METHOD TO CALCULATE THE VAPOUR PRESSURE OF HYDROCARBON SOLVENTS FROM SIMPLE PHYSICO-CHEMICAL PROPERTIES

Erik Olsen
National Institute of Occupational Health,
Lersø Parkalle 105,
DK2100 Copenhagen Ø.

Work sponsored by CEFIC - HSPA (Hydrocarbon Solvent Producers Association)
February 1997 – July 2002

Summary

The determination of vapour pressures for solvents of low volatility can be very difficult and time-consuming, especially for complex substances such as hydrocarbon solvents. Therefore the need for a simple calculation tool was identified in order to determine whether such solvents are VOCs under the definition of the EU Solvent Emissions Directive (or VOC Directive). The tool should be simple to run, widely accessible and, after validation, aimed to ensure consistent designation of the VOC status of hydrocarbon solvents in the EU.

A suitable tool based only on distillation range and aromatic content of the product has been developed and validated with experimental data. The tool is applicable to hydrocarbon solvents with an initial boiling point above 200℃ (ASTM D 86). It can be used by solvent suppliers but also by solvent users such as the coatings, adhesives and printing inks producers.

1. Introduction

The Solvent Emissions Directive[1] (EU Directive 1999/13/EC) limits emissions of Volatile Organic Compounds (VOCs) in many industrial processes. This directive defines a VOC as any organic compound having a vapour pressure of 0.01 kPa or more at 293.15°K (20°C), or having a corresponding volatility under the particular conditions of use. The directive, however, does not specify any reference method to be used to determine the vapour pressure of organic substances.

In OECD Guideline 104 (adopted on 27 July 1995)[2] for the testing of chemicals, seven methods to measure vapour pressure are included. Each method has its own range of applicability and variability (Figure 1). The gas saturation method is interesting since it covers a wide range including the cut-off value of the directive. At vapour pressures below 0.1 kPa, many of the measurement techniques, such as ASTM D323[3], are not applicable. For suitable methods, sample preparation and handling, and actual measurement are extremely time-consuming hence, in practice, such methods cannot be applied routinely. Another difficulty stems from the fact that most commercial hydrocarbon solvents are complex mixtures of hydrocarbons with up to 50 or more individual components. Furthermore, compositions can vary slightly from batch to batch.

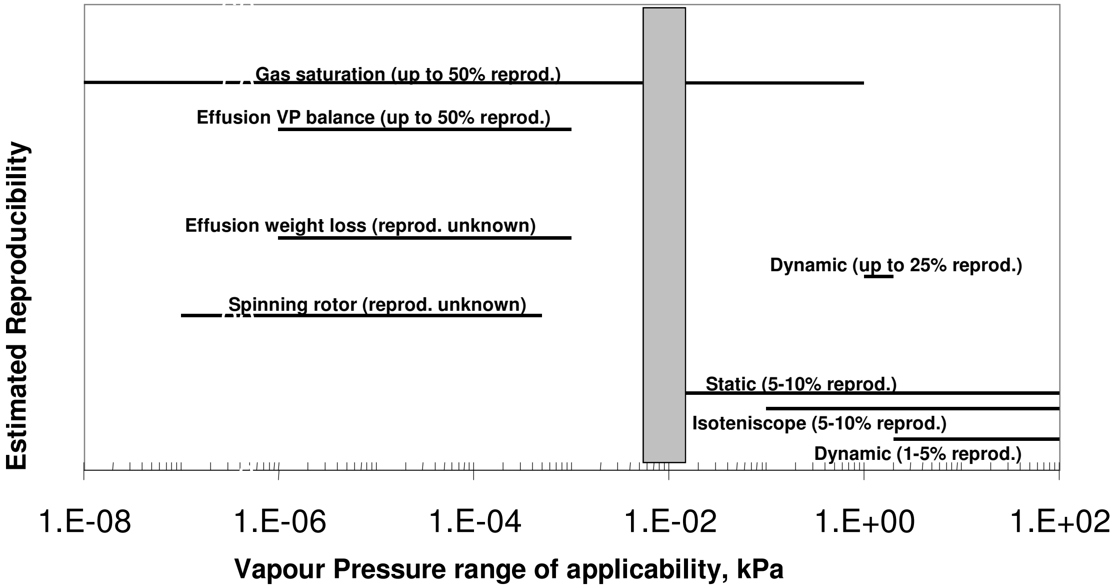

Figure 1. Overview of methods to measure vapour pressures according to OECD Guideline 104 (27 July 1995)

