Discrimination of Biodiesel-Diesel of B7 and B10 by Infrared Spectroscopy with Dendogram

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Abstract: *Spectroscopists face an ongoing challenge in identifying fuel spectra due to a wide range of fuel formulations and the increasing abuse of biodiesel-diesel blends. In Malaysia, a new type of biodiesel-diesel blend known as B7 and B10 has been introduced, which requires rapid and reliable discrimination methods. However, current identification methods are costly and time-consuming. To overcome this issue, a spectroscopy study was conducted using a portable Fourier transform infrared (FTIR) spectrometer to identify biodiesel-diesel blends. The study found that direct identification using spectral libraries was reliable in identifying complex samples but unable to differentiate B7 and B10 due to the libraries' focus on hydrocarbons rather than esters. Instead, FTIR spectroscopy provided unique spectral peaks for each blend. Spectral range influences the discrimination, and the truncated region 1697–1777 and 1164–1224 cm^{-1} was shown to be reliable for discriminating the B7 and B10. The study concluded that a combination of algorithms, libraries, and hierarchical cluster analysis (HCA) in FTIR spectroscopy could effectively differentiate the blends. The primary objective was to differentiate B7 and B10 by analyzing liquid samples collected in Malaysia using HCA and IR spectroscopies. FTIR spectroscopy provides molecular-specific vibrational signals and is proven as a rapid identification method.*

Keywords: *biodiesel; diesel; discrimination; FTIR; Hierarchical Cluster Analysis*

■ INTRODUCTION

Petroleum is a naturally occurring, oily, and flammable liquid composed mainly of hydrocarbon materials. On the other hand, vegetable oils consist of glycerol fatty acid esters (triglycerides). Vegetable oils are different from conventional diesel fuels, and vegetable oils are bigger in size than the ones found in petroleum diesel. Meanwhile, biodiesel blends are a renewable and oxygenated fuel that has properties close to petroleum diesel. It is a combination of methyl esters (C15–C17) with any level of petroleum diesel i.e., 1% of pure biodiesel blended with 99% of petrol-diesel [1].

In many countries, including Malaysia, biodiesel-diesel blends, and petrol are the main energy sources consumed for road and maritime transportation. These fuels consist of hundreds of different hydrocarbon molecules. For example, petrol consists of alkanes (paraffin), alkenes (olefins), and aromatics, while diesel fuel contains paraffin, aromatics, and naphthene. Petroleum products (fuels and oil products) are also the most common environmental contaminants in most industrial countries [2].

The identification and discrimination of fuels and other related fuels is always needed because they are always abused by fuel traffickers in criminal activities such as fuel smuggling and fuel adulteration. For

example, the smuggling of petroleum products across the border regions is an international issue for many countries. Illicit trade of fuel, especially gasoline, along the borders of Brazil is a problem that concerns the authorities responsible for the inspection and surveillance of these areas. The main reason is the significant difference between prices in neighboring countries, including Peru, Paraguay, Bolivia, and Venezuela [3].

Fuel adulteration is a national issue in developing countries, including Brazil, India, Kenya, and Nigeria [4]. Typical adulterated fuel products are high-quality motor oils, kerosene, and diesel. In the case of high-quality motor oil samples, they are adulterated with lower-quality oils such as used oils and standard oils [5]. The higher volume "cocktail" or "adulterated" fuel is then sold as taxed fuel, with the evader keeping the tax revenue. It was reported that the detection of adulterated fuel could be problematic since many potential cocktailing products include compounds that are already present in fuel [6]. Besides the forensic needs, the discrimination of the sample's source in oil spills in the maritime area also raises a big concern for researchers [7].

