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Structural Information from Ratio Bands in the FTIR Spectra of Long Chain and Branched Alkanes in Petrodiesel Samples

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Abstract

FTIR is a widely used equipment for determining the chemical structure of organic materials. Vibrational analysis was employed to characterize hydrocarbon structure from which depends their quality and environmental effect. The results showed that the FTIR spectrum of petrodiesel allowed structural information about degree of branched or aliphatic chain hydrocarbons. The ratios of aliphatic carbons especially CH_2/CH_3 (A_{2920}/A_{2950}) and $A_{1376}/(A_{1376}+A_{1460})$ appeared to be suitable indicators for identifying type of alkanes present in petrodiesel samples.

Keywords: FTIR, Petrodiesel, Hydrocarbon structure

1 Introduction

Most of air contaminants have origin from diesel petroleum which is urgent problem in most world countries and simplicity of determination of fuel quality is still challenge. Today all European countries have strong quality control of quality diesel fuel, but all these quality parameters do not involve petroleum hydrocarbons (PHCs) which can contain a lot of contaminants, or can initiate formation of other air contaminants which can be chemical product in engine combustion of diesel petroleum. Nakakita et al. reports about diesel fuel which contain branched and ring hydrocarbon compounds under engine combustion produced high level of PM precursors, such as benzene and toluene which are in high level produced from branched paraffins compare with n-paraffins where their formation are in low level (1, 13). Their funding's suggest branched hydrocarbons to be in low level in diesel fuel because of possibility to increase PM emissions in air also particle matter of are in strong correlation with composition and physico-chemical parameters (1, 14). Anyway, high level of n-paraffins or long chain aliphatic hydrocarbons have lower impact in PM emissions compared with branched paraffins; but also has other negative effect which originates from their higher boiling point and under engine incomplete combustion some of them can be exhaust gases or can be condensed droplets from unburned fuel (2). From this point of view it is very important to know what type of hydrocarbons contain diesel fuel branched or long chain hydrocarbons. Cetane number and molecular composition of petrodiesel properties was done by gas chromatography (3), others applied NIR-Spectroscopy (4, 15), or NMR (5, 16). Most of them use a lot of toxic chemicals also need a lot of time for sample preparation and cost analysis are very expensive.

Other important parameter used in fuel quality is cetane number which depends from organic structure of molecules and can be in correlation with molecular structure of hydrocarbons but from cetane number is not possible to know more details about type of hydrocarbons. Most of methods used in cetane number determination are expensive and time consuming but using this cetane number is possible to know molecular structure of fuel hydrocarbons (6). Cetane Number has minimum legislative limit, but not the maximum, based on European Commission legislation. Cetane number, combustion level and PM emissions are in strong correlation between and as a conclusion high cetane number provide complete and faster combustions and lower PM emissions (7, 17). Our research group proposed FTIR-spectroscopy application which has a lot of benefits compared with other methods for the reason that it does not need any sample preparation, it does not use any hazardous chemicals, the cost analysis is cheaper and FTIR-Spectroscopy known as green but also as fast and sensitive method of analysis. FTIR spectroscopy was applied in order to estimate structural information of hydrocarbon molecules present in coal using single wavenumber and using ratio of frequencies from asymmetric stretching vibrations of CH_2/CH_3 ratio (8, 18). Cetane number is one fuel parameter which corresponds with ignition delay, but in general this depends on the type of hydrocarbons content in fuel. Similar application in coal sample characterization was reported

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about using same ratio of frequencies to find branched aliphatic degree and long chain side of hydrocarbons (9). They found correlation between intensity ratio and type of hydrocarbons (long or short chain and branched degree) as follows:

- Decrease or lower ratio- High level of branched degree or shorter aliphatic chain
- Increase or high ratio-Longer aliphatic chain of alkanes are present or less branched.

Other authors' reports about other ratio combinations that determine the branched degree of alkanes following $A_{1376}/(A_{1376}+A_{1460})$ apply in oils from reservoirs (10). The intensity of this ratio is in correlation with branched degree of hydrocarbons which means that high intensity of this ratio corresponds with the highest branched hydrocarbon structure. There are published reports about the use of the ratio of frequencies, but not directly about fuel analysis and their usage as indicators for type of hydrocarbons which still remain unclear. Novelty of this proposed method is the promotion of FTIR-Spectroscopy as an alternative method of cetane number determination and to give information about type of hydrocarbons. This FTIR offers opportunities to detect the type of hydrocarbons branched or long chain which is sufficient information for monitoring contaminants in air and their origin of contamination. The aim of this research is to optimize FTIR-Spectroscopy method by using those two types of ratio frequencies from two different IR region of methyl and methylene vibrations. Challenge is to determine exact type of hydrocarbons in petrodiesel samples present in different diesel fuels from 5 different brands of fuel companies around Kosovo in comparison with cetane number as a standard method.

