

Study of diesel with oxygenated fuel blends for its prominence using high performance thin layer chromatography

Kalil Rahiman M, Balakrishnan K, Venkatachalam R, Murugappan S, Santhoshkumar S

Abstract--- Alternative fuel is found broad utilization in compression ignition engines in terms of its decreased harmful exhaust emissions. In the present work, tri-fuels namely diesel, di-butyl ether and ethanol were blended in various proportions and the resultant fuel blends were validated through high performance thin layer chromatography (HPTLC). Eight different fuel proportions were experimentally validated with the chromatography by comparing with the diesel fuel. Qualitative analysis of various fuel blends such as retention factor, absorption unit, peak height and peak area were carried out depicting the variations in the migration distances and proportional concentrations of different individual components in the tri-fuel samples. The chromatogram resulted from the HPTLC were analyzed for its significance. The one-way ANOVA test was performed to check the formulated null and alternate hypothesis. The critical values for experimental wise error rate lies between 3.28 for the significance value of 5% to 3.80 for significance value of 1%.

Keywords: Oxygenated fuel; High Performance Thin Layer Chromatography; Retention Factor; ANOVA.

1.0 INTRODUCTION

Fossil fuels plays an important role in the carbon-based economical sources, whereas the substances originated have been turn out from the inadequate natural resources. Moreover, the increase in demand and supply of fossil fuels is often unstable due to the rapid increase of world's population with improved standards of livelihood [1]. Diesel as a hydrocarbon fuel contains 8-28 carbon atoms of derived from the fractional distillation of crude oil between 200°C and 350°C at atmospheric pressure. The worldwide petroleum products consumption including diesel fuel showed an increased fuel price, transportation vehicles, depletion of petroleum resources are likely to cause their consumption to decline in classic industrial nations. Continuing accumulation of greenhouse gases is considered as another strong reason for the expansion in alternative fuels [2, 3]. Renewable raw material components (bio-fuel) blended with diesel fuel in low concentrations have been reported by various researchers [4, 5] Alternative fuels

should be environment friendly, fulfill energy demands and easily available at low cost [6, 7]. Employing ethanol as a fuel shows potential alternative to fossil fuel, contributing and substantially lowering the exhaust emissions by decreasing the non renewable fuel usage [8, 9].

Biomass includes a wide range of energy resources which comprises of energy crops, aquatic biomass, urban and forest waste materials. Bio-derived solvents create a center of attraction towards the energy demand in the recent years. [10, 11]. Several researchers [12, 13] reported that the addition of oxygenated compounds to diesel fuel improves the lubricity, stability, combustion efficiency (by increasing the Cetane number), miscibility and reduces the knock and ignition temperature of particulates. The use of oxygenated fuels such as ethanol or branched ethers resulted in the decrease of carbon dioxide emission from vehicles has been the focus for substantial consideration [14]. Ethanol has cleaner burning characteristics, which reduce environmental pollution, strengthen agricultural economy and is technically feasible for diesel engines. Ethanol was deemed to be the 'fuel of the future' as stated by Henry Ford. The advantage of ethanol is that it can be generated from renewable fuels like biomass [15, 16]. The characteristics of Di-butyl ether (DBE) are colorless liquid, immiscible, odor, flammability and toxic. DBE is known as diesel Cetane enhancer (Cetane number is 91-100) and is considered as a potential oxygenated fuel. The oxygenated fuels with oxygen components ranged between 12.3 and 53.3 wt%. The oxygenated fuel with high Cetane number resulted in lower particulate, smoke and NOx emission than a conventional fuel [17].