Various analytical methods were used for the analysis of petroleum fuel products. For example, gasoline samples were studied using gas chromatography coupled with flame ionization detection (GC-FID) [8]. Next, chromatography-mass spectrometry (GC–MS) was used for the characterization of ninety-one samples of petrol, diesel, and biodiesel [9]. Variety of the obtained compounds in petrol, diesel, and biodiesel were detected with the help of National Institute of Standards and Technology (NIST) mass spectral search program for the NIST/EPA/NIH mass spectral library (version 2.0) [9]. Spectroscopy methods were often used to characterize fuels such as Fourier transform infrared (FTIR), Raman, [10] and ^{1}H-nuclear-magnetic-resonance (NMR) spectroscopy [11]. Attenuated total reflection (ATR) configuration provides a larger spectral range and better signal-to-noise ratio during the study of diesel samples. Comparisons with commercialized and in-house vibrational spectral libraries were proven for rapid identification of unknown samples [12-14].

Quantitative and qualitative analysis of petroleum diesel, biodiesel, and a number of hydro-processed esters and fatty acids (HEFA) was achieved using Raman spectroscopy. When analyzing a complex mixture of gasoline samples, NMR spectroscopy is useful because regions of the chemical components' regions are unique and can be integrated for quantitative analysis [15].

The increased number of recorded crimes related to petroleum fuels has led many researchers to use multiple strategies either by analyzing various adulterants in fuels using the spectroscopy method [16], analysis of explosion residue related to ammonium nitrate fuel oil (ANFO) explosives using Raman spectroscopy [17], analysis of fire debris for the determination of fuel constitution, and ignition source using laser-induced breakdown spectroscopy [18].

ATR-FTIR method is non-destructive and requires no sample preparation. The advantages of FTIR methodology include a rapid method to analyze many samples and rapid identification of samples with the help of the spectral library. Besides being an identification method, it also has evolved as an excellent tool for the detection of many substances with the help of chemometric tools [19]. This study aims to develop and differentiate biodiesel-diesel (B7 and B10) through the analysis of liquid samples collected at various pump stations in Mersing, Malaysia using Hierarchical Cluster Analysis (HCA). First, the local authority in Putrajaya, Malaysia, granted sampling permission to acquire samples from major brands in Mersing. Then, the samples were acquired and characterized using a portable ATR-FTIR spectrometer in the laboratory. Finally, the study used the strong raw FTIR spectra to differentiate biodiesel-diesel (B7 and B10) samples using HCA.

■ EXPERIMENTAL SECTION

Materials

Mersing is a small fishing town in Johor. It is located 136 km north of Johor Bahru, the state capital. Mersing covers a total area of 761 km^2. According to KPDNHEP Putrajaya, there are ten petrol pump stations operating in this town, including Petronas, Shell, Caltex, BHP, and Petron, in 2021. The specific locations of all pump stations in Mersing are shown in Fig. 1.

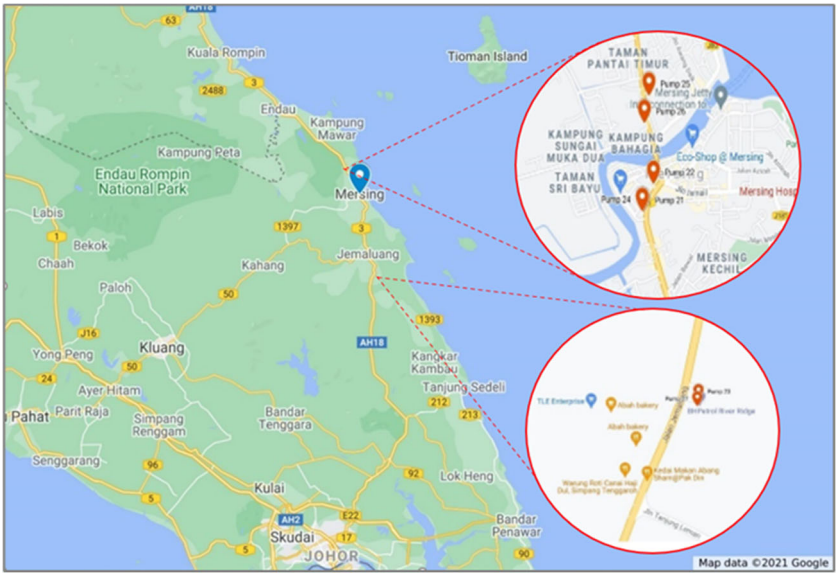

Fig 1. Location of fuel pump stations in Mersing

As many as 10 samples with various fuel brands, as shown in Table 1, were obtained from various company petrol stations that operated in Mersing. This list was produced by the *Kementerian Perdagangan Dalam Negeri dan Hal Ehwal Pengguna* (KPDNHEP). However, only 7 fuel pump stations in Mersing were eligible for sampling.