2 Experimental

2.1 Samples and applied Measurements

Diesel fuel purchased from local and international brands in Kosova were used and analyzed by FTIR-Spectroscopy. An Irrafinity-1 Shimadzu FT-IR spectrophotometer equipped with a deuterated triglycine sulfate (DTGS) detector was used to acquire FT-IR spectra. Fuel sample were deposited between two CaF_2 transparent windows. All spectra were recorded from 4000 to 1000 cm^{-1} and processed using IR-Solution Software for Windows (Shimadzu). After each operation, the CaF_2 window was thoroughly cleaned up, washed with acetone and then dried. For comparison between branched and long chain compounds was used two standard compounds one as a long chain aliphatic compounds was used hexadecane >99 % Sigma-Aldrich (below STD1) and isocetane as highly branched alkane reference compound 2.2.4.4.6.8.8-heptamethylnonane Sigma-Aldrich, 98 % (below STD2).
The assignment of bands was done by comparison with literature spectral data and with reference compounds spectra included in the software spectral library. Height and area of each band were measured and calculated by the essential FTIR software. Cetane Number were determined according to the standard methods EN ISO 5165 method (11).

3 Results and Discussion

Based on reported results (Table 2a) sample number 4 has higher cetane and also based FTIR results has similarity in ratio 2925/2954 and conclusion is they are not different which means their chemical structure is very similar between standard long chain molecule and real analyzed sample. From this point of view higher cetane number are in correlation with long chain aliphatic molecules. All other analyzed petrodiesel samples are classified as different compared with standard long chain compound because relative difference is higher than 10 %. Same samples were analysed by FTIR Spectroscopy and all results were compared with branched aliphatic standard compound results presented in Table 2b, relative difference is lower than 10 % classified as Not Different chemical structure except in sample 4 where relative difference is higher than 10% and it is classified as different chemical structure. Conclusion based on a standard compounds was confirmed from both compounds long and branched aliphatic compounds and based on this sample 1,2,3 and 5 contain branched aliphatic compounds and only sample 4 has long aliphatic chain molecules. In Figure 1 are shown scanned FTIR spectra of petrodiesel compounds and their characteristic band of methylene and methyl vibrations of hydrocarbon molecules and in Table 1 are presented group frequencies for crucial type of vibrations in petrodiesel samples. Ratio I was used to compare standard analyzed compounds and both reference compounds and sample 4 has similarity with STD1 or long chain aliphatic compounds and all other samples has similarity in intensity ratio with STD2 or branched aliphatic reference compounds Figure 2.

Table 1: Selected FTIR spectra peak frequencies in petrodiesel (12).

Functional Group	Region (cm^{-1})	Intensity*	Comments
Ar–H	3010~3080	m	Str.
$–CH_3$	2950~2975	m-s	asym.str.
	2865~2885	m	sym.str.
$–CH_2$	2915~2940	m-s	asym.str.
	2840~2870	m	sym.str.
–CH	2880~2890	w	Str.
$–CH_3$	1440~1465	m	asym.def
	1370~1390	m-s	sym def.
$–CH_2$	1440~1480	m	acissors vib.

*w = weak; m = medium; s = strong; vs = very strong; v = variable; asym= asymmetric; str.= streching

Table 2: Comparison of peak height ratio 2924/2954 cm^{-1} data for the petrodiesel samples with standard long aliphatic chain hydrocarbon. (a), and comparison of peak height ratio 2924/2954 cm^{-1} data for petrodiesel samples compared with standard branched aliphatic hydrocarbon (b). If the relative difference for a single peak height ratio is greater than the threshold of 10%, the peak height ratio is classified as 'different'; vice versa, the peak height ratio is classified as 'not different'

a)

Sample	Ratio I Long Aliphatic chain standard compound	Ratio I Real sample	Cetane Number	Mean	Absolute Difference	Relative Difference	Conclusion
1	1.75	1.544	52	1.65	0.2	12.50	Different
2	1.75	1.522	51.5	1.64	0.22	13.91	Different
3	1.75	1.545	53.6	1.65	0.2	12.39	Different
4	1.75	1.7	55	1.72	0.05	2.83	Not Different
5	1.75	1.58	53.8	1.66	0.17	10.27	Different

b)

Sample	Ratio I for real sample	Ratio II for Branched Aliphatic standard compounds	Mean	Absolute Difference	Relative Diffference	Conclussion
1	1.54	1.5	1.52	0.044	2.89	Not Different
2	1.52	1.5	1.51	0.022	1.47	Not Different
3	1.545	1.5	1.52	0.045	3	Not Different
4	1.7	1.5	1.6	0.201	12.56	Different
5	1.58	1.5	1.53	0.079	5.13	Not different

