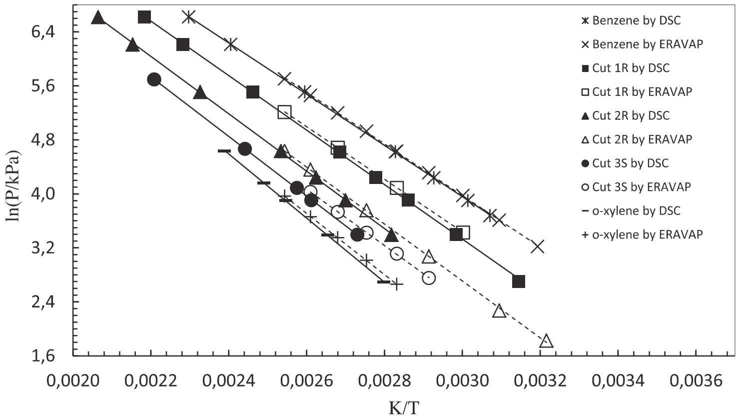

Fig. 4. Experimental vapor pressure data by DSC and by ERAVAP. Solid lines present trendlines for DSC measurements and dash lines for ERAVAP. From top to bottom by DSC and ERAVAP: benzene, Cut 1_R, Cut 2_R, Cut 3_S and *o*-xylene.

compounds. The apparent distribution is quite symmetric, usually well represented by a three parameter Gaussian distribution function [44,45]. As each cut has a characteristic boiling range, then for visualization purposes the indicative boiling point distribution of each cut was roughly evaluated using a DuPont Instruments 951 Thermogravimetric Analyzer (TGA) and shown in Figs. 2 and 3. For this 5 mg of sample was heated at a rate of 5 K min^{-1}. The sample was placed into a hermetic aluminum crucible (volume of 100 μl) with a pinhole of 50 μm in the lid. We found that under these conditions the differential mass loss curve is roughly representative of the boiling point distribution curve. As an additional step, indicative molecular weight distributions for the cuts in Fig. 3 were derived from the boiling point curves using a derived relationship between boiling point and molecular weight. For this, the original light shale oil fraction was separated into 17 fractions using the rectification column and into 9 fractions with a simple batch distillation, and corresponding properties of the fractions were measured. Figs. 2 and 3 indicate that the cuts selected for the study have quite symmetric distributions with different distribution widths: the rectification cut 1_R has the narrowest distribution followed by rectification cut 2_R, and the simple distillation cut 3_S has the widest distribution. This is consistent with the shape of the DSC endotherms.

Fig. 4 presents graphically, in the form of the integrated Clausius–Clapeyron equation, experimental vapor pressure curves obtained by the DSC method. The vapor pressure curves from a static method (by means of the ERAVAP commercial vapor pressure tester, in accordance with ASTM D 6378) are shown for comparison. It can be seen that the DSC based vapor pressure curves of the cuts can be adequately fit using the integrated Clausius–Clapeyron equation since linear behavior is observed on an $\ln P$ over $1/T$ plot. For both narrower rectification cuts and the wider distillation cut the coefficients of determination of the linear regression (R^2) were seen to be very high ($\geq$0.9998).

Fig. 4 reveals that the data obtained for narrow boiling range cuts by the two methods, the DSC method and the static method (using the ERAVAP vapor pressure tester), show close trends. It can be noted that the vapor pressures measured by DSC are somewhat smaller than the data obtained by the ERAVAP vapor pressure tester, both for cuts and pure compounds. However, for pure compounds the DSC values coincide well with the literature values, as seen in Table 3, and the data from the ERAVAP vapor pressure tester show a similar kind of deviation from both the literature values and the DSC data for oil cuts. Therefore, the minor deviation between the DSC and ERAVAP data for oil cuts could result mostly from the ERAVAP's performance. Actual experimental data, that numerically support the outcomes above, are shown in Tables 3 and 4 for pure compounds and in Table 5 for narrow boiling range cuts. These results indicate that compositional changes of the narrow boiling point fractions, when the sample is evaporated through a pinhole from a hermetically sealed container, does not significantly influence boiling temperature determination from the onset of the endotherm (determined as the extrapolated onset temperature, where the tangent to the baseline intersects the tangent to the boiling endotherm). In this regard, the behavior of narrow boiling point fractions can be viewed as close to that of pure compounds.

4. Conclusions

Comparative vapor pressure measurements of narrow boiling range cuts by a static method (ERAVAP commercial vapor pressure tester, in accordance with ASTM D 6378) and a DSC based method (in accordance with ASTM E 1782) indicate that the DSC based method can reliably be used for these complex, multi-component substances. Thus, the adequate experimental results presented and the advantages of the DSC method (small sample size, use of commercial equipment, no need for degassing, relatively wide temperature–pressure range) allow the DSC based vapor pressure technique to be suggested as a simple, robust and convenient alternative for determining vapor pressure characteristics of narrow boiling range oil cuts.