The issues associated with measurement could be overcome if a user-friendly calculation tool was available. However, no standard method is available to calculate vapour pressures of higher boiling hydrocarbon solvents (typically above 150°C) without a detailed breakdown of the composition. This has led most hydrocarbon solvents producers to develop their own calculation tools. This resulted in the need to develop a simple and consistent calculation method to determine whether a hydrocarbon solvent is a VOC under the Solvent Emissions Directive.

It is important to note that hydrocarbon solvents, in spite of their complex composition, are regarded as substances and therefore have one vapour pressure value, just as they have one flash point value.

The objective of this work was to develop and validate a calculation tool, hereunder designated ‘VP Tool’, applicable for the determination of the vapour pressure of hydrocarbon solvents based on readily available physico-chemical properties of the substances.

2. Methodology

The calculation tool was designed, as explained later, to use only distillation data and composition details of the product as input. To validate the calculation method, data were compared with measurement results for a number of products of known composition. This is schematically shown on Figure 2.

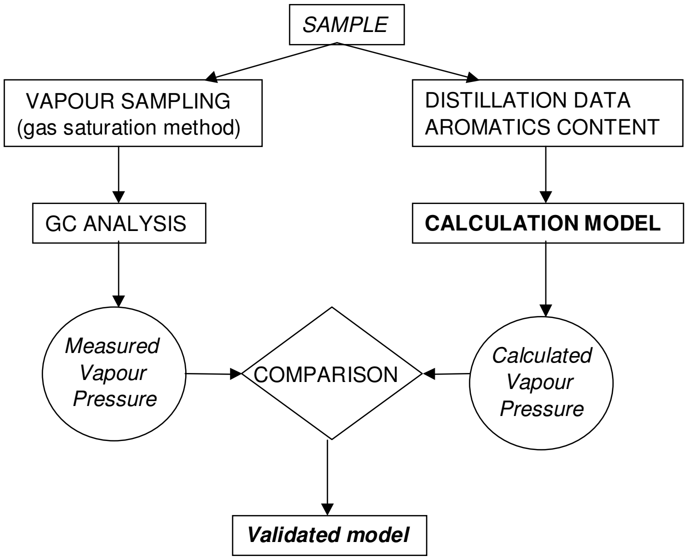

Figure 2. Validation of the calculation tool

In a second stage, the VP Tool was used to calculate the vapour pressure of commercial products and compared with results obtained by individual companies using other calculation tools. Some products have also been analysed using the static method for vapour pressure determination (5 to 10% estimated reproducibility).

2.1. Vapour pressure measurements of reference hydrocarbon mixtures using the gas saturation method

The gas saturation method is explained in detail in OECD Guideline 104[2]. The principle of this method is to slowly pass a flow of nitrogen through a horizontal thermostated tube containing sufficient sample of the test substance for gas saturation. (Figure 3). The nitrogen stream saturated with vapour is led through charcoal tubes to collect the vapours (ASTM D 3686[4]). Quantitative analysis of the charcoal tubes is carried out by gas chromatography (ASTM D 3687[5]).

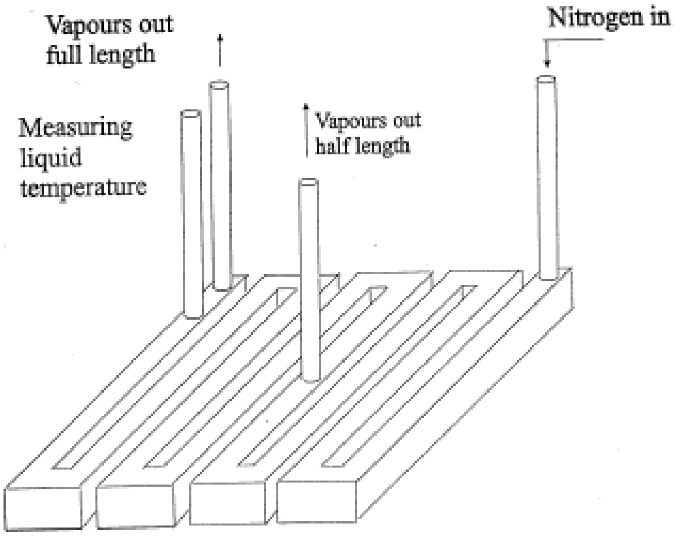

Figure 3. Scheme of the sampling apparatus

In order to obtain reliable results with the gas saturation method, sampling and analytical procedures must be carefully controlled to ensure that:

- Vapours are truly saturated
- Liquid sampling composition is constant
- Experimental conditions are stable throughout the experiment
- Quantitative measurement of vapours adsorbed on the charcoal is reliable

These requirements were fulfilled during our experiments.

The vapour pressure is calculated as follows:

$$p = W/V \times RT/M \qquad [1]$$

where:
p = vapour pressure (Pa)
W = mass of adsorbed test substance (g)
V = volume of nitrogen through charcoal tube (m^3)
R = 8.314 (J mol^{-1} K^{-1})
T = temperature (°K)
M = molar mass of the test substance (g mol^{-1})

2.2. Vapour pressures of hydrocarbon solvents calculated from their physico-chemical properties

In the petrochemical industry, it is well recognised that petroleum fractions (and therefore hydrocarbon solvents) can be characterised with two parameters: (1) a "size" parameter such as the distillation range and (2) a "structure" parameter such as the ratio of aromatics to non-aromatics. The distillation characteristics (according to ASTM D 86[6]) and the aromatics content are usually part of the specifications of commercial hydrocarbon solvents. ASTM D 86 measures the boiling point temperature as a function of the volume of the test substance distilled in a standard apparatus at atmospheric pressure. An example of a distillation curve is shown in Figure 4.

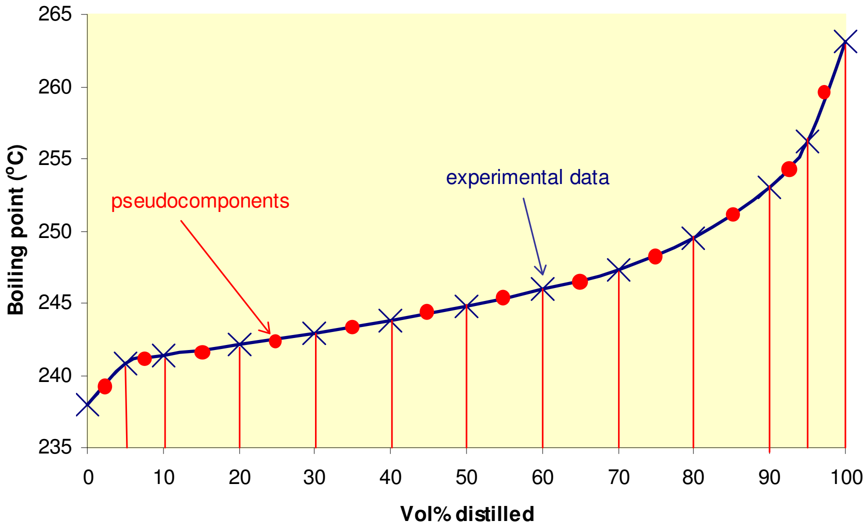

Figure 4. Typical distillation curve and selection of pseudo-components

The distillation curve obtained using ASTM D 86 can be divided into a number of fractions in line with the volume intervals recorded. Subsequently each fraction is regarded as a "pseudo-component". Taken together, these pseudo-components mimic the distillation properties of the actual sample. The boiling point of each pseudo-component is the average of the boiling points at the beginning and at the end of the volume interval concerned. (Figure 4).

For the VP Tool, thirteen points were chosen to describe the distillation curve, in line with the reporting format of ASTM D 86. This corresponds to twelve pseudo-components.

