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Determination of Vaporization Properties and Volatile Hazardous Components Relevant to Kukersite Oil Shale Derived Fuel Oil Handling

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The aim of this study was to investigate vaporization properties of shale fuel oil in relation to inhalation exposure. The shale fuel oil was obtained from kukersite oil shale. The shale oil and its light fraction (5 % of the total fuel oil) were characterized by vapor pressure curve, molecular weight distribution, elemental composition and functional groups based on FTIR spectra. The rate of vaporization from the total fuel oil at different temperatures was monitored as a function of time using thermogravimetric analysis (TGA). It is shown that despite its relatively low vapor pressure at room temperature a remarkable amount of oil vaporizes influencing air quality significantly. From the TGA data the changes in the vapor pressure during vaporization process were estimated. Although the shale fuel oil has a strong, unpleasant smell, the main hazards to workplace air quality depend on the vaporization rate of different toxic compounds, such as benzene, toluene, xylene or phenolic compounds. The presence of these hazardous substances in the vapor phase of shale fuel oil was monitored using headspace analysis coupled with selective ion monitoring (SIM) and confirmed by the NIST Mass Spectral library and retention times of standards.

Keywords: oil shale kukersite, shale fuel oil, vapour pressure, vaporization sate, volatility of compounds.

1. INTRODUCTION

Environmental impacts of shale fuel oil include potential damage to the local and regional environment, including humans. Over the last 20 years, there has been rapid growth in the environmental legislation affecting the petrochemical industry. The relationship between the industry's performance and the environment are complex and not fully understood, but environmental regulations and indicators are widely used [1, 2]. There are several new analysis methods available for determination of environmental and workplace air pollution [3, 4]. Environmental indicators cover global warming, photochemical oxidation potential, ozone depletion, acidification potential, eutrophication potential, the potential for human toxicity by ingestion, inhalation or dermal exposure, as well as the potential for aquatic and terrestrial toxicity.

Petroleum products include crude oil, residual oil, heating oil, diesel fuel, gasoline, jet fuel, kerosene, propane and liquefied gases. The consumption in the world increased from 1990 – 2011 by 32 % [5]. The hazardousness of fuel oil products to humans and the environment depends on the composition of the initial oil; for example, heavier petroleum products, such as residual fuel oil, are carcinogenic on mouse skin and mutagenic both in vitro and in vivo [6]. Residual (heavy) fuel oil has been classified by IARC as possibly carcinogenic to humans [7]. These fuel oils contain carcinogenic polyaromatic hydrocarbons (PAH), have a high sulphur content and contain ash, carbon residue and asphaltene compounds (aromatic compounds containing nitrogen, sulfur and oxygen) [8].

The toxicity and mutagenicity of combustion particles, including fuel oil emissions, were first reported in the 1980s [9]. Studies of inflammation and acute lung injury in rats when residual oil fly ash (ROFA) was administered by intratracheal instillation [10] stimulated an interest in ROFA as a model particle. The biologic effects and potential mechanisms of ROFA toxicity associated with transition metals have been reviewed by Ghio et al. [11]. Limited research has been reported on the organic constituents and the mutagenicity or other genetic or potential cancer risks of ROFA. The occupational study of boilermakers exposed to ROFA particles and metal fume that contain carcinogenic PAH and metals is presented by Mukherjee [12].

World oil shale resources are estimated to exceed 8 trillion barrels of recoverable oil equivalent [13]. The properties and yield of shale oil, a product of oil shale upgrading via a retorting process, are known to vary widely depending on the oil shale [14, 15]. Although the relative proportions and types of hazardous components are quite variable, a potential health hazard exists from exposure to any shale oil. For example, the exposure of test animals to aerosolized raw shale oil was associated with inflammatory and hyperplastic lesions in the lungs and upper respiratory tract. Inhalation of raw shale aerosol can be toxic to major organs [16].

In Estonia Kiviter type internal combustion vertical retorts and Galoter type solid heat carrier retorts are presently in commercial use for shale oil production, and there is about 350 to 400 thousand tons (or up to 2.5 mln bbl) of shale oil produced per year. Raw kukersite shale oil (synthetic crude oil) is a mixture of thousands of compounds and has wide molecular weight and boiling point distributions [17]. Table 1 presents an example of the basic chemical composition groups in the middle oil

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fraction (middle distillate). The middle fraction is the part of the overall kukersite shale oil with the boiling range of 200 °C – 300 °C [18, 19].