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Paper III

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Application of a DSC based vapor pressure method for examining the extent of ideality in associating binary mixtures with narrow boiling range oil cuts as a mixture component

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ABSTRACT

This study is aimed to extend an application of the differential scanning calorimeter (DSC) based vapor pressure method to evaluate vaporization of a target substance from a complex matrix that exhibits several times lower vapor pressure. The experiments involved preparing mixtures of known composition and measuring their vapor pressure by a DSC based vapor pressure method (following ASTM 1785 guidelines). The vapor pressure of two types of associating "binary systems" were examined: (1) a narrow boiling range oil fraction (or distillation cut) mixed with a pure compound (nicotine or 2-*tert*-butylphenol); (2) a mixture of two narrow boiling range oil fractions. Emphasis was placed on 50:50 mol% mixtures. To evaluate deviation from ideality, the total vapor pressure curves measured were compared to values calculated from Raoult's law. Narrow boiling range oil fractions (distillation cuts) were treated as single pseudocomponents in these calculations. The vapor pressure curves obtained suggest that the DSC based vapor pressure method is a useful tool for characterizing these kinds of multicomponent systems. The results presented can be viewed as a preliminary indication of the extent of ideality in systems containing "synthetic crude oil" from Kukersite oil shale, which is rich in alkyl-phenolic moieties.

1. Introduction

One of the basic goals of chemical engineering thermodynamics is estimating the deviations from ideality. Although the problem seems quite fundamental, there are often no answers when it comes to undefined complex mixtures. Undefined complex mixtures are mixtures containing hundreds to thousands of compounds with a wide range of molecular weights, polarities and functionalities. These mixtures can be described by conventionally defined average properties rather than by detailed chemical composition [1]. Examples of these undefined mixtures could be oils or tars from different origins, for example from heavy petroleum [2], biomass [3] or oil shale [4]. For these types of complex mixtures even rough estimates of the extent of ideality are of great interest for many research communities (biomass thermo-chemical conversion, fossil fuel thermo-chemical conversion, environmental engineering and risk assessment communities).

The current work presents some experimentally measured data aimed at gaining preliminary insight into the degree of ideality of systems exhibiting the selected level of complexity. We have selected narrow boiling range distillation cuts (fractions) of oil rich in phenolic moieties as the samples to study. The current study is an initial investigation into the degree of ideality or non-ideality by looking at deviations from Raoult's law at the selected liquid phase concentration, and describing the full vapor-liquid behavior is out of the scope of this study. For this initial investigation, mostly 50:50 mol% mixtures were used because the work was driven by a specific interest in converting the vapor pressure curve of a narrow boiling range fraction (which corresponds to the initial boiling point) to those of average parameters (the average boiling point of the fraction).

A Differential Scanning Calorimeter (DSC) based technique (ASTM E 1782) was chosen to determine the vapor pressures of binary mixtures of narrow boiling range distillation cuts or of a narrow boiling range cut mixed with a pure compound. The pure compounds were selected to be potentially capable of strong polar interactions (hydrogen bonds) with the phenolic moieties present in the oil. The DSC based vapor pressure measurement technique is a standardized vapor pressure measurement technique for pure compounds (ASTM E 1782 [5]). The vapor pressure curve is determined by measuring, via separate experiments, a number of boiling points at various specified pressures. During an experiment the

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sample is evaporated, being heated at a constant rate, through a pinhole from a hermetically sealed sample pan. Insights into fundamental aspects of the technique can be found in previous studies [6,7]. This pure compound vapor pressure measurement method has also been extended to measure vapor pressures of multicomponent systems (see the latest summary of DSC based vapor pressure experiments, as of 2014 [8]). Some applications of the DSC technique have been on binary mixtures of pure compounds [9–11] or on multicomponent mixtures containing one dominant compound [12]. And lately, the literature shows an application of the DSC technique to measure the vapor pressures of narrow boiling range oil fractions [8]. Here, we extend the scope of application to measuring the total vapor pressures of "binary mixtures" containing narrow boiling range fractions, which is another somewhat uncommon application of this ASTM E1782 approach. Therefore, an underlying goal was to evaluate the suitability of the DSC technique (ASTM E 1782) for "binary mixtures" containing narrow boiling range oil fractions as pseudocomponents.

2. Experimental

2.1. Materials

The narrow boiling range oil fractions used were distilled from a wide middle shale oil fraction provided by the Estonian Energy Narva Oil Plant. The shale oil was manufactured from Estonian Kukersite oil shale by one type of industrial retorting process, known as the Galoter process [13–15]. Oil shale is a sedimentary rock (solid fossil fuel) with organic matter being mostly in the form of kerogen, which is an insoluble highly cross-linked macromolecular organic material [16,17]. In order to produce synthetic crude oil from oil shale, the kerogen is broken down by heat to monomers and oligomers (or oil size species) in an inert environment in a process called retorting.

The narrower boiling range cuts, or fractions, were distilled under reduced pressure ($10^{-1} - 10^{-2}$ Torr) by simple batch distillation (also called Engler distillation). These narrow cuts were taken from a distillation temperature range that was about 10–15 K wide. Three of these distillation cuts or fractions, which essentially did not overlap (the difference between their average boiling points was about 50 K), were selected for this study. The narrow boiling point fractions were considered to be pseudocomponents and were described by average properties. Characteristics of the oil fractions selected for this study are shown in Table 1. It can be seen that the fractions have a highly phenolic character (OH wt% values shown correspond to a phenolic compound content of about 30–60 wt% [18]). Vaporization curves, which are representative of the variation of boiling points of progressively less volatile oil, measured by TGA using hermetic capsules with 50 μm pinholes, are given in Fig. 1. Fig. 1 also indicates that the boiling ranges of these fractions are only slightly overlapping (Fractions A and B had less than 10% overlap, and Fractions B and C had less than 30% overlap).