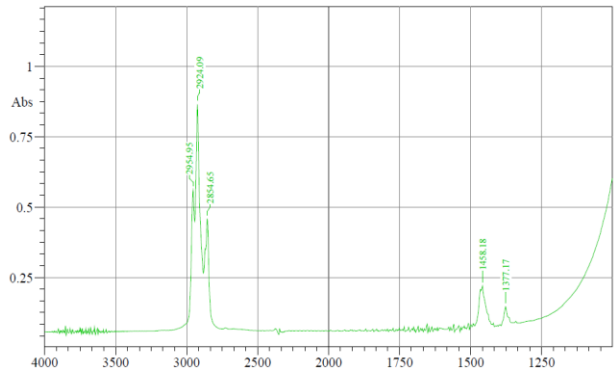

Figure 1: FTIR-Spectra of petrodiesel sample

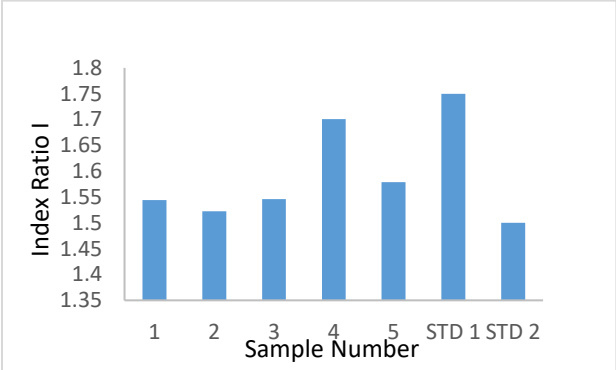

Figure 2: Ratio I comparison analyzed sample with both standard compounds

During research we also used and other frequency combinations which is combination of two frequencies 1377cm^{-1} and 1458 cm^{-1}. (Ratio II) used reported formula before and also correlation of this intensity ratio of frequencies analyzed for real samples reference compounds are in strong relation between Figure 3. More similarity has Sample 4 with STD1 and sample 1 is very close with STD 2 but all other samples are between two standard compounds and this can be explained with their different components present in every sample with different alkane type.

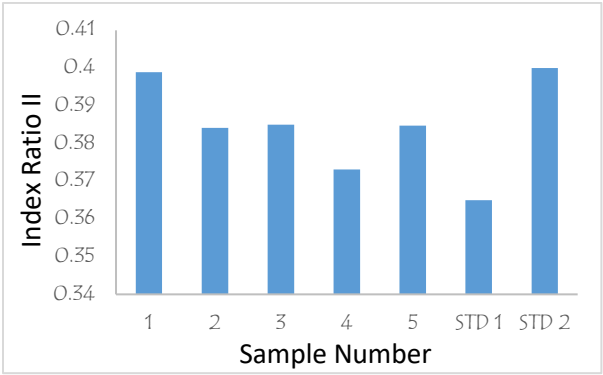

Figure 3: Ratio II comparison analyzed sample with both standard compounds

Based on both Ratios sample 4 corresponds with longer aliphatic chain and all other samples contain more branched aliphatic compounds. Both ratios from FTIR Spectroscopy results can be in correlation with Cetane Number meausered for same samples.

4 Conclusions

Based on our investigations most of brands in Kosovo use petrodiesel classified as branched molecular structure. This can be confirmed by both FTIR ratio confirming each

other, and they are also in complete agreement with cetane number. Petrodiesel in Kosovo petrol companies` brands contains branched alkanes which can be powerful sources for benzene and toluene precursor for PM formation. These are critical air pollutants in Kosovo and have high negative environmental and health impact. We strongly recommend analysis of air particles for their chemical structure and their contaminants origin. Branched molecular structures of petrodiesel converted in benzene and toluene during engine conditions which are precursor for formation of PM. Based on this, most of petrodiesels can be source of benzene and toluene emissions. Only one brand sample contains long aliphatic chain which can be unburned from engine conditions which can be source of emission for other exhaust gases. FTIR tool can be very suitable because this tool known as green method, cheaper, faster, easily operated and sensitive to monitor chemical structure of petrodiesel components, especially parameter ratio I. As such, we suggest to start optimizing the FTIR method and its validation with the purpose of its application in fuel analysis to monitor molecular structure of hydrocarbons.

Ethical issue

Authors are aware of, and comply with, best practice in publication ethics specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that there is no conflict of interest that would prejudice the impartiality of this scientific work.

Authors' contribution

Author of this study have a complete contribution for data collection, data analyses and manuscript writing

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