The vapour pressure of each pseudo-component can be determined using a regression of vapour pressures versus boiling points (Figure 5). The regression was obtained from boiling point and vapour pressure data available for pure hydrocarbons in the DIPPR database[7]. For hydrocarbon compounds it is widely accepted that mixtures can be regarded as ideal and that their vapours behave as perfect gases. The total pressure of a mixture of ideal gases is the sum of the partial pressures p_i of the individual gas components(Raoult's law):

$$P_{mixture} = \Sigma p_i = \Sigma\ x_i P_i \qquad [2]$$

where:

$P_{mixture}$ = vapour pressure of hydrocarbon solvent
p_i = partial pressure of pseudo-component i
x_i = molar fraction of pseudo-component i
P_i = vapour pressure of pseudo-component i

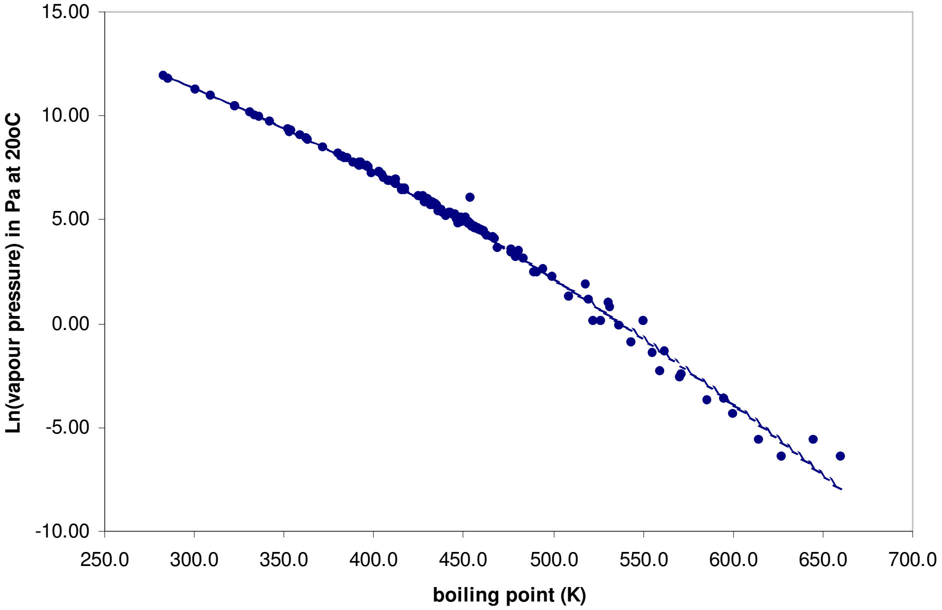

Figure 5. Relationship between vapour pressure and boiling point for pure hydrocarbons (data from DIPPR, 1998)

In order to calculate the total vapour pressure according to equation [2], the molar fractions of the pseudo-components have to be derived from volume % using the liquid molar densities. A plot of the molar densities of various hydrocarbon families versus their normal boiling points is shown in Figure 6. To simplify the calculation, only aromatic and paraffinic regression curves from Figure 6 were used.

From the distillation temperature data and the aromatics content (ASTM D 1319[8]) the molar density of each pseudo-component can be calculated using the regression curve of mono-aromatics for the aromatic fraction and the regression curve of n-paraffins for the non-aromatic part.

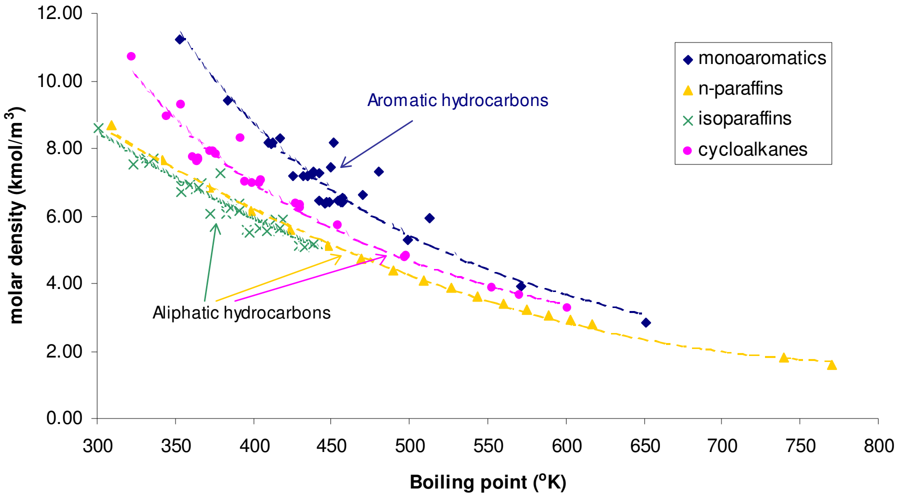

Figure 6: Relationship between liquid molar density and boiling point for various pure hydrocarbon types (data from DIPPR, 1998)

