Universiti Sains Malaysia

UNIVERSITI SAINS MALAYSIA

Discrimination of diesel by gas chromatography

Dissertation submitted in partial fulfillment for the
Degree of Bachelor of Science in Forensic Science

Muhamad Sufiyan Bin Azah

School of Health Sciences
Universiti Sains Malaysia
Health Campus
16150, Kubang Kerian, Kelantan
Malaysia

2009

CERTIFICATE

This is to certify that the dissertation entitled

"Discrimination of Diesel by Gas Chromatograph"

is the bonafide record of research work done by

Mr. Muhamad Sufiyan Bin Azah

during the period **21st December 2008** to **30th April 2009**

under my supervision.

ACKNOWLEDGEMENTS

I praise to Allah who gives me the strength and the healthiness to complete this final year project. Nothing I can do without Him.

Thanks to Associate Professor R. Kuppuswamy for coordinating the final year research project and for allocating enough time for us to complete our research. Special thanks to my supervisor, Dr. Ahmad Fahmi Lim Abdullah who is also my lecturer in Universiti Sains Malaysia, for giving me opportunity to complete my final year research project supervised by him along with the technical help and recommendations. I have gained a lot of experience during the course of this project. My special also goes to Mr. Rosliza, the scientific officer and Mr. Azwan, the technician who gave technical advice in handling the instrument. Many thanks also to my colleagues, Mohd Rashid and Shaiful Anuar for their technical help and to Mohd Ikram and Izmer Sukri for the help during samples collection.

Thanks to my parents who always pray for my success in completing my study and give me full support in all matters. Finally, special word of thanks to Zainor Ridzuan who always motivated me in my study and says the right words at the right times to keep me on track.

Contents

Table of Contents

List of Figures

List of Tables

ABSTRACT

Diesel samples from 27 service stations in Kota Bharu were collected over a period of a week were subject to GC-MS analysis. Using extracted ion chromatograms, peak area of 41 selected peaks at various mass per charge were integrated. These peak areas were then self-normalised to ion 220b prior to Principal Component Analysis (PCA).

The results show that principal component analysis is able to group the samples into a few clusters. Using the distance between replicates, however, some samples are tightly group indicating that these samples are relatively similar based on the data treatment and statistical analysis used in this study.

A blind test matched the target sample indicating that the data treatment is reliable. The reliability of this approach is further supported by the close proximity between duplicates.

Four samples collected from a selected service station over a period of four weeks were spread out by PCA indicating that these diesel profiles change over time. This is true if the service station received new batches of diesel after each collection of the samples.

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

This thesis studies the variability of diesel fuels collected from service stations in the district of Kota Bharu, Kelantan. Principal Component Analysis (PCA) was used to discriminate the 41 selected peaks of each of the chromatograms from the 27 samples studied. Three samples other than diesel, namely charcoal lighter, tupertene, and petrol were also analysed. One service station was arbitrarily chosen where diesel samples were collected in one-week interval over a period of four weeks to observe the variability of the diesel fuels.

1.2 STATEMENTS OF THE PROBLEMS

Diesel is one of the refined products of crude oil that has been used worldwide as one the fuels for motor vehicle. Most heavy load vehicle uses diesel as the fuel compare to other type of fuel. According to Malaysia Energy Database & Information System (MEDiS), diesel and petrol had been leading in the demand for petroleum product in Malaysia in 2006 [1]. Prior to 2008, diesel fuels were subsidised by the government for selected sectors such as land and sea transportation as well as for fishing boats [2].

Crimes relating to petroleum products are often reported in arson, theft, smuggling [2]. Smuggling of diesel was often reported in Malaysia. For instance, about 1000 litres of diesel were smuggled to nearby country by various as reported by Malaysia Police Marine [2].

Hence, it may be necessary to compare a seized diesel sample believed to be subsidized by the government to its known source if smuggling is suspected.

The detection of diesel at a fire scene, where one is not normally present, is a very strong indication of arson. Therefore, its presence "is almost conclusive evidence of intent and preparation provided they are not normal to the premises" as mentioned by DeHaan [3]. Arson crime had led to the lost in properties over other types of fire cause [3]. In the forensic point of view, it is important to establish a link between the evidence recovered in the scene of crime to its origin in settling legal liabilities for the affected parties. A link can be established by analysing the accelerant recovered from the crime scene using GC-MS to produce a profile that could be either associate with or discriminate from the suspected accelerant [4].