Table 1
Characteristics of the oil fractions A, B and C: initial boiling point (T_b^{DSC}) measured by DSC, average boiling point (T_b^{TGA}) measured by TGA, number average molecular weight (MW), hydrogen-carbon atomic ratio (H/C), wt% of OH-groups and number of OH groups per average molecule.

Fraction	T_b^{DSC}/K	T_b^{TGA}/K	MW/g mol^{-1}	H/C	OH/wt%	OH per molecule
A	543	569	191	1.41	5.9	0.7
B	606	626	227	1.32	7.9	1.1
C	648	675	284	1.27	6.7	1.1

Standard uncertainties u for measured values are u(T_b^{TGA}) = 2.5 K, u(T_b^{DSC}) = 0.6 K for Fraction A, 0.7 K for Fraction B and 1.4 K for Fraction C, u(MW) = 5 g mol-1, u(wt% OH) = 0.44 wt%, and u(wt% C) = 0.15 wt%, and u(wt% H) = 0.05 wt%.

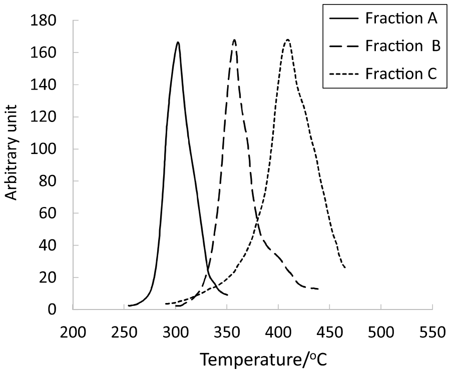

Fig. 1. Indicative boiling ranges of the fractions studied.

The polar pure compounds used to prepare potentially associating binary mixtures with these oil fractions were nicotine and 2-*tert*-butylphenol. Nicotine (CAS No. 54-11-5; systematic IUPAC name: 3-(methylpyrrolidin-2-yl)-pyridine; $C_{10}H_{14}N_2$) with a purity of 99%+, was obtained from Acros Organics. 2-*tert*-butylphenol (CAS no. 88–18–6; systematic IUPAC name: 2-(2-Methyl-2-propanyl)phenol; $C_{10}H_{14}O$) with a purity of 99% (≥0.985%) was purchased from Sigma Aldrich. The chemicals were used without further purification as seen in Table 2. The molecular weight of nicotine is 162.2 g mol^{-1} and the boiling point is 531 K (measured). 2-*tert*-butylphenol has a similar molecular weight (150.2 g mol^{-1}) and a boiling point of 496.2 K (measured). The vapor pressure data, measured in our laboratory, for 2-*tert*-butylphenol are given in Table 3 and for nicotine can be found from our previous study [19]. The vapor pressure values measured were in good agreement with previous literature data (for the reference literature vapor pressure data used for nicotine see our previous study [19]; for 2-*tert*-butylphenol see a comparison with references [20–23] presented in Table 4).

Each binary mixture was prepared by mixing two shale oil fractions or a shale oil fraction and a pure compound to give the desired composition (mass basis) in hermetically sealable vials. To ensure homogeneity, the mixture (in a hermetically sealed vial) was then placed in an ultrasonic bath at 313 K for about 50 min. Vapor pressures were measured the next day to give extra time for normal mixing. No indications of immiscibility were observed for these

Table 2
Sample table of pure compounds used.

Chemical name	Source	Initial Purity [a]	Purification Method	Final Purity	Analysis Method [a]
Nicotine	Acros Organics	≥0.99[b]	–	≥0.99[b]	GC [c]
Toluene	Sigma-Aldrich	≥0.998[b]	–	≥0.998[b]	GC [c]
Benzene	Sigma-Aldrich	≥0.998[b]	–	≥0.998[b]	GC [c]
2-*tert*-butylphenol	Sigma-Aldrich	≥0.985[b]	–	≥0.985[b]	GC [c]

[a] By a Supplier.
[b] Mass fraction.
[c] Gas chromatography.

Table 3
Experimental values of boiling temperatures at pressures p (or vapor pressure data) for toluene, 2-*tert*-butylphenol and oil fractions A, B and C. Expanded uncertainties with a 95% confidence level for temperatures and pressures are given.