Table 1. Chemical groups in the middle oil from Kiviter and Galoter retorts

Chemical groups, %	Kiviter	Galoter
Carbohydrates, saturated	12	6
Carbohydrates, unsaturated	20	12
Aromatic compounds	30	35
Neutral oxygen and sulfur compounds	19	27
Phenols	19	20

The middle oil fraction is the main source of the shale fuel oil produced for use in boilers and in industrial furnaces. As can be seen from Table 1 there are a lot of phenols in kukersite middle oil from both Kiviter and Galoter industrial processes. Therefore the shale fuel oil from kukersite oil shale differs from the petroleum-based oils in that it is much more heterogenous. In the previous study it was determined that at room temperature the vapor phase of shale fuel oil from kukersite oil shale contained benzene, toluene, xylene and phenol [20]. The sample under study was produced from shale oil obtained from the Kiviter process [21] and the same is used in this research.

The shale fuel oil has a strong, unpleasant smell, but main hazards to workplace air quality, the concentration of different compounds in air, depend on vaporization rate of these compounds. Therefore a study was carried out to characterize shale fuel oil vaporization and changes in vapor pressure during the vaporization process that takes place, for example, in the case of an oil spill. The need to investigate shale fuel oil vaporization at different temperatures is due to the different handling temperatures: in storage room for tanks the temperature is approximately 22 °C, during loading it is close to 40 °C and during every-day cleaning of the injector in the boiler system it can even be close to 70 °C.

2. MATERIALS AND METHODS

The shale fuel oil (heating oil) used in the studies was produced from kukersite oil shale using the Kiviter process. It is used in boiler houses during winter when it is not possible to use other fuels. The properties of the sample are taken from the material safety data sheet [22] and given in Table 2. It can be seen that there are no vaporization related physical properties reported, such as vapor pressure or boiling point.

Table 2. Properties of the sample

Quality characteristics	Values	Norms
Flash point (°C)	Min 61	68
Freezing point (°C)	Max –15	–17
Sulphur (%) content	Max 0.80	0.61
Density at 15 °C (kg/m^3)	Not measured	1005.4
Moving viscosity at 80 (°C)	Max 2.80	2.49
Ash (%)	Max 0.10	0.03
Water (%)	Max 1.0	0.1

The vaporization properties of total shale fuel were investigated using a commercial static vapor pressure tester and a thermogravimetric analyzer. The ERAVAP commercial vapor pressure tester [23] was used to characterize the volatility of the fuel by determining a vapor pressure curve. Due to the low vapor pressure of the fuel oil and its constituents, as the lighter fraction is vaporized it is harder to measure the vapor pressure using the ERAVAP. Therefore, a DuPoint 951 thermogravimetric analyzer (TGA) was used to determine fuel oil vaporization rates at temperatures of interest as a function of time. Isothermal TGA measurements were performed using an open sample pan (of 5 mm diameter) under a purge gas flow of 1500 ml/min that corresponds to a gas (wind) speed of 0.3 m/s over the sample. The TGA was also used to simulate distillation as is done in the case of coal tars [24]. In these experiments a sample was placed into a 70 µl alumina crucible (with a 1 mm hole in the lid) and heated at a rate of 10 °C/min under an inert gas flow of 50 ml/min.

Gas chromatography mass spectrometry (GC-MS) with headspace sampling was used to determine the organic compounds contained in shale fuel oil. The samples were heated at various temperatures in the range of 40 °C – 60 °C for 15 min prior to headspace sampling. The GC column was a HP-5ms (length 30 m, internal diameter 250 µm, stationary phase 0.25 µm) and the carrier gas was helium (purity 6.0). The temperature was programmed to increase from 30 °C (5 min isothermal) to 200 °C (5 min) at a rate of 20 °C/min. The system used was composed of the Agilent Technologies GC 7890A, Agilent Technologies MS 5975C and Agilent 7694E headspace sampler.

As fuel oil vaporization properties depend on fuel oil characteristics, the fuel oil was characterized according to elemental composition, phenolic OH content, number average molecular weight and molecular weight distribution. The Elemental analyzer used was an Exeter Analytical Inc. model CE-440. An infrared spectroscope (FT-IR), Thermo Scientific Nicolet IR100 with attenuated total reflection (ATR, ZnSe crystal) system, was used to characterize fuel oil functional groups and specifically to evaluate quantitatively the phenolic OH content. For quantification a correlation was used that relates the area of the 3600 cm^{-1} – 3100 cm^{-1} region to the phenolic OH group content of shale oil fractions. The phenolic content of the narrow boiling point shale oil fractions used to develop the correlations was determined using a chemical method [25]. Gel permeation chromatography (GPC) was used to measure molecular weight distribution and average molecular weights. The column was kept at 25 °C and the eluent (dichloromethane) flow rate was 0.6 ml/min. The system was calibrated using narrow boiling point shale oil fractions for which the number average molecular weights were predetermined using a Osmomat 070 vapor pressure osmometer. The GPC system was composed of a Waters e2695 separations module with a Waters Styragel HR 0.5 column and a Waters 996 PDA detector.