Polycyclic aromatic compounds (PACs) identifies the significant challenges for accurate quantitation which signifies the poly-cyclic aromatic hydrocarbons (PAHs) (nucleus and isomers) with aliphatic side chains containing up to a total of four saturated carbons [18]. However, the influence of poly nuclear aromatic hydrocarbons shows that the reduction in di- and tri-aromatics reduces the emissions of HC, PM, and NOx [19]. Fuel blend quality and monitoring need to be important, since the quality of natural products vary more vividly. The high quality is secured with broad quality assurance and prominence control measures. An extensive array of meticulous instrumental system can be utilized in the fuel property and its quality analysis [20, 21]. The octadecyl silanized

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Kalil Rahiman M, Centre for Thermal and Fluid Sciences, Bannari Amman Institute of Technology, Sathyamangalam 638401, Tamil Nadu, India. (E-mail: kalilrahimanm@bitsathy.ac.in)

Balakrishnan K, Technology Business Incubator, Bannari Amman Institute of Technology, Sathyamangalam 638401, Tamil Nadu, India.

Venkatachalam R, Department of Automobile Engineering, Institute of Road and Transport Technology, Erode 638 316, Tamil Nadu, India.

Murugappan S, School of Management studies, Bannari Amman Institute of Technology, Sathyamangalam 638401, Tamil Nadu, India.

Santhoshkumar S, Centre for Thermal and Fluid Sciences, Bannari Amman Institute of Technology, Sathyamangalam 638401, Tamil Nadu, India.

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silica gel and acetylated cellulose TLC plates be evidence for good selectivity in separation of aromatic hydrocarbons. The better resolution of these mixture results in less separation time using multiple development. The response ratio determines the peak homogeneity as an assessment of consistency in quantitative data [22, 23]. The HPTLC plays an imperative role in analyzing the mixture components. The major advantages are i) it requires very small sample size, ii) results in better resolution, iii) spot intensity and quantitative information, iv) accurate and precision control function and v) computer assisted performance. Invariably it endorses with superior separation efficiencies, lesser analysis time, lowers the amount of mobile phase with efficient data processing and acquisition [24, 25].

Investigations were carried out on the detection profiling of alternative fuel blends with suitable proportionate of diesel, DBE and ethanol. The samples were tested using HPTLC and the chromatographs were identified by the peaks resulted at 254 μm ultra violet (UV) absorbing light for polar compounds, aromatics and saturates. In addition, the experimental results obtained for different fuel blends were compared for their peak height, peak areas and retention factors. Further, the mean and standard deviation resulted with the performance measure and a one-way analysis of variance (ANOVA) test determines the chromatograph peaks in terms of absorption unit for different fuel blends compared with reference diesel fuel. From this feasibility study, it appears that there are meaningful similarities and differences in connection with diesel and the tri-fuel blends as a fingerprint data. When elution pattern and inertness are both evaluated, it can be observed that this study suggests that similar fuels such as diesel, DBE, ethanol and its blends could be the better options to be enhanced as a fuel.

2.0 EXPERIMENTATION

2.1 Materials and Methods

2.1.1. Samples

The fuel samples for various fuel blend combinations chosen as tri-fuel blends, i.e. diesel, ethanol and DBE. Diesel was purchased from the local petroleum sales outlet, ethanol as the product of distilled fermented sugarcane molasses wash was purchased from m/s Sakthi Sugars Ltd, India. The analytical grade di-butyl ether with 99% purity, n-hexane and n-butyl ethyl acetate were obtained from Sigma Aldrich.

2.2 Sample Preparation

The fuel samples of diesel, ethanol and di-butyl ether selected with different proportions and mixed thoroughly. Ethanol was added with DBE as a co-solvent in various proportions ranging from 0 to 100%, this in turn was blended with diesel at different proportions. The major concern with the use of ethanol as a bio-fuel found immiscible in diesel, resulting in fuel instability due to its phase separation. However, this is because of its difference in chemical structure and characteristics [26]. Conversely, instability rivets the chemical conversion of antecedent leads to higher molecular weight fraction which tends to limited fuel solubility with reactive compounds. The prevention of

this phase separation can be accomplished by adding DBE as the co-solvent, which performs as the conduit through molecular compatibility to create a homogenous blend. In the experiments, stability of the fuel blends mentioned above was determined by visual observation during a time period of 48 hours post mixing. Each such blend sample was found exhibiting different interfacial appearance and different drop size when allowed to disperse on a glass slide. From our laboratory observations, ethanol 25% and DBE 75% mixture, blending with any proportion of diesel found to be stable, miscible and no phase separation. Further, it was observed that increase in ethanol proportions resulted in phase separation and immiscibility. Diesel when varied from 0 to 100% blended with ethanol 25% and DBE 75% (v/v) were taken for analysis of fuels as tri-fuel blends in this study.