The lot number was used to record the physical characteristics of the sample. The lot number elements are fuel type, brand, company, and city. The lot number was generated prior to sample collection. All the lot numbers for the samples were printed on a labeling sticker and stuck on the bottle samples. The element of the lot number used in this study is shown in Table 2.

The lot number began with the fuel type, which it contains 6 different labels, P95 (petrol RON95), P97 (petrol RON97), D0 and B10 (biodiesel B10), and DE5 and B7 (biodiesel B7). There are two different labels that indicate the same fuel type, such as D0 and B10, which refer to biodiesel B10 same goes for DE5 and B7, which refer to biodiesel B7. This is due to the improvement made after being informed about the new biodiesel naming in Malaysia.

All the labels with the alphabet 'P' indicated petrol type followed by the Research Octane Number (RON) number, whereas RON 95 and 97 indicate the percentage of unleaded petrol. The alphabet 'D' and 'B' indicate biodiesel type. Biodiesel B7 is a biodiesel with 7% methyl ester blended with diesel. Meanwhile, biodiesel B10 is a biodiesel with 10% methyl ester blended with diesel.

Table 1. Detail of the fuel samples used in this study

Sample number	Fuel type	Fuel brand	Lot number
69	B7	BHPetrol	DE5_BP3_868
70	B7	Petronas	DE5_PS5_868
71	B7	Petron	DE5_PN6_868
72	B10	BHPetrol	D0_BP2_868
73	B10	BHPetrol	D0_BP3_868
74	B10	Petronas	D0_PS5_868
75	B10	Caltex	D0_CX3_868
76	B10	Petron	D0_PN5_868
77	B10	Petron	D0_PN6_868
78	B10	Shell	D0_SL5_868

Table 2. Description of the lot number

Fuel type		Fuel brand		Company		City	
P95	Petrol RON 95	PS	Petronas	1	Each number represents a different	868	Mersing
P97	Petrol RON 97	PN	Petron	2	company within the city area		
D0	Biodiesel B10	BP	BHPetrol	3			
B10	Biodiesel B10	CX	Caltex	4			
DE5	Biodiesel B7	SL	Shell	5			
B7	Biodiesel B7			6			

The middle of the lot number indicates the fuel brand, followed by the number that indicates a different branch/company. The end part of the lot number indicates the postcode of '868' (Mersing). Table 2 shows the list of samples with Lot numbers for infrared spectroscopic purposes.

Instrumentation

ATR-FTIR measurements were carried out using an Alpha II (Bruker) spectrometer equipped with a platinum diamond ATR module, a ZnSe beam splitter, and an RT-DLaTGS detector. The transmission spectra were recorded between 550 and 4000 cm^{-1} with a spectra resolution of 4 cm^{-1} and an accumulation of 32 scans.

The acquired FTIR spectra were corrected using the H_2O compensation function of the OPUS software (Bruker, version 7.5) that also drives the spectrometer operation. The instrument status was self-tested prior to data acquisition. The spectra were recorded at room temperature (~25 °C). Once the solvent (acetone) was evaporated to dryness, the spectra of the liquid samples were recorded immediately after placing one droplet of sample on the ATR. The pressure applicator was applied to enhance the quality of the spectra. A spectrum of the polymeric material of a hand glove was acquired to verify the performance of the instrument prior to sample analysis. The online instrument monitoring of all relevant system components, including PerformanceGuard and PermaSure was performed to ensure proper instrument operation. The acquired spectra were obtained in .0 (OPUS) file format and analyzed using OPUS software.