In order to discriminate the petroleum product especially diesel, background information on the variability of the product at service stations must be established. This paper intends to find out the existence of chemical variability in diesel product that comes from various service stations around Kota Bharu, Kelantan. In order to characterise the variability in the chemical composition, chemical fingerprinting and data interpretation of the diesel were used so that association or discrimination of the diesel can be made [5-8]. For that purpose, an understanding of the chemical composition of diesel is vital.

Variability in the chemical fingerprints of diesel especially when it is released to the environment is determined by four factors [9]; crude oil genesis, petroleum refining, weathering in the environment, and mixing in the environment. Weathering and environmental mixing are important and must be considered during investigation of oil spill. In fresh diesel, additional factors such as the mixing of residual fuels in the tank of the service station with the new fuels that fill up the tank can also contribute to the variability of diesel fuels because the variability or uniqueness will be inherent when the tank is filled with a new batch of oil [10].

1.3 DEFINITION OF DIESEL FUELS

Oxford English Dictionary defines diesel as a heavy petroleum fraction used as fuel in diesel engine. The range of petroleum fraction is in the C_{11} to C_{18-27} with its own boiling range. Boiling range as defined by Song [11] "is the initial boiling point and the final boiling range in the distillation curve and the boiling point of diesel fuels is within the range of 150°C to 380°C."

Diesel fuel is one of the products of distillate fuels from vaporization of crude oil which is then re-condensed in the refining process to form the final product. If distillate fuels are not to be used in diesel engine, they are termed as fuels oil [12]. However, in Europe, fuels oil refers to the residual oils in the process of refinery.

The classification of diesel fuels are based on the established specifications by the American Society for Testing and Materials (ASTM) on both land and marine diesel fuels (ASTM D975) [13]. It designates diesel fuel grades into diesel no. 1, diesel no. 2, and diesel no. 4 [12]. Grade no. 3 fuels is not being use anymore because the specifications were dropped and replaced by those grade no. 2 [14].

The most common diesel fuel grades used are diesel no. 1 and diesel no. 2. Both of them are frequently used in transport vehicles and locomotives while diesel no. 4 is commonly used in stationary diesel motors or furnaces that requiring constant load [12]. In some cases, not all diesel engines use distillate diesel fuels. Diesel no. 5 and no. 6 are those come out from refinery process as residual fuels. Marine diesel engine used fuel oil no. 6 which is commonly referred to as ‘bunker C’.

CHAPTER 2

LITERATURE REVIEW

2.1 DIESEL CHEMISTRY

Crude oil is made from a complex mixture of hydrocarbons and nonhydrocarbons [9]. The distribution of these compounds in crude oil affects their physical properties. Based on the variability in physical properties, crude oils are classify as conventional and heavy [15]. These physical properties will determine the composition of the refinery products. However all refinery product will have three major hydrocarbon classes; paraffinic, naphthenic, and aromatics with which each of class posses a very broad range of molecular weight [9, 16].

2.1.1 Molecular Components of Diesel

Diesel contains paraffin, naphthene, aromatic, non hydrocarbon compounds, and sometimes olefins, with different proportions that depend on which crude oil they come from [9, 11, 17] and also the nature of distillation process [12]. Different proportions of the first three classes is one of the factors that makes a grade of diesel fuel different from another [16]. Each member in a class shares a common structural feature but differ in the number of carbon atom or geometry. The differences among classes are in the ratio of hydrogen to carbon atoms and the type of bonding among the carbon atoms [16].

2.1.1.1 Paraffins

Paraffin is a collective name of aliphatic hydrocarbon which include normal paraffins (also known as normal alkanes) and iso-paraffins (also known isoalkanes or acyclic isoprenoids) [12, 16]. The general formula for paraffins is C_nH_{2n+2} where “n” is the number of carbon atoms in the molecules.

All carbons atoms in normal paraffins are bonded to two others except those at the ends to form long chain-like molecules, Figure 1. Isoparaffins has same chain-like molecule but they have one or more carbons branching off from the backbone. Normal nonane and 2,4-dimethylheptane has the same chemical formula of C_9H_{20}, but different in chemical and physical properties, Figure 1. Though 2,4-dimethylheptane is an isomer of nonane that exhibits similar chemical formula, it has different chemical structure.