T/K	p/kPa	T/K	p/kPa	T/K	p/kPa	T/K	p/kPa	T/K	p/kPa
Fraction A		Fraction B		Fraction C		Toluene		2-*tert*-butylphenol	
514.6 ± 0.4	39.42 ± 0.09	539.3 ± 0.4	19.91 ± 0.05	584.4 ± 0.4	19.90 ± 0.05	345.5 ± 0.2	29.65 ± 0.07	418.5 ± 0.2	9.90 ± 0.02
522.1 ± 0.4	49.42 ± 0.12	553.4 ± 0.4	29.82 ± 0.07	602.0 ± 0.4	29.82 ± 0.07	360.6 ± 0.2	49.44 ± 0.12	438.6 ± 0.2	19.82 ± 0.05
535.5 ± 0.4	69.18 ± 0.16	553.7 ± 0.4	29.58 ± 0.07	619.8 ± 0.4	49.71 ± 0.12	371.1 ± 0.2	69.20 ± 0.16	451.7 ± 0.2	29.75 ± 0.07
552.9 ± 0.4	101.60 ± 0.24	564.5 ± 0.4	39.48 ± 0.09	627.5 ± 0.4	59.64 ± 0.14	384.3 ± 0.2	101.60 ± 0.24	469.4 ± 0.2	49.63 ± 0.12
		565.7 ± 0.4	39.77 ± 0.09	646.7 ± 0.4	102.26 ± 0.24	418.6 ± 0.4	247.50 ± 0.76	479.2 ± 0.2	64.61 ± 0.15
		576.3 ± 0.4	49.72 ± 0.12						
		605.1 ± 0.4	101.23 ± 0.24						
		605.4 ± 0.4	101.40 ± 0.24						

Table 4
Comparison of experimental vapor pressure data of 2-*tert*-butylphenol to literature values.

T/K	p/kPa[a]	p/kPa	Δp/%[b]	p/kPa	Δp/%[b]	p/kPa	Δp/%[b]	p/kPa	Δp/%[b]
		Ref. [17]		Ref. [18]		Ref. [16]		Ref. [19]	
418.5	9.9	10.16	−2.6	9.8	1.4	9.97	−0.7	9.97	−0.7
438.6	19.82	20.05	−1.2	20.1	−1.4	19.93	−0.6	19.93	−0.6
451.7	29.75	30.05	−1.0	31.1	−4.4	30.02	−0.9	30.02	−0.9
469.4	49.63	49.8	−0.4	54	−8.0	49.93	−0.6	49.90[c]	−0.6
479.2	64.61	64.66	−0.1	71.9	−10.2	64.90	−0.44	64.80[c]	−0.3

[a] Measured in this work.
[b] $\Delta p\% = \frac{|x-X|}{X} * 100$, where x is measured value and X is reference value.
[c] Extrapolated values.

Table 5
Experimental values of boiling temperatures at pressures p (or vapor pressure data) for 50:50 mol% binary mixtures of benzene + toluene and of 2-*tert*-butylphenol and oil fraction A or B. Expanded uncertainties for random errors with a 95% confidence level for temperatures and pressures are given.

T/K	p/kPa	T/K	p/kPa	T/K	p/kPa
benzene + toluene[a]		Fr A + 2-*tert*-butylphenol[b]		Fr B + 2-*tert*-butylphenol[b]	
338.2 ± 0.2	41.72 ± 0.10	456.5 ± 0.4	19.74 ± 0.05	453.2 ± 0.4	14.75 ± 0.04
343.3 ± 0.2	49.54 ± 0.12	470.6 ± 0.4	29.65 ± 0.07	475.2 ± 0.4	28.46 ± 0.07
351.2 ± 0.2	64.00 ± 0.15	481.2 ± 0.4	39.54 ± 0.09	512.4 ± 0.4	76.04 ± 0.18
365.6 ± 0.2	99.21 ± 0.24	489.6 ± 0.4	49.45 ± 0.12	527.5 ± 0.4	108.93 ± 0.76
390.6 ± 0.2	196.68 ± 0.76	501.7 ± 0.4	64.26 ± 0.15		
		519.0 ± 0.4	101.90 ± 0.24		

[a] Standard uncertainty u in the mole fraction based concentration basis is u(x) = 0.005.
[b] Standard uncertainty u in the mole fraction based concentration basis is u(x) = 0.015.

binary mixtures. The measured vapor pressure data for the binary mixtures are given in Tables 5, 6 and 7. A total vapor pressure curve for each of the binary mixtures, as if they were ideal solutions, was calculated at a given temperature from Raoultís law as

$$P = \sum_{i}^{N} x_i P_i = x_1 P_1 + x_2 P_2 \tag{1}$$

where x_i is the component's (or distillation cut's) mole fraction in the solution and P_i is the vapor pressure of the component (or distillation cut). It is worth noting, that the mole fraction of the distillation cut or fraction is an average property, it is calculated using the average molecular weight of the fraction, whereas the vapor pressure is the actual vapor pressure of the fraction, which provides an indication of the fraction's initial boiling point, not its average boiling point. The measured vapor pressure data for oil fractions (or distillation cuts) A, B and C are given in Table 3.

Table 6
Experimental values of boiling temperatures at pressures p (or vapor pressure data) for 50:50 mol%[a] binary mixtures of nicotine and oil fractions A, B or C. Expanded uncertainties for random errors with a 95% confidence level for temperatures and pressures are given.

T/K	p/kPa	T/K	p/kPa	T/K	p/kPa
Fr A + nicotine		Fr B + nicotine		Fr C + nicotine	
478.3 ± 0.4	20.13 ± 0.05	478.4 ± 0.4	15.06 ± 0.04	443.4 ± 0.4	4.74 ± 0.01
492.0 ± 0.4	29.63 ± 0.07	491.4 ± 0.4	21.85 ± 0.05	490.7 ± 0.4	20.15 ± 0.05
502.7 ± 0.4	39.93 ± 0.09	512.4 ± 0.4	38.31 ± 0.09	512.4 ± 0.4	35.80 ± 0.09
511.3 ± 0.4	49.45 ± 0.12	527.5 ± 0.4	55.80 ± 0.13	527.5 ± 0.4	51.93 ± 0.12
522.0 ± 0.4	64.71 ± 0.15	539.3 ± 0.4	73.78 ± 0.18	539.3 ± 0.4	68.45 ± 0.16
542.5 ± 0.4	102.04 ± 0.24	542.9 ± 0.4	80.15 ± 0.19	542.9 ± 0.4	74.29 ± 0.18
		553.4 ± 0.4	101.41 ± 0.24	553.4 ± 0.4	93.75 ± 0.22

[a] Standard uncertainty u in the mole fraction based concentration basis is u(x) = 0.015.