Procedure

Library search identification

Molecular identification of petrol diesel samples in Table 1 and their composition were accomplished through spectral library searches using commercial IR spectral libraries (796 reference spectra). Spectral library searches were performed using a standard and mixture search algorithm in the OPUS software v.7.5 (Bruker Optik Gmbh 2014). The quality of the match between the query spectrum and the various library spectra was evaluated based on calculated hit quality index (HQI) values.

Hierarchical Cluster Analysis (HCA)

HCA is used to identify the similarities between the spectra of samples with the use of distances between spectra [20]. A dendrogram showing similarities between the spectra was generated. Spectra were acquired and processed by the OPUS software v8.5 (Bruker Optik Gmbh 2020) and Spectragryph software v.1.2.16.1 [21]. For multivariate analysis, the 1697–1777 and 1164 and 1224 cm^{-1} region of the FTIR spectral data, rather than the full spectrum, were subjected to HCA. Dendrograms of each fuel type were generated. Ward linkage algorithm and Euclidean distance were used for cluster analysis, which was provided in the OPUS software v.8.5 (Bruker Optik Gmbh 2020).

■ RESULTS AND DISCUSSION

Spectral Identification Using Spectral Libraries

Three OPUS spectral libraries were used to identify liquid query spectra, which consist of two different types of biodiesel-diesel samples of B7 and B10, by using the "spectrum search" option available in the OPUS 7.5 (Bruker Optik Gmbh 2014) software. To evaluate the appropriate comparison criteria of the samples, two different search algorithms: standard and mixture algorithms, were used. Initially, the aim of spectral matching is to identify the composition of the samples.

Table 3. OPUS 7.5 library search results of different samples on the same spectral libraries, in which the best match Hitlist at standard search algorithm and main three components content in mixture search algorithm

Samples/search algorithm	Standard		Mixture	
	Identification hit	HQI	Content	%
DE5_BP3_868*	Parvan 3150, f.n. 3502*refined paraffin wax	662	**Vaseline 8401**	42.7
	Octane	557	Poly(ethylene), low density	31.0
	Epcar 5875*ethylene/propylene/diene terpolymer	543	Octadecane	26.4
DE5_PN6_868*	Parvan 3150, f.n. 3502*refined paraffin wax	625	**Vaseline 8401**	78.5
	Epcar 5875*ethylene/propylene/diene terpolymer	544	Poly(ethylene), low density	21.5
	Octane	543		
DE5_PS5_868*	Parvan 3150, f.n. 3502*refined paraffin wax	625	**Vaseline 8401**	79.3
	Vaseline 8401	583	Poly(ethylene), low density	20.6
	Epcar 5875*ethylene/propylene/diene terpolymer	545		
D0_PS5_868**	**Epcar 5875*ethylene/propylene/diene terpolymer**	545	**Vaseline 8401**	44.3
	Rumiten 250 cq*low density polyethylene	541	Poly(ethylene), low density	32.4
	Parvan 3150, f.n. 3502*refined paraffin wax	539	Octadecane	23.3
D0_SL5_868**	Octane	633	**Vaseline 8401**	43.3
	Parvan 3150, f.n. 3502*refined paraffin wax	620	Poly(ethylene), low density	30.2
	Epcar 5875*ethylene/propylene/diene terpolymer	543	Octadecane	26.5
D0_BP2_868**	Octane	555	**Vaseline 8401**	83.1
	Epcar 5875*ethylene/propylene/diene terpolymer	543	Poly(ethylene), low density	16.9
	Rumiten 250 cq*low density polyethylene	539		
D0_BP3_868**	**Epcar 5875*ethylene/propylene/diene terpolymer**	542	**Vaseline 8401**	83.6
	Rumiten 250 cq*low density polyethylene	540	Cumar r-15 (formerly cumar mh-1 1/2 resin) *coumarone-indene resin	16.4
	Parvan 3150, f.n. 3502*refined paraffin wax	539		
D0_CX3_868**	**Epcar 5875*ethylene/propylene/diene terpolymer**	543	**Vaseline 8401**	41.1
	Rumiten 250 cq*low density polyethylene	541	Poly(ethylene), low density	33.7
	Parvan 3150, f.n. 3502*refined paraffin wax	539	Octadecane	25.2
D0_PN5_868**	Parvan 3150, f.n. 3502*refined paraffin wax	544	**Vaseline 8401**	81.3
	Epcar 5875*ethylene/propylene/diene terpolymer	544	Cumar r-15 (formerly cumar mh-1 1/2 resin) *coumarone-indene resin	18.7
	Rumiten 250 cq*low density polyethylene	542		
D0_PN6_868**	**Epcar 5875*ethylene/propylene/diene terpolymer**	544	Vaseline 8401	40.9
	Rumiten 250 cq*low density polyethylene	541	Poly(ethylene), low density	34.1
	Parvan 3150, f.n. 3502*refined paraffin wax	540	Octadecane	25.0