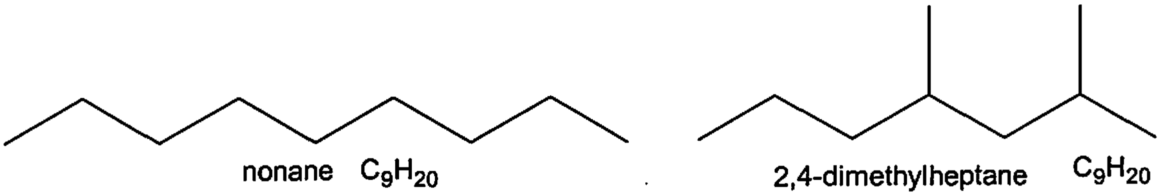
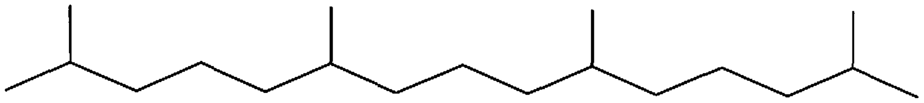


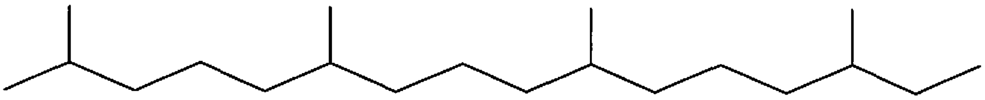
Figure 1: Structure of normal paraffin (nonane) and isoparaffin (2,4-dimethylheptane)

The range of carbon atoms of normal paraffin in diesel fuels is from C_{10} to C_{20} with the boiling points from 174°C (n-C_{10}) to 344°C (n-C_{20}) respectively [11]. Diesel fuels may also contain small proportions of lighter (C_9-) and heavier (C_{20}+) components.

Isoalkanes are mostly found in the C_6 to C_8 range, especially methyl-hexane and methyl-heptane [18]. Isoalkanes with methyl group branching off from the main carbon chain are called isoprenoids and they fall in the range of C_9 to C_{25} [18]. Pristane (Pr) and phytane (Ph) are the most abundant isoprenoids in crude oils [18], Figure 2.



Pristane



Phytane

Figure 2: Structures of pristane and phytane

2.1.1.2 Naphthenes

Naphthene, cycloalkane, or cycloparaffin is a saturated cyclic hydrocarbon where the carbon atoms linked to each other to form a ring. The number of carbon atoms in rings of naphthalene of diesel fuels is commonly five or six [16]. In other instances, some carbons are shared by adjacent ring to form two or more rings. The general formula for those with single ring is C_nH_{2n}.

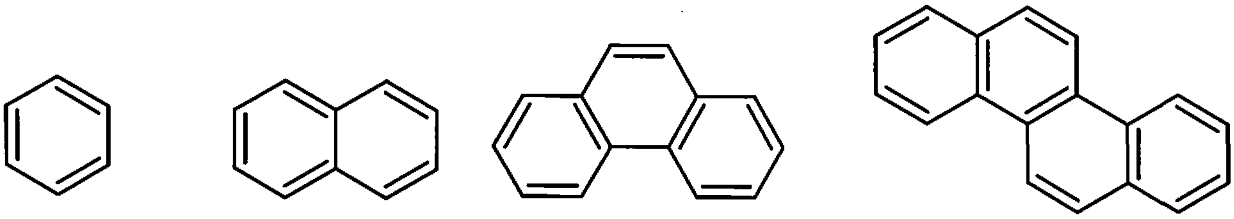
Sometimes one or more alkyl groups are attached to the ring to form alkylated cycloalkanes. Typical examples of alkylated cycloalkanes in diesel fuels are alkylcyclohexanes, decahydronaphthalenes, and perhydrophenanthrenes with one to two rings. The nature of crude oil, the blending stocks, and the processing parameter during refinery process will determine the contents of naphthenic components in diesel fuels [11].

2.1.1.3 Olefins

Olefin, also known as alkene, is similar as paraffin but in its structure, it contains at least one double bond. Because of this, the numbers of hydrogens are reduced compare to paraffins. Olefins also can have isomer when the number of carbon atoms is more than four. The general formula for an olefin is same as a naphthene, C_nH_{2n} when it has one double bond in its structure [16]. Note that olefins are unsaturated hydrocarbon. They are rarely found in the crude oil because they are relatively unstable [18].

2.1.1.4 Aromatic Hydrocarbons

Carbon atoms in aromatic are arranged in such a way that it is linked by one another to form a ring called aromatic ring such as those seen in naphthenes. The ring contains six carbon atoms and aromatic bonds join them. Aromatic hydrocarbon can exist in a single aromatic ring and chains or combination of more than one aromatic rings with addition of five-carbon ring [16, 18]. The examples of compounds that exist in single aromatic ring and chains include benzene, naphthalene, phenanthrene, and chrysene as in Figure 3.