3. RESULTS

3.1. Vaporization characteristics and vapor composition of the total fuel oil

Vaporization characteristics (vapor pressure, heats of vaporization, boiling point) are important parameters that can be used to describe the behavior of fuels during storage and also to specify safety measures that need to be taken to avoid possible accidents. Vaporization to the ambient environment is related to vapor pressure. The vapor pressure of the shale fuel oil, used in this study, was relatively low at room temperature. Therefore the vapor pressure of the total fuel oil was measured in the temperature region from 80 °C to 120 °C using a commercial static vapor pressure tester ERAVAP. Vapor pressure data measured were described through the Clausius-Clapeyron equation:

$$\ln p^S = A - \frac{B}{T} = A - \frac{\Delta H_{vap}}{RT}, \qquad (1)$$

where p^S is in [kPa] and T in [K]. The corresponding coefficients for the Clausius-Clapeyron equation found were $A = 14.7115$ and $B = 4569.663$. The data gave a heat of vaporization (ΔH_{vap}) of 38 kJ/mol and atmospheric boiling point of 180 °C. Fig. 1 presents the vapor pressure curve extrapolated down to room temperature that was derived from the data.

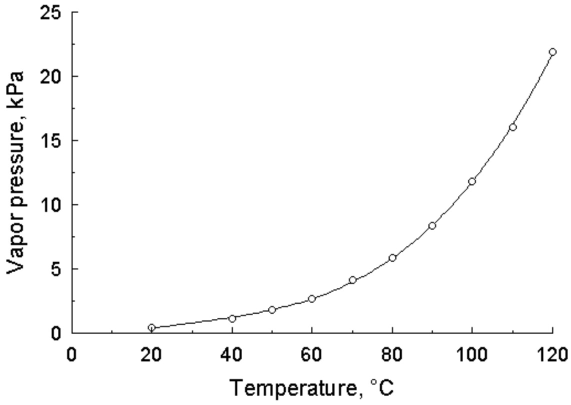

Fig. 1. Temperature dependence of vapor pressure of shale fuel oil used

It can be see that at room temperature (20 °C) the shale fuel vapor pressure is low, only 0.42 kPa. Despite this, the unpleasant smell of shale fuel is very strong and easily spreads throughout the work environment. Although the smell is bothersome, it does not provide a good measure of the exposure to hazardous chemicals. There is wide variability in human sensitivity to odor specific compounds, including detection of concentrations in the parts per million range.

Fig. 2 presents GC/MS based headspace analysis of the total shale fuel oil. The figure shows the GC-MS spectra of the vapor phase which is in equilibrium with the liquid fuel oil at 40 °C (corresponds to the shale fuel oil vapor pressure of 1.13 kPa). The dotted line presents total ions chromatogram (TIC) of shale fuel oil indicating that a wide range of compounds vaporize from the total fuel oil. The solid line shows selective ions monitoring (SIM) of specific target compounds with known retention times. The compounds were hexane, benzene (carcinogenic for humans, [26]), toluene, n-decane, o-xylene and phenol. These gave the expected elution times based on ions peaks. Results were compared to a library of mass spectra. The ions peak of phenol appears to be very low, but there is reason to believe that phenol vaporizes under these conditions from kukersite oil shale derived fuel oil [20].