2.3 High Performance Thin Liquid Chromatography

High performance thin liquid chromatography was used to determine the mixture components and promotes higher separation efficiencies, shorter analysis time, lowers the amount of mobile phase, and efficient data acquisition and processing. The different fuel combinations were analyzed using HPTLC (CAMAG, Switzerland) as shown in Figure 1. The windows CAMAG automated TLC software (WinCATS) was used to process all the data facilitating function of the automatic thin layer chromatography (TLC) applicator and the post development processing of the TLC plates for interpretations. The hamilton syringe of 0 to 10 μl volume was selected for sample collection. The sample volume of 6 μl was filled in the syringe and the quantity required was 4 μl for dosing spot and the dosage speed was set as 150 nl/s. The syringe was cleaned every time with HPTLC grade methanol after each sample dosage. N₂ gas with moderate pressure was applied for injecting the syringe sample as spot layering. The chromatography was performed on TLC aluminium coated silica gel plate of size 10cm x 10cm (0.3cm, thickness). The sample spotted onto the TLC plate is analyzed with spot band width of 8 mm size and 8 number of samples preferred on a single plate covering 64 mm as track width. The TLC plate developed in a chamber containing eluting fluid, or mobile phase via capillary action, carrying the analytes along with it. The TLC plates were dipped appropriately in select solvent system of n-hexane and n-butyl ethyl acetate with a volume ratio of 92:8 (v/v) and a quantity of 20 mL filled in a twin trough automatic HPTLC developing chamber for duration of 20 min was used for separation of components in the samples. The TLC plates were then dried thoroughly using hand held mini air blower for 5 min. The spots developed on the TLC plates were detected and identified using HPTLC scanner for UV reflectivity and porosity. The developed TLC plate with bands for ethanol, diesel and DBE and its blends were shown in Figure 2. The scanning speed was 20 mm/s with a data resolution speed of 100 μm / step. The compounds present in the sample resulted with dark spots on the green background. The silica gel coated aluminum foil



TLC plates were scanned for chromatographic separation by using UV light with $\lambda = 254$ nm. Moreover, the corresponding peak for different samples obtained as 2D peak areas were taken up for qualitative analysis.

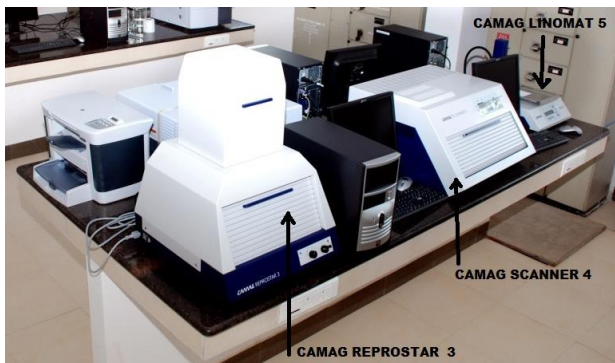


Fig. 1 Experimental set up of HPTLC.