Benzene Naphthalene Phenanthrene Chrysene

Figure 3: Structure of benzene, naphtalene, phenanthrene, and chrysene

2.1.1.5 Nonhydrocarbon compounds

Some of nonhydrocarbon compounds present in diesel include polar compounds, which contain one or more nitrogen, sulphur, and oxygen that give polarity to the compounds. The nitrogen-containing compounds that may present in diesel fuels include benzocarbazoles, quinolines, and porphyrins, while sulphur-containing compounds include benzo-, dibenzo-, and polynuclear thiophenes. Examples of oxygen-containing compounds include furans, phenol, and acids [9].

2.2 ANALYSIS OF DIESEL

Analytical methodology for diesel includes the used of gas chromatography-flame ionization detection (GC-FID) for screening purpose and giving the description of the distribution of the dominating hydrocarbon in the sample. Gas chromatography mass-spectrometry (GC-MS) can then be used to give more detail characterization and identification of the sample [8, 19, 20]. Both GC-FID and GC-MS are the most widely used instruments in characterization of hydrocarbon. Other techniques that can also be used include high-performance liquid chromatography (HPLC), size exclusion HPLC, infrared spectroscopy (IR), supercritical fluid chromatography (SFC), thin layer chromatography (TLC), ultraviolet (UV) and fluorescence spectroscopy, isotope ratio mass spectrometry, and gravimetric methods [7].

American Standard for Testing and Material Method (ASTM D5739-06) is a standard practice for oil spill source identification by gas chromatography and positive ion electron impact low-resolution mass spectrometry [21]. This method is used to assess the source for an oil spill. As this practice assumes that, a screening of suspect source has been done by, for example, using GC-FID, it focuses on the generation of data using predetermined compounds. Unfortunately, these compounds, which are mainly present in crude oil, may be at trace level for diesel samples as a result of refinery process.

Nordtest NT CHEM 001, an oil spill identification system, is a procedure to identify oil spills [22]. Similar to ASTM method, it uses GC-MS at selected ions to compare and establish "identity" or "nonidentity" of a sample taken from a spill with samples taken from suspected sources. The lists of ions are as shown in Table 1.

m/z	Component type
183.21	Alkanes and acyclic isoprenoids
113.13	Alkanes
177.16	Norhopanes
191.18	Hopanes
205.20	Methyl hopanes
208.22	Bicyclonaphthalenes
217.20	14α (H) steranes
218.20	14β (H) steranes
253.20	Monoaromatic steranes
231.12	Triaromatic steranes
156.09	C_2-naphthalenes
170.11	C_3-naphthalenes
184.13	C_4-naphthalenes
178.08	Phenanthrene, anthracene
192.09	C_1-phenanthrenes
206.11	C_2-phenanthrenes
220.13	C_3-phenanthrenes
184.03	Dibenzothiophene
198.05	C_1-dibenzothiophenes
212.07	C_2- dibenzothiophenes
226.08	C_3- dibenzothiophenes

Table 1: Selected mass to charge (m/z) ratio of ions with its corresponding component [22]

ASTM D5739-06 compares samples by overlying and direct visually comparing the specific extracted ions chromatograms. As stated by Hibbert et al., [23] there might be a risk of subjective error associated with visual comparison of spectra [23].

The used of statistical analysis have been proved successful in discriminating petroleum origin including petrogenic, biogenic, and pyrogenic hydrocarbon source as conducted by Page and co-workers using double plot ratio and principal component analysis [24]. One of the statistical analysis in exploratory nature is principal component analysis (PCA) which is a multivariate statistical analysis has been used widely in science and engineering fields [7].

PCA will transforms the original data set into new, smaller, and uncorrelated variables called principal component.

The aim of PCA is to help examine data by simplification, and help understand the structure of the variables, thus summarises a multivariate data set by relatively few components with minimal loss of information. PCA is based on the derivation of linear combinations of the p variables X_1, X_2..., X_p to produce "indices", or "derived variables" that are uncorrelated. Each of these uncorrelated derived variables, commonly referred to as "principal components" (PCs), explain a different "dimension" within the data. Note that the PCs are derived in such a way that they are all mutually orthogonal. In other words, they are independent and at right angles to one another in multidimensional space. These components are also arranged in order such that the first PC account for the largest portion of explainable variability in the measured dataset, followed by the second PC and so on. This can be visualise in a scree plot as in Figure 4.