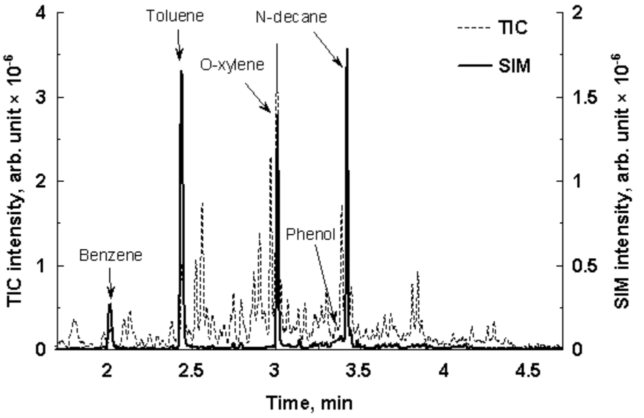

Fig. 2. Mass-spectrum from headspace analysis of the shale fuel oil vapor phase at 40 °C

The shale fuel oils are complex mixtures with wide boiling point distributions. Therefore, a TGA (with 15 mg of the sample) was used to roughly simulate (experimentally) the Engler distillation behavior of the fuel oil. The Engler distillation is a standard test to characterize the volatility of fuels (ASTM D86). Fig. 3 shows the simulation of the boiling point distribution of shale fuel oil in a distillation – i. e. the fraction of the mass of shale fuel oil that will evaporate at different temperatures. The mass of the sample that has evaporated from the start of mass loss at 70 °C up to 300 °C is represented by the area under the curve and corresponds to 61 % of total mass. At temperatures starting from approximately 300 °C shale oil starts to slowly decompose. The decomposition proceeds more rapidly at higher temperatures. The boiling point range of the first fraction (the filled area under the curve represents 5 mass% of total shale fuel oil) is shown in Fig. 3. According to the TGA measurements, at 190 °C only 5 % of the sample had evaporated confirming that the shale fuel oil has a relatively low volatility. The graph also indicates that the fuel oil contains relatively low amounts of fractions classified as volatile organic compounds (VOC) and semi-volatile organic compounds (SVOC), about 15 % of each [27].

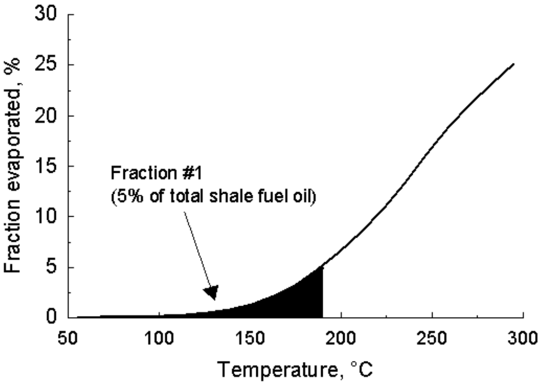

Fig. 3. TGA based boiling point distribution simulation of the shale fuel oil. Fraction 1 corresponds to the first 5 % of the mass evaporated from the total shale fuel oil

3.2. Average characteristics of the total fuel oil and its lightest fractions

In order to analyze the average properties of the lightest components that evaporate from the total fuel oil, the two lightest fractions (fraction #1 and fraction #2) were collected by Engler distillation (from 100 ml of sample). The separation was performed in accordance to the ASTM D86-046 standard. The 1st fraction (first 5 % vaporized from the shale fuel oil) was collected at temperatures up to 207 °C and the 2nd fraction (second 5 %) up to 222 °C. Fraction #1 had a vapor pressure at room temperature (20 °C) of 1.97 kPa, heat of vaporization (ΔH_{vap}) of 34 kJ/mol, atmospheric boiling point of 135 °C, and the following coefficients for the Clausius-Clapeyron equation: $A = 14.6211$ and $B = 4087.71$.

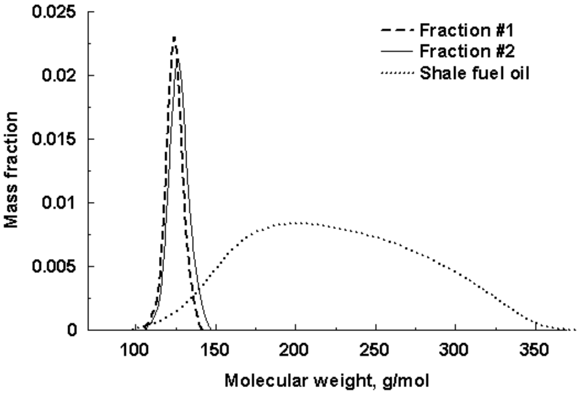

Fig. 4. Molecular weight distribution of shale fuel oil, and its two lightest Engler distillation fractions

Table 3. Characterization of samples

Material	Vapour pressure (at 20 °C), kPa	Average molecular weight, g/mol	OH^- group	H/C/O atomic ratio
Shale fuel oil	0.42	216	3.85	1/1.36/18.14
Fraction #1	1.97	124	1.97	1/1.72/27.21
Fraction #2	not measured	127	2.30	1/1.68/24.86

Table 3 summarizes the main characteristics of the shale fuel oil and its 1st and 2nd fractions separated via Engler distillation. The values of weight average molecular weights shows that both fractions contain compounds with similar molecular weights, however fraction #2 is less aliphatic (H/C ratio is lower) and contains more OH^- groups.