* Refers to the B7 type of fuel

** Refers to the B10 type of fuel; the repeated compound in each algorithm is highlighted as Bold

Hence, 10 biodiesel-diesel samples, as shown in Table 1, were analyzed using FTIR spectrometers, and the acquired spectra were evaluated by the algorithm search. During the spectrum search methodology, the spectral region was consistent between 600 and 4000 cm^{-1} for both search algorithms. The spectrum search results are summarized in Table 3 for 10 unknown biodiesel-diesel samples using two algorithms search.

In the standard search algorithm, the search parameter was set as one main component with min hit value of 100 and a maximum hit value of 30. The standard search algorithm produced a table that contained the HQI values and library spectra with higher similarities to the query spectrum. Each biodiesel-diesel sample was evaluated by HQI values. The HQI can range from 0–1000, in which 0 corresponds to very unlikeness and 1000 corresponds to perfect likeness. As a result, three main identification hits were recorded. All the B7 and B10 samples show the matching spectrum of Epcar 5875*ethylene/propylene/diene terpolymer with HQI value 542–545. Parvan 3150, f.n. 3502*refined paraffin wax, octane, vaseline 8401, and rumiten 250 cq*low density polyethylene were also found in most samples. This result is very likely indicating the presence of hydrocarbon materials in B7 and B10 samples. The low HQI values are probably because of the absence of fuel spectra in the tested library.

In the mixture algorithms, three main components were evaluated to match the query spectrum. Similarly, this algorithm produces a table containing the reference spectra and their percentage composition. It can be defined that the samples are a mixture of compounds with different levels of composition. Vaseline 8401 was found as one of the components in all the studied biodiesel-diesel samples. For example, D0_BP3_868 displayed the highest composition of Vaseline 8401 (83.6%), followed by D0_BP2_868 (83.1%). Vaseline is known as a product made from paraffin wax, which is a by-product of petrol [22]. There is also the presence of poly(ethylene), low-density octadecane cumar r-15 (formerly cumar mh-1 1/2 resin) *coumarone-indene resins in most of the studied samples. Similarly, this result also indicates the presence of hydrocarbon materials in the samples.

To sum up, the spectrum search methodology is less suitable for the direct identification of biodiesel-diesel samples by using both standard search and mixture search algorithms. Despite the presence of different levels of esters in all studied samples, the spectrum search methodology only shows the major component of the hydrocarbon in all biodiesel-diesel samples. Another classification method is needed to identify different levels of esters and hydrocarbons in biodiesel and diesel, respectively. Prior to this approach, FTIR spectral analysis is needed for the characterization of the samples.

FTIR Spectral Analysis of Biodiesel-Diesel of B7 and B10

In this study, samples were obtained from various pump stations in Mersing, Malaysia, according to the methodology. The presence of local authorities and pump managers ensures the integrity of the sampling procedures. The overlay FTIR spectra of B7 and B10 are given in Fig. 2.

Upon visual inspection, spectra were found similar for both B7 and B10. There are many overlapping peak positions and peak intensities between B7 and B10. However, different FTIR intensities at selected spectral regions were also observed between B7 and B10 after spectral expansion. Distinct regions are shown in Supplementary Information.