Deviation from ideality is evaluated using the relative deviation (RD%) and average absolute relative deviation (ARD%) the measured pressure (P_m) and the pressure estimated by Raoult's law (P_R)

$$RD\% = 100\frac{P_m - P_R}{P_R} \tag{2}$$

$$ARD\% = 100\frac{1}{N}\sum \left|\frac{P_m - P_R}{P_R}\right| \tag{3}$$

So a negative RD% indicates negative deviation from Raoult's law and a positive RD% indicates positive deviation from Raoult's law. As this paper focuses on the applicability of the DSC based method to evaluate deviation from ideality (qualitative study), and does not emphasize vapor pressure data, then a complete uncertainty analysis is out of the scope of the current paper. The uncertainties, as a random errors reported in Tables 5–7, are shown because of journal requirements.

2.2. Apparatus and procedure

2.2.1. DSC technique

Vapor pressure curves were measured by the DSC technique according to recommendations given in the ASTM E 1782 standard. The heating rate was 5 °C/min and the purge gas (nitrogen) flow rate was 40 ml/min. Hermetically sealable pans, with a 50 µm diameter pinhole in the lid, were used. A Netzsch DSC 204 HP Phoenix, equipped with a standard DSC cell and a pressure and flow control system, was used. The technical data for the apparatus, procedure for performance tests with reference materials and temperature calibration were described in detail previously [19]. The performance of the method for studying the vapor pressures of narrow boiling point oil fractions is shown in [8]. Because three papers were found that cover the application of the DSC based technique to binary mixtures of pure compounds [9–11], then the corresponding performance here was verified by only a single experiment using a 50:50 mol% binary benzene (purity of 99.9%; Sigma-Aldrich; used without further purification as seen in Table 2) and toluene (purity

Table 7
Experimental values of boiling temperatures at pressures p (or vapor pressure data) for binary mixtures of narrow boiling oil fractions A, B or C at given compositions. Expanded uncertainties for random errors with a 95% confidence level for temperature and pressure are given.

T/K	p/kPa	T/K	p/kPa	T/K	p/kPa	T/K	p/kPa	T/K	p/kPa
Fr A + Fr B	50:50 mol%[a]	Fr A + Fr B	10:90 mol%[a]	Fr A + Fr B	90:10 mol%[a]	Fr B + Fr C	50:50 mol%[a]	Fr A + Fr C	50:50 mol%[a]
516.9 ± 0.4	24.68 ± 0.06	532.7 ± 0.4	19.73 ± 0.05	493.5 ± 0.4	19.72 ± 0.05	555.2 ± 0.4	19.72 ± 0.05	501.9 ± 0.4	19.75 ± 0.05
527.0 ± 0.4	34.55 ± 0.08	539.0 ± 0.4	24.66 ± 0.06	512.5 ± 0.4	34.55 ± 0.08	572.3 ± 0.4	29.60 ± 0.07	514.8 ± 0.4	29.63 ± 0.07
542.2 ± 0.4	49.44 ± 0.12	552.1 ± 0.4	34.55 ± 0.08	525.8 ± 0.4	49.41 ± 0.12	583.4 ± 0.4	39.53 ± 0.09	526.7 ± 0.4	39.58 ± 0.09
550.1 ± 0.4	59.31 ± 0.14	565.1 ± 0.4	49.44 ± 0.12	536.5 ± 0.4	64.14 ± 0.15	592.6 ± 0.4	49.45 ± 0.12	537.2 ± 0.4	49.46 ± 0.12
572.4 ± 0.4	100.72 ± 0.24	595.6 ± 0.4	101.13 ± 0.24	554.7 ± 0.4	100.81 ± 0.24	624.3 ± 0.4	100.10 ± 0.24	565.2 ± 0.4	101.98 ± 0.24

[a] Standard uncertainty u in the mole fraction based concentration basis is u(x) = 0.03.

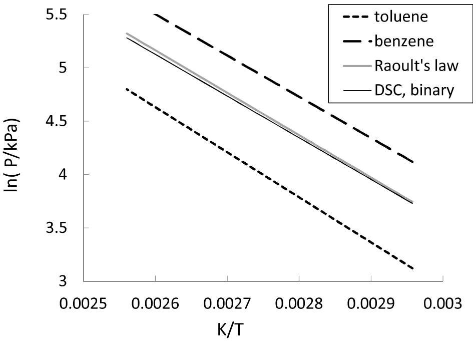

Fig. 2. Vapor pressure behavior of an equimolar mixture of benzene and toluene as an example of application of the DSC based technique to binary mixtures.

Table 8
Comparison of experimental vapor pressure data of toluene to values from selected literature references.