In Fig. 4 the molecular weight distributions are shown. The peaks of the distributions represent weight average molecular weights. Shale fuel oil has a wide molecular weight distribution ranging from 100 g/mol to 450 g/mol. This is also a reason for its rather low volatility.

Fig. 5 presents infrared spectra of total fuel oil and the fractions collected. Infrared spectroscopy has good qualitative aspects which allow determination of the different functional groups in a sample [28]. The infrared spectrum for shale fuel oil, and also for the 1st and 2nd fraction collected by Engler distillation, confirm the presence of phenolic OH groups. All spectra show absorption in the 3600 cm^{-1} – 3100 cm^{-1} infrared region. This could be caused by phenols, carboxylic acids and alcohols OH^- groups. The exact species are difficult to identify because the area is large and the absorbance of all these substances is in the same range. However, it is known from previous studies that the kukersite shale oil contains mostly phenolic OH groups (from alkyl phenols) [29, 30, 31]. The IR spectra of the oil samples also contain aromatic, aliphatic, carbon-oxygen bands [32].

3.3. Changes in vapor pressure and vaporization rate due to the vaporization of the lightest compounds

The rate of vaporization for a fuel at different temperatures is determined by its saturated vapor pressure, which in turn is determined by the fuel composition. As the vaporization process progresses, the composition, and therefore, the vapor pressure of the shale fuel oil (a complex mixture), changes as more volatile compounds are lost over time. This also means that the main health hazard, the concentration of different fuel based compounds in the air, changes over time.

Experimental vaporization curves of the shale fuel oil (as a mass loss in % per unit area) from an open container under constant gas flow rates and different temperatures (isothermal conditions) are presented on Fig. 6. The experiments were performed in a thermogravimetric analyzer.

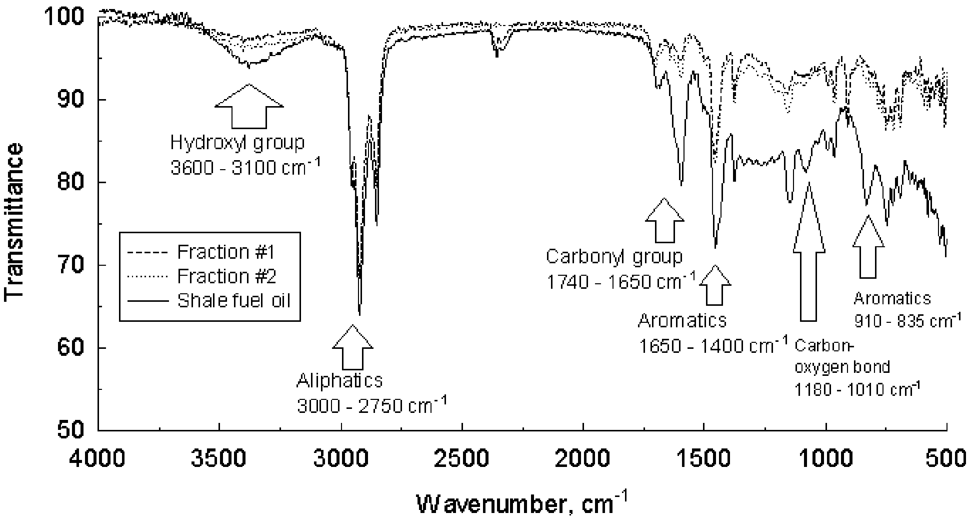

Fig. 5. IR-spectra of the shale fuel oil and the 1st and 2nd Engler distillation fractions