The FTIR spectrum represents multiple compositions of the samples. B7 and B10 have slightly different chemical compositions. B7 and B10 are biodiesel-diesel compositions that are 7 and 10% biodiesel mixed with petrodiesel, respectively [23].

Diesel is a complex mixture with hundreds of hydrocarbon components, including alkanes, monocyclic cycloalkane, bicyclic cycloalkanes, tricyclic cycloalkanes, alkylbenzene, hydrindene, tetrahydronaphthalene, indene, naphthalene, acenaphthene, biphenyl, acenaphthylene, and phenanthrene [24]. Although the biodiesel-diesel sample is a complex mixture with hundreds of compositions, vibrational assignment is simple. For this study, the FTIR spectra of B7 and B10 are comparable with palm oil methyl ester in the biodiesel-diesel blend. The FTIR features that are found to be associated with B7 and B10 are 700, 722, 740, 765, 806, 1169, 1196, 1247, 1377, 1459, 1746, 2853, 2922, and 2954 cm^{-1}. Most of them are associated with hydrocarbon signals. However, 1169, 1196, and 1746 cm^{-1} are associated with fatty acid methyl ester.

For diesel samples that contain many hydrocarbons, IR signals at 2900 and 2830 cm^{-1} are associated with symmetric CH_3 stretch and symmetric CH_2 stretch,

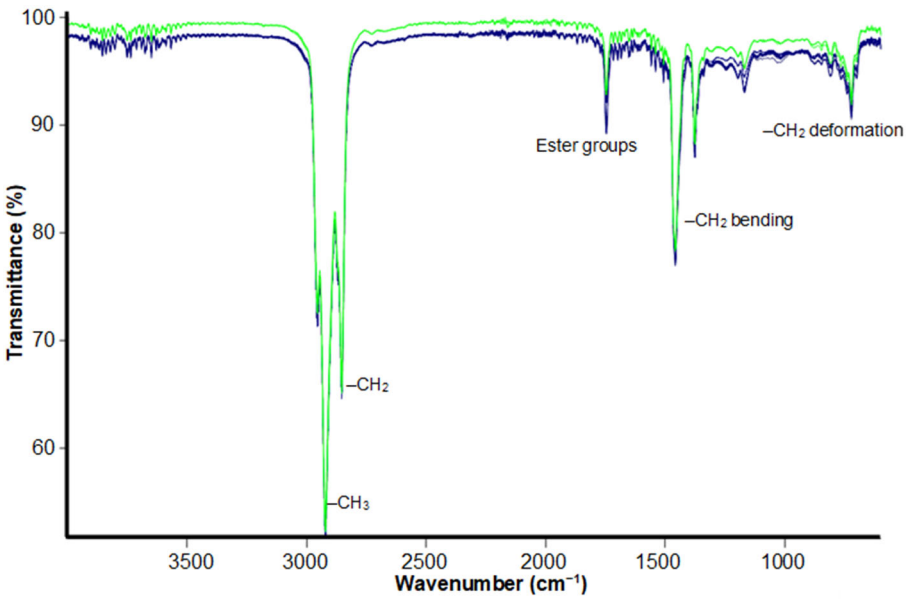

Fig 2. FTIR spectra of B7 (green) and B10 (black) were collected at different pump stations in Mersing whereas the FTIR intensity of B10 was decreased by 0.01

respectively. Two other weak peaks were observed at 1445 and 1400 cm^{-1} caused by the CH_3 and the CH_2 bending vibration, respectively [25]. A signal at 720 cm^{-1} is assigned to the asymmetric angular deformation of CH_2 [26]. Meanwhile, peaks at 1703 and 1728 cm^{-1} correspond to the ester functional group.

Alkanes were determined to be the most common functional group in the FTIR spectra data, with the majority of characteristic wavenumber peaks located between 700 and 1200 cm^{-1} [27]. The main characteristic that distinguishes biodiesel-diesel blend from diesel is its absorption at 1169, 1196, 1247 and 1746 cm^{-1}. Fig. 3 shows the comparison of wavenumber differences with B10. High agreement of wavenumber was found in the mid-infrared spectra region.