T/K	p/kPa[a]	p/kPa	Δp/%[b]	p/kPa	Δp/%[b]	p/kPa	Δp/%[b]	P/kPa	Δp/%[b]
		Ref. [21]		Ref. [22]		Ref. [23]		Ref. [24]	
345.5	29.65	29.87	−0.8	29.22	1.5	29.73	−0.3	29.25	1.4
360.6	49.44	49.85	−0.8	49.43	0.02	49.87	−0.9	49.49	−0.1
371.1	69.2	69.45	−0.4	69.48	−0.4	69.47	−0.4	69.55	−0.5
384.3	101.6	102.68	−1.1	103.80	−2.1	102.39	−0.8	103.93	−2.2
418.6	247.5					246.99	−0.2		

[a] Measured in this work.
[b] $\Delta p\% = \frac{|x-X|}{X} \times 100$, where x is measured value and X is reference value.

of 99.5%, Sigma-Aldrich; used without further purification as seen in Table 2) mixture (a common example of an ideal binary mixture). The vapor pressure results are graphically shown in Fig. 2. The vapor pressure data, measured in our laboratory, for toluene are given in Table 3, for benzene can be found from our previous study [8] and for the 50:50 mol% binary mixture are given in Table 4. The vapor pressure values of the pure compounds measured were in good agreement with literature data (for the reference literature vapor pressure data used for benzene see Refs. [8,24]; for toluene see a comparison with selected references [25–28] given in Table 8). The average absolute relative deviation (ARD%) of the binary mixture from the values calculated by Raoult's law was below 3% (RD% varying from −1.4% at 65.0 °C to −4% at 117.4 °C), which is a satisfactory level given the purpose of the current paper. The absolute deviation from Raoult's law of current experimental data and selected literature data from references [29–36] is illustrated comparatively in Fig. 3. Note that due to the existence of a systematic error, the deviations from Raoult's law observed are somewhat larger than the deviations coming only from the reported random error uncertainties in Table 5.

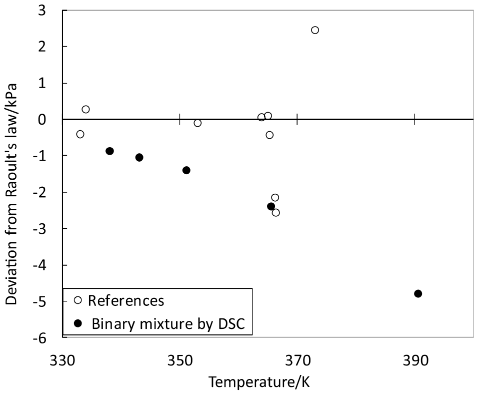

Fig. 3. Deviation of measured vapor pressures of an equimolar mixture of benzene and toluene from corresponding Raoult's law values. Deviations from Raoult's law with selected literature data [29–36] are shown for comparison.

2.2.2. Characterization techniques of oil cuts

Initial boiling temperatures of the fractions, shown in Table 1, are calculated from linear regression (from the integrated Clausius-Clapeyron equation) of vapor pressure data obtained by DSC. The estimated accuracies, as a standard error of the estimation of these boiling temperatures, were 0.6 K for Fraction A, 0.7 K for Fraction B and 1.4 K for Fraction C. Other characteristics (molecular weight, atomic H/C ratio, average boiling point, OH content) in Table 1 describe average properties of the fractions. The average boiling points of the cuts were determined by a TGA based method (developed in our laboratory), which had an accuracy of ±2 K (given based on an absolute average deviation of 29 reference fractions) [7]. The average molecular weights were determined using the cryoscopic method with benzene as the solvent, which had an accuracy of ±5 g mol^{-1}. Elemental composition as wt% H, wt% C and wt% (S,N,O) (by difference) was measured with an Exeter Analytical model CE440 elemental analyzer (which had an accuracy of ±0.15 wt% C and ±0.05 wt% H). The OH group content (dominantly phenolic [37]) was determined by an FTIR technique (developed in our laboratory, a RMSE of 0.44 wt% OH) using an Interspec 301-X spectrometer fitted with an ATR accessory [18]. H/C ratios and the number of OH groups per average molecule were calculated from the data.

3. Results and discussion

3.1. Binary mixtures of oil cuts with pure compounds

Here the application of DSC to study the total vapor pressure of a binary system is evaluated, where a pure compound vaporizes from a complex matrix, or in this study from a narrow boiling range

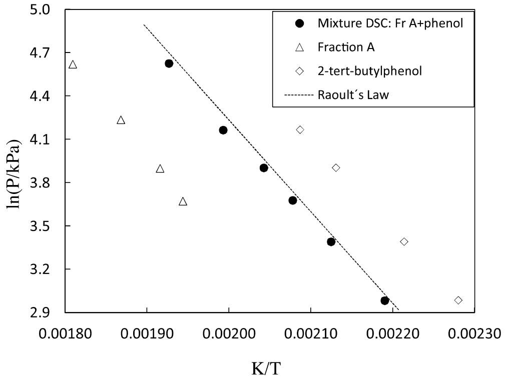

Fig. 4. Vapor pressure behavior of an equimolar mixture of Fraction A and 2-*tert*-butylphenol.