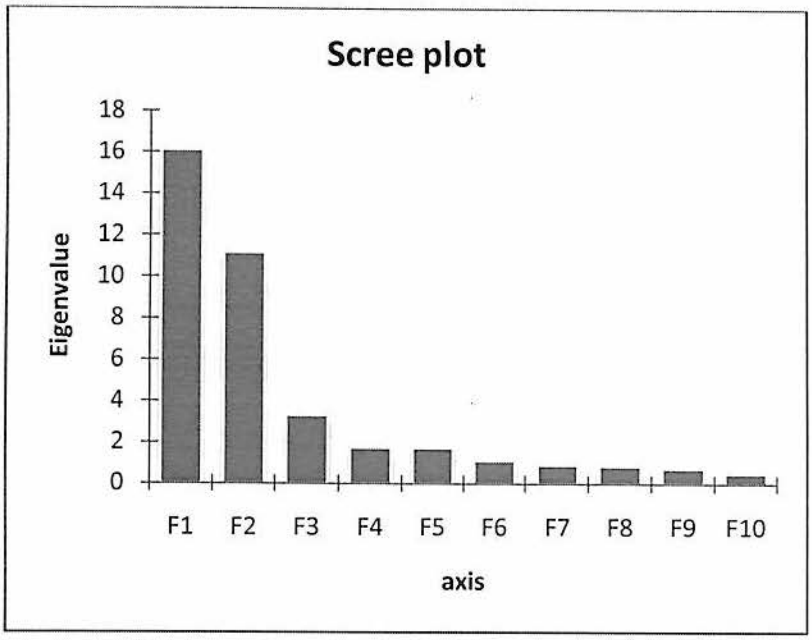


Figure 4: Scree plots of 10 PCs.

Note that, as there are *p* response variables within the data set, *p* principal components can be derived, i.e. number of components equal to number of response variables. It is expected that most of the explainable variability in the can be explained by *n* components where *n* is very much less than *p*.

The first is usually denoted by PC_1. It can be expressed as (Eq. (1)):

$$PC_1 = \alpha_{11}X_1 + \alpha_{12}X_2 + \ldots + \alpha_{1p}X_p \tag{1}$$

Where α terms refer to the weights or loadings, for each variable within this principal component. The second PC, denoted as PC_2 is expressed as (Eq. (2));

$$PC_2 = \alpha_{21}X_1 + \alpha_{22}X_2 + \ldots + \alpha_{2p}X_p \tag{2}$$

provides the linear combination, orthogonal to PC_1.

In this study, the variables of the principal component analysis are the normalised peak area of the selected ions. The importance of each PC is specified by its eigenvalue (λ), with $\Sigma\lambda$ representing the total of the eigenvalues. A measure of the proportion of data variation accounted for each PC is provided by $\lambda/(\Sigma\lambda)$. This will always be the large for the first PC, PC_1 and less for the second, PC_2 and so on. Note the general guideline in PCA application is to select those PCs that account for an accumulation of at least 80%.

Wang et al. [7] claimed that PCA is a powerful statistical method for analyzing the structure of the data and reducing the dimensionality of the pattern vectors. A few researchers have implemented PCA in analyzing their data [25, 26]. Lavine et al. analysed 85 GC peaks obtained from the chromatograms of 284 neat jet fuels that were weathered and unweathered [25]. The PCA performed successfully discriminate the two types of neat jet fuels.

Kennicutt et al. also apply the PCA who study the sediments contamination on Casco Bay, Maine for source identification [26]. In the study, a large number of analytical data with a variety of analytes were analysed using PCA [26]. From the analysis, the contaminants in Casco Bay were identified to be petroleum and petroleum by-product [26].

CHAPTER 3

OBJECTIVES

The objectives of this research are therefore to:

1. Investigate the variability of diesel samples collected from service stations around Kota Bharu.
2. Perform data transformation of gas chromatograms.
3. Discriminate collected diesel samples using Principal Component Analysis.

CHAPTER 4

METHODOLOGY

4.1 SAMPLES COLLECTION

Sampling was carried out in such a way that all the samples were collected in a day (Appendix I) [27]. This however was not achieved and the subsequent 5 samples were collected after a week, Table 2. A Shell service station was sampled four times in an interval of a week for each sampling to investigate the diesel profiles over time.

Prior to sampling, about 100 mL of diesel was dispensed into a metal can. This is to flush out any contaminant at the pump. Then, a brown bottle was used to content about 200 mL of diesel. The bottle was then capped and labeled.