In general, no differences in wavenumber and intensity were found among the FTIR spectra for 3 samples of B7 and 7 samples of B10 samples, regardless of brands. However, a spectrum of B10 (D0_SL5_868) interferes with spectra collected from B7 since it contains an overlapping peak position below 1800 cm^{-1} as seen in Fig. 2. Spectral expansion for different regions is shown in Supplementary Information.

Although various spectral regions were interrogated for the small number of samples, discrimination of B7 and

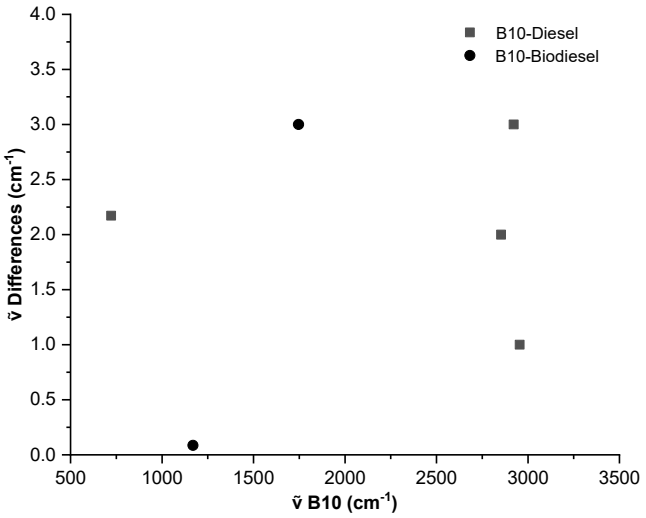

Fig 3. Comparison of the wavenumber differences and B10 wavenumber

B10 using visual inspection would be challenging if the same methodology is used for a large number of samples in the forensic analysis. On top of this, multiple spectral formats prevent rapid data analysis because of incompatibility issues. Thus, the HCA method was performed much easy with the use of the clustering function in OPUS (Bruker) for discrimination of B7 and B10 samples after sample acquisition with Bruker spectrometer.

Cluster Analysis Using HCA

In this study, the results of the HCA on the truncated region between 1697–1777 cm^{-1} using the standard Ward linkage algorithm and Euclidean distance are presented in the form of a dendrogram as shown in Fig. 4.

The dendrogram in Fig. 4 shows the classification of B7 and B10 diesel, where the biodiesel-diesel samples are divided into two major clusters with high heterogeneity levels at 0.25. Cluster B7 groups the samples of D0_SL5_868.0, DE5_BP3_868.0, DE5_PS5_868.0, and DE5_PN6 _868.0, while Cluster B10 consists of samples of D0_BP2_868.0, D0_PS5_868.0, D0_PN5_868.0, D0_BP3_868.0, D0_CX3_868.0, and D0_PN6_868.0. Within the particular clusters, it is possible to distinguish additional sub-clusters. Accordingly, in cluster B7, the following sub-clusters may also be distinguished: sub-cluster B7.1 grouping diesel samples DE5_BP3_868.0, DE5_PS5_868.0, and DE5_PN6_868.0. However, two sub-cluster can be identified in B10, which are B10.1 and B10.2 clusters. B10.1 cluster containing grouping diesel samples of D0_BP3_868.0, D0_CX3_868.0, and D0_PN6_868.0 while B10.2 consists of D0_BP2_868.0, D0_PS5_868.0, and D0_PN5_868.0.