2.3. Samples

Six mixtures of hydrocarbon compounds of known composition were prepared. Five of those mixtures were made of various amounts of n-paraffins in the C11-C15 range. The sixth mixture contained approximately 18% of 1,4-diisopropylbenzene, in addition to n-paraffins.

Further, four commercial hydrocarbon solvents with expected vapour pressures below 50 Pa at 20°C were selected: two solvents free from aromatics (< 0.1%), one containing approximately 17% aromatics, and a pure aromatic solvent.

3. Results and discussion

3.1 Samples of known composition

The new VP Tool program, based on the aforementioned methodology, was used to calculate the vapour pressures of the six test samples of known composition (samples A to F). A comparison was made with the calculated results obtained with the SUBTEC program[9] and with the vapour pressure measurements using the gas saturation method (Table 1).

Table 1: Comparison of calculated vapour pressures for samples of known composition and measurement with the gas saturation method (values in Pa at 20ºC)

Sample	A	B	C	D	E	F
VP Tool calculation	6.3	2.8	2.4	6.4	6.5	8.9
SUBTEC calculation**	4.7	2.6	2.2	4.7	4.9	12.1
Gas Saturation Measurement	3.8	2.2	2.0	4.1	4.3	10.0*

* Result of one measurement, whereas other data are averages of three laboratories

** SUBTEC is a software that calculates the vapour pressure of mixtures of known composition.

Vapour pressures calculated with the VP Tool tended to be higher than vapour pressures obtained by measurement or with the SUBTEC software, except for sample F that contains about 18% of an aromatic compound. The bias between the measured and the calculated vapour pressures using the VP Tool ranges from 0.4 to 2.5 Pa with an average of 1.5 Pa (about 30%). These discrepancies are considered acceptable since they fall well within the variability found from actual measurements by various methods at these vapour pressure levels (Figure 1).

3.2 Commercial products of "unknown" composition

Calculated vapour pressures obtained with various models for four commercial hydrocarbon solvents are shown in Table 2. Results of the calculations show that:

- The differences between the various models can be significant, reinforcing the need for a standard tool.
- Data obtained with the VP Tool fall within the range of calculated values obtained by different company models.

Table 2. Comparison of VP Tool with existing (company internal) calculation methods for commercial samples

Sample	**I**	**II**	**III**	**IV**
Distillation range (°C), *ASTM D 86*	207-242	218-242	192-234	222-237
Aromatics content (vol%), *ASTM D 1319*	0.0	16.5	99.8	0.0
Vapour pressure (Pa at 20°C):				
VP Tool calculation	11.3	10.0	34.8	10.2
Company 1 model	9	8	38	-
Company 2, model 1	14.5	14.1	43.7	14.2
Company 2, model 2	-	11.2	-	10.8
Company 3 model	10.7	6.5	39.5	6.1

A limited number of measurement data are available on the commercial products, as shown in Table 3. Again, the VP Tool generated a higher vapour pressure than the gas saturation method for the one commercial sample where data was available, but was in line with the results obtained by the static method at Company 2. The higher value achieved with the static method by the university laboratory is thought to result from low level water contamination, a well-known interference effect.

Table 3. Comparison of VP Tool results with measured vapour pressures for commercial samples (Pa at 20ºC)

	I	**II**	**III**	**IV**
VP Tool calculation	11.3	10.0	34.8	10.2
Gas Saturation Measurement	-	-	-	5.4
Static Measurement at University Lab	31	29	65	26
Static Measurement at Company 2	-	11.7	-	10.6

In Figure 7, the VP Tool results are plotted against the measurement data. The plot indicates that the VP Tool generally takes a conservative approach as most results of the calculations give slightly higher vapour pressures than the actual measurements.