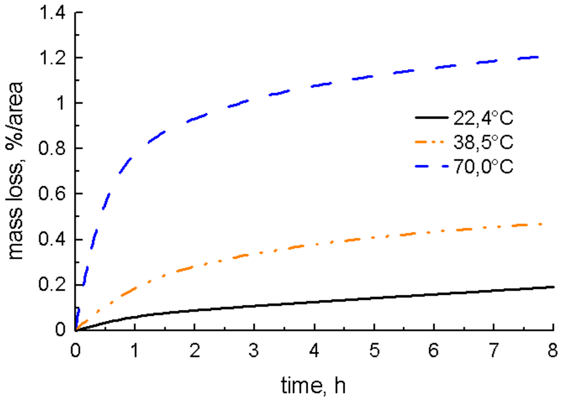

Fig. 6. Changes in mass loss per area in time

Vaporization data are presented as the mass loss in % per unit area in the Fig. 6 because vaporization is a surface phenomenon. In addition to the change in the mixture composition (that determines the change in vapor pressure), the rate of mass loss as function of time (i. e. the time it takes for a certain percentage of shale fuel oil to vaporize) depends on the surface area. As the surface area is increased, the quantity of the shale fuel oil exposed to the atmosphere increases, hence the rate of mass loss also increases (meaning that it takes less time for an equal mass of shale fuel oil to vaporize as the area is increased). Because fuel vapor pressure increases with temperature (see Fig. 1), the higher the temperature the greater the fraction of the mass that evaporates and the higher is the rate of mass loss (in the studied range). The figure also indicates that during the first half hour at 70 °C about 5 % vaporizes, the amount equivalent to the lightest fraction collected via Engler distillation. This indicates that during the everyday cleaning of the injector in the system of the boiler plant, where the shale fuel oil is at 70 °C, large quantities of harmful substances are released into the work environment. Although the process takes only 15 minutes to complete, all workers in the boiler plant complain about the disgusting smell. This clearly demonstrates the need to provide information about the vaporization properties of shale fuel products.

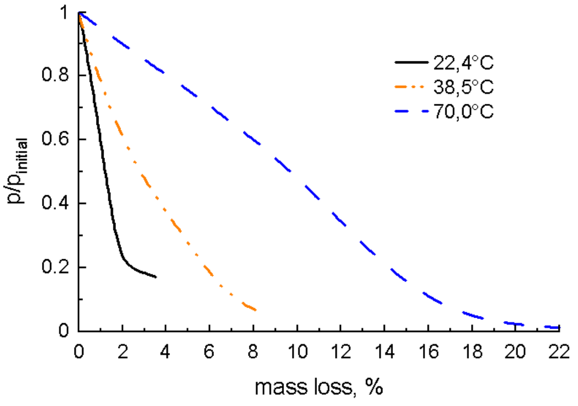

Fig. 7. Changes in relative vapor pressure during vaporization at different temperatures

The TGA based mass loss data given in Fig. 6 can be used to track changes in saturated vapor pressure as shown in Fig. 7. The change in the vapor pressure during vaporization can be roughly tracked by knowing the vapor pressure of the initial fuel (measured here using the ERAVAP) and estimating the relative vapor pressure change from the rate of mass loss (obtained using the TGA). This is a fast and convenient method that requires only a small amount of sample.

The mass loss data from TGA were converted to vapor pressure data using the following classic equation that relates the rate of vaporization, or mass loss rate (*dm*/*dt*), to the driving force (Δp) [33]:

$$\frac{dm}{dt} = k \cdot A \cdot \Delta p \,, \tag{2}$$

where k is the mass-transfer coefficient, A is the vaporization area and Δp is the difference in the partial pressure of the compounds between two points in space. The mass-transfer coefficient, k, depends on the properties of vaporizing compounds and ambient conditions. In this study it is assumed that for light fractions it is mostly a device/configuration dependent coefficient. In the case of vaporization into the environment the driving force of the mass-transfer process, Δp, may be taken as the saturated vapor pressure (p^S) of the vaporizing liquid, since the partial pressure of the compound in air, away from the liquid itself, is negligible. Therefore the equation above simplifies to become:

$$\frac{dm}{dt} = k \cdot A \cdot p^S \,. \tag{3}$$

4. CONCLUSIONS

In the current study the vaporization of shale fuel oil at different temperatures was investigated. The analysis of the vapor phase composition revealed the presence of several hazardous compounds, including toluene, xylene, phenol and carcinogenic benzene, even at room temperatures. The easily vaporizable fraction of the liquid was estimated to have an average molecular weight close to 125 g/mol (distribution between 100 g/mol and 150 g/mol), and according to the FT-IR analysis it contained aromatics, aliphatics, phenols, alcohols and carbonyl compounds.

The uniqueness of this study is the use of TGA to estimate the changes in vapor pressure during vaporization at different temperatures. This technique could be useful in describing the changes in fuel properties and behavior during storage or spills. This work also showed that the higher the ambient temperature the more potentially harmful compounds evaporate – the higher the rate of mass loss and vapor pressure. Despite the low volatility at room temperature (20 °C), significant increases in vapor pressure were observed at working temperatures, which also remarkably affects the air quality.

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