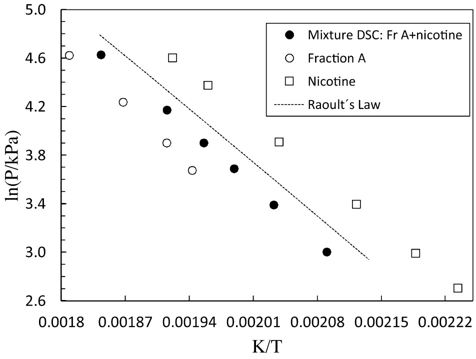

Fig. 5. Vapor pressure behavior of an equimolar mixture of fraction A and nicotine.

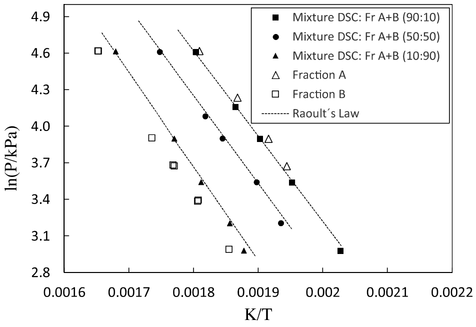

Fig. 6. Vapor pressure behavior of 90:10, 50:50 and 10:90 mol% binary mixtures of Fractions A and B.

oil fraction. The pure compounds were selected to be more volatile (or to exhibit several times higher vapor pressure) than the oil fractions they were mixed with. The pure compounds selected contain heteroatoms with the capability of forming hydrogen bonds (nicotine contains a nitrogen base and 2-*tert*-butylphenol contains an acidic or phenolic functional group) with oil fraction constituents.

The pure phenolic compound, 2-*tert*-butylphenol, was used to prepare binary mixtures with oil Fractions A and B. Fractions A and B had molecular weights of 191 and 227 $g\,mol^{-1}$ and 0.7 and 1.1 OH groups per average molecule, respectively. This means that for Fraction A roughly every other molecule contained an OH group, and for Fraction B every oil molecule contained an OH group. Fig. 4 presents graphically an example of the behavior of 2-*tert*-butylphenol when mixed with Fraction A (50:50 mol% mixture), and the other binary mixture exhibited similar behavioral trends. In the mixture with Fraction A, the average absolute relative deviation (ARD%) is 8.5%. The relative deviation varies from −4.1% to −11.1% as temperature increases from 180 °C to 280 °C. Fig. 4 shows that the DSC technique provided a vapor pressure curve of the binary mixture on an ln P versus 1/T plot that exhibits good linearity. The linear regression (R^2) coefficient was 0.998 for the mixture with Fraction A and 0.9994 for the mixture with Fraction B. The mixture with Fraction B shows similar behavioral trends, with an average relative deviation of 7.7% (RD% varying from −10.2% at 180 °C to −5.7% at 254.3 °C). Remember that an average absolute difference of 3% was seen for the practically ideal benzene-toluene mixture (see Fig. 2); however, for oil fractions a larger error could be expected due to somewhat poorer vapor pressure measurement accuracy (see Ref. [8]) and uncertainties in molecular weight determination (in the range of 5%). As seen from Table 1, the oil fractions selected have 0.7 and 1.1 OH groups per average molecule and are known to contain large amounts of phenolic alkyl-aromatic structures [37,38]. Therefore, the addition of another alkyl-phenolic compound to the narrow boiling range oil fraction should not alter the existing chemical nature considerably, which is likely the reason these 50:50 mol% mixtures exhibit behavior quite close to ideal mixture behavior (with an ARD% from Raoult's law of 8%). There was essentially no dependence on whether fraction A or B was mixed with 2-*tert*-butylphenol. This observation of behavior close to ideal mixture behavior is similar to that seen with a mixture of a phenol-rich Illinois coal tar and 1-hydroxypyrene (50:50 mol% pre-prepared mixture), determined by the Knudsen effusion technique in references [39,40]. In this study it was found that the average molecule of Illinois coal tar contains about two hydroxyl groups.

The pure compound with nitrogen base character, nicotine, was used to prepare 50:50 mol% binary mixtures with oil Fractions A, B and C. The addition of nicotine to the oil fractions resulted in mixtures that exhibited observably lower total vapor pressures than those predicted by Raoult's law (negative deviation). Moreover, the deviation trends and also relative deviation values were similar for all three mixtures, despite the fact that the average molecule of Fractions A, B and C contained 0.7, 1.1 and 1.1 phenolic OH groups, respectively. Fig. 5 shows graphically the situation for the mixture with Fraction A, as an example. The ARD% of the 50:50 mol% mixture in this case was 16.4%. The deviation varies from −20.0% to −13.6% as temperature increases from 205 °C to 270 °C, so deviation is greater at lower temperatures. The mixture with Fraction B had an ARD% of 16.9% (RD% varies from −24.6 to −10.8% as temperature increases) and the ARD% for the mixture with Fraction C was 16.4% (RD% varies from −29.1% to −8.9% as temperature increases). It can be seen from Table 1 that these Kukersite oil fractions contain practically no nitrogen (below 1 wt%, that suggests that, on average, every fifth or sixth molecule contains nitrogen). Therefore, the presence of a compound containing a nitrogen base in the binary mixture with the oil fraction should exhibit exchanged molecular interactions, and as a result, have a lower total vapor pressure than expected from Raoult's law. This is consistent with, although not as pronounced as, the trend seen with the Illinois No. 6 coal tar and phenanthridine 50:50 mol% mixture determined by the Knudsen effusion technique in Refs. [39,40]. Note that in this study the average molecule of Illinois coal tar was found to contain about two hydroxyl groups and only about one in five molecules contained a nitrogen group.