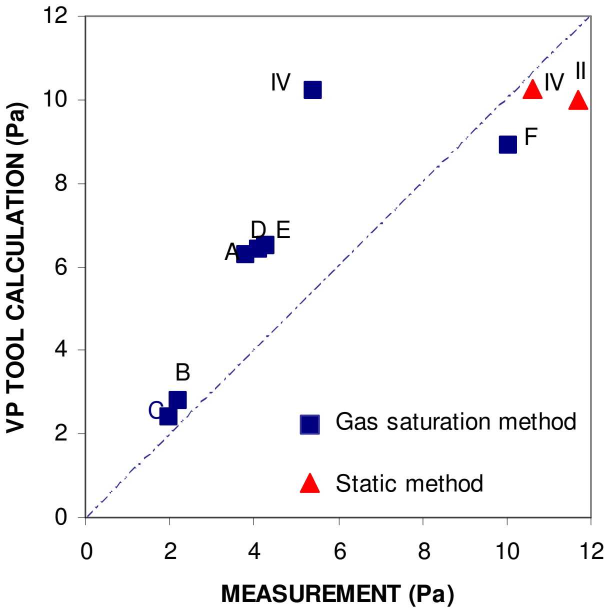

Figure 7. Comparison of vapour pressures obtained by VP Tool calculation and measurement methods

Taking into account the unavoidable sources of error inherent to vapour pressure determination for low volatility products and the assumptions that needed to be made to keep the tool simple, the VP Tool is believed to be suitable as a standard tool to calculate vapour pressures of commercial hydrocarbon solvents. Since the VP Tool was not validated over a broad range of vapour pressures, it is proposed to limit its application range to products with initial boiling points higher than 200°C by ASTM D 86 method (corresponding to vapour pressures lower than approx. 0.1 kPa).

Based on this study, the members of CEFIC-HSPA (Hydrocarbon Solvents Producers Association) have accepted the tool as an industry standard. The VP Tool can be freely downloaded from the European Solvents Industry Group website: www.esig.org .

4. Conclusions

- A new computer programme called VP Tool has been successfully developed to calculate, at 20°C, the vapour pressure of complex hydrocarbon solvents having a relatively low volatility. The calculation method is based on a set of pseudo-components selected in such a way that they represent an accurate approximation of the hydrocarbon solvent composition.
- The VP Tool is recommended by HSPA as an industry standard to calculate vapour pressures of hydrocarbon solvents around the 0.01 kPa (10 Pa) level and subsequently determine their VOC status under the EU Solvent Emissions Directive.
- The VP Tool has shown a good correlation with time-consuming experimental measurements and with various companies' calculation methods.

- The VP Tool is simple to use and applicable to hydrocarbon solvents with an initial boiling point above 200℃.

REFERENCES

1. More information about the Solvent Emissions Directive can be found at: www.voc-infoex.uni-karlsruhe.de/en/index.html
2. Available from: www.oecd.org/oecd/pages/home/displaygeneral/0,3380,EN-document-524-14-no-no-5720-0,00.html
3. ASTM D 323 *Standard Test Method for Vapor Pressure of Petroleum Products (Reid Method),* American Society for Testing Materials, West Conshohocken PA, USA (1994).
4. ASTM D 3686 *Standard Practice for Sampling Atmospheres to Collect Organic Compound Vapors (Activated Charcoal Tube Adsorption Method),* American Society for Testing Materials, West Conshohocken PA, USA (1995).
5. ASTM D 3687 *Standard Practice for Analysis of Organic Compound Vapors Collected by the Activated Charcoal Tube Adsorption Method,* American Society for Testing Materials, West Conshohocken PA, USA (1995).
6. ASTM D 86 *Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure,* American Society for Testing Materials, West Conshohocken PA, USA (1997).
7. DIPPR: Design Institute for Physical Property Data. Technical Databases Services, New York (1998).
8. ASTM D 1319 *Standard Test Method for Hydrocarbon Types in Liquid Petroleum Products by Fluorescent Indicator Adsorption,* American Society for Testing Materials, West Conshohocken PA, USA (1995)
9. Olsen at al., *The Subtec software package*, Occupational Hygiene, **1997**, 5(4), 1-21.