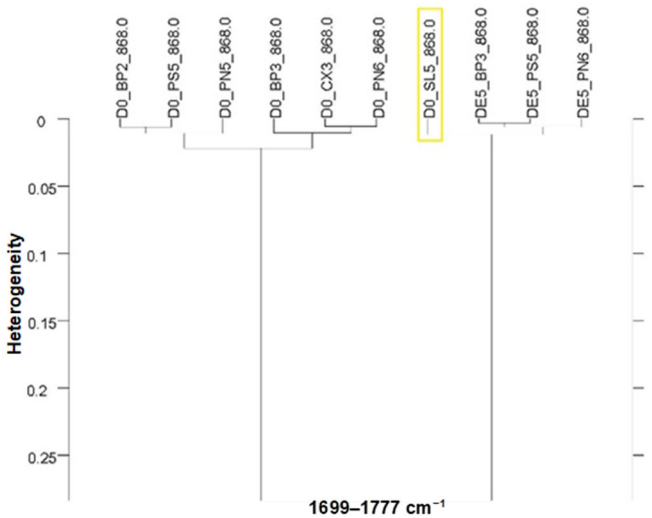

Fig 4. Dendrogram obtained from the HCA of raw spectra of B7 and B10 (10 spectra) partitioned into 2 main groups corresponding to two different types of biodiesel-diesel fuels. The clustering was performed between 1699 and 1777 cm^{-1}

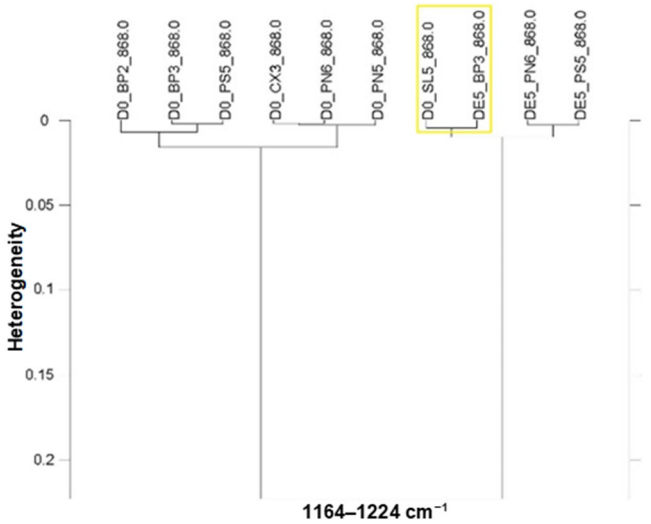

Fig 5. Dendrogram obtained from the HCA of raw spectra of B7 and B10 (10 spectra) partitioned into 2 main groups corresponding to two different types of biodiesel-diesel fuels. The clustering was performed between 1164 and 1224 cm^{-1}

The only sample signed out of their cluster was the D0_SL5_868.0 sample highlighted in yellow color shown in Fig. 4. This sample overlapped with the B7 cluster. In separate clustering between 1164–1224 cm^{-1} (heterogeneity level at 0.2), the samples of D0_SL5_868.0 are clustered together with DE5_BP3_868.0 as shown in Fig. 5.

However, the wrong discrimination of this method still has the potential to find the sample similarity. HCA result shows the region between 1697–1777 cm^{-1} in the mid-infrared spectra containing relevant information than 1164–1224 cm^{-1} to discriminate between B7 and B10 without pre-processing.

■ CONCLUSION

The current research evaluated the capability of FTIR combined with chemometric analysis. FTIR spectra data were characterized by analyzing the functional groups in different types of samples (B7 and B10). A comparison of spectra between B7 and B10 samples was made to identify overlapping and non-overlapping peaks for clustering. Upon visual inspection, two regions for clustering were successfully selected. With the help of the add-on function of Cluster

Analysis in OPUS, rapid HCA analyses were successful in distinguishing B7 and B10 from Mersing. HCA result shows the region between 1697–1777 cm^{-1} in the mid-infrared spectra containing relevant information than 1164–1224 cm^{-1} to discriminate between B7 and B10 without spectral pre-processing. This discrimination is very likely because of the significant differences in FTIR intensity present.

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■ AUTHOR CONTRIBUTIONS

Mohd Rashidi Abdull Manap and Ramizah Azis conducted the design of the experiment and experimental works. Ahmad Fadly Jusoh, and Nur Diana Farhana Muhamad Zulkifli conducted the clustering work and experiment, Lim Xiang Chuin, Qhurratul Aina Kholili, Fatin Abu Hasan, and Danish Aiman Akmal Mohd Effendy conducted the spectral analysis.

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