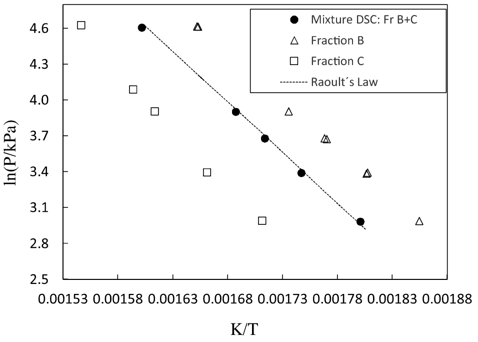

Fig. 7. Vapor pressure behavior an equimolar mixture of Fractions B and C.

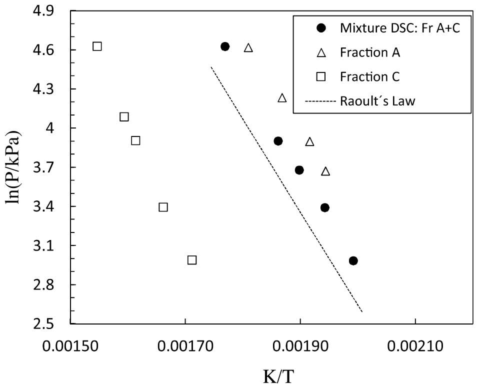

Fig. 8. Vapor pressure behavior an equimolar mixture of Fractions A and C.

3.2. Binary mixtures of narrow boiling range oil fractions

Here we evaluate the application of DSC to studying the vapor pressure of a system where two discrete narrow boiling range oil fractions form a binary mixture. One of fractions in the mixture was more volatile (or exhibited several times higher vapor pressures) than the other. It can be seen from Figs. 6, 7 and 8 that the DSC technique could provide vapor pressure curves of binary mixtures of two narrow boiling range fractions on an ln P over 1/T plot that exhibit quite good linearity (R^2 better than 0.998).

Fig. 6 presents total vapor pressure curves of three binary mixtures of oil Fractions A and B (the difference between the average boiling points of Fractions A and B is about 50 K, as seen from Table 2). The mixture ratios were approximately 90:10, 50:50 and 10:90 mol% of Fractions A and B, respectively. The results in Fig. 6 show that behavior is close to that predicted by Raoultís law. The ARD% are 3.4% for the 50:50 mol%, 5.0% for 10:90 mol% (10 mol% of Fraction A) and 1.6% for 90:10 mol% (90% of Fraction A) binary mixtures.

Fig. 7 presents data for the 50:50 mol% binary mixture of Fractions B and C (again, the difference between the average boiling points of Fractions B and C is about 50 K, as seen from Table 2). Once again, behavior that is quite close to ideal is seen, with the ARD% being 1.8%. Fig. 8 shows a 50:50 mol% mixture of Fractions A and C. These fractions have an even larger difference in boiling points: about 100 K. The direction of deviation from the curve calculated by Raoult's law is towards higher pressure, indicating that interactions in Fraction A are weakened in the presence of the larger molecules from Fraction C (positive deviation from Raoult's law). The ARD% was 36%.

4. Conclusions

This preliminary study examined the extents of deviation from ideality in two types of binary mixtures containing undefined oil fractions as at least one of the mixture component: (1) a mixture of a narrow boiling range oil fraction and pure compound; (2) a mixture of two different narrow boiling range oil fractions. For both types of systems the DSC based vapor pressure measurement method (that followed ASTM E 1782 guidelines) provided vapor pressure curves that exhibit good linearity on an ln P over 1/T plot.

The study indicated that 50:50 mol% mixtures of alkyl-phenolic compounds (2-*tert*-butylphenol in this study) with oil fractions rich in alkyl-phenol give close to ideal behavior (i.e. close to Raoult's law behavior). However, 50:50 mol% mixtures of a compound containing a nitrogen base (nicotine) with these alkyl-phenol rich oil fractions showed lowered vapor pressure relative to Raoult's law.

The study also suggested that for binary mixtures of fractions taken closer together during the distillation, but still with boiling point ranges essentially not overlapping (difference in average boiling point of about 50 K) the ideal mixture behavior could be a fair approximation. However, the binary mixture of fractions further apart (difference in average boiling point of about 100 K) indicated considerable deviation from ideality (i.e. from Raoult's law).

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Inglise keel	Kesktase (B2)
Saksa keel	Kesktase (B1)

Teenistuskäik

2016-…	Veterinaar-ja Toiduamet, kvaliteedijuht
2012-2014	Tallinna Tehnikaülikool, Keemia ja materjalitehnoloogia teaduskond, Keemiatehnika instituut, Keemiatehnika õppetool, assistent (0.30)
2009-2016	AS Liviko, tehnoloog, kvaliteedispetsialist
2007-2008	Tallinna 37.keskkool, matemaatikaõpetaja
2007 suvi	Terviseamet, praktika