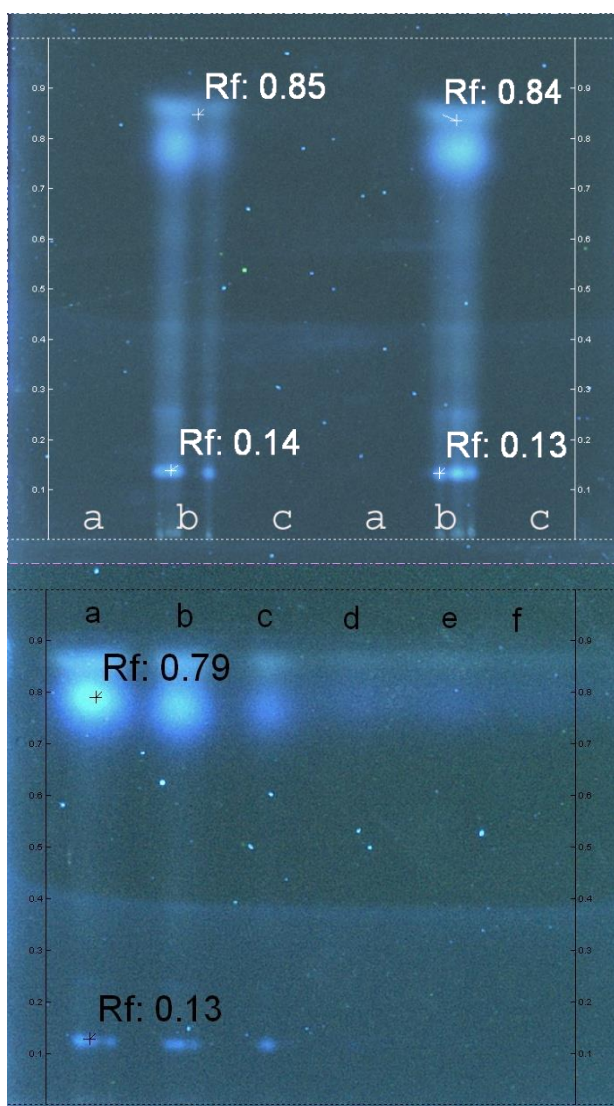


Fig. 2 Developed TLC plate for various fuel blends.

3.0 RESULTS AND DISCUSSION

Petroleum hydrocarbons can be generally separated into saturated, aromatic and polar compounds. Saturates found to be the major hydrocarbons in crude oils, which comprises of straight and branched chain structures (paraffin and naphthenes). A separation method indicating the profile of

blends helps in the prediction of suitability or adulteration or contamination which helps in analyzing and identifying the discrepancies within these blends [27]. Liquid chromatography (LC) is used extensively in characterizing petroleum distillates (ASTM D20073 for saturates, aromatics, and polar compounds) and diesel fuel (ASTM D25494 for saturates and aromatics). Peaks from the sample due to the solvents with the retention times were also identified and analyzed from the mass spectral analysis [28]. Based on the observations mentioned above, the investigations on qualitative analysis for the tri-fuel blends were carried out. These investigations necessitate the broader understanding of fuel blends in terms of qualitative profiles and helps in identifying the specific profile of the best miscible tri-fuel blend.

3.1 Detection and Visualization of Compounds using HPTLC

The composition of the prepared fuel blends was determined based on the TLC analyses. In order to verify the residues and to analyze the blended samples the HPTLC technique was employed [29]. Thin layer chromatography used silica gel coated aluminium plate and n- hexane and butyl ethyl acetate as solvent mix to acquire rapid class separation of saturates, aromatics, and polar compounds was dealt by American Society for Testing Materials (ASTM) D2007. This technique involves separating and detecting the components of mixtures as efficiently as possible and it is thus, capable of indicating a blend if used efficiently as fuel. Hydrocarbon type analysis had been a preferred choice for the characterization of fuel samples by separation of polar, aromatic and saturate compounds. Diesel fuel was typically composed of about 60 to 90 % saturated aliphatic and 10 to 40 % aromatics [30 - 32]. Since the change in the chemical group in tri-fuel blends as envisaged in our experimentation can determine the chemical properties and quality of the fuel blends. Hydrocarbon type analysis executed as finger print of tri-fuel blends through HPTLC attains significance. In our work, HPTLC had been applied to reveal appreciable differences in hydrocarbon types between various tri-fuel blends employed in this investigation. HPTLC finger printing could be completed in less than an hour for fuel blends. The HPTLC quantification of different blends signifies a quite realistic precision of 5 - 10% error for the triplicate measurement of fuel blends. However, the chromatogram signifies the Retention factor and its ability to resolve the analytes [33].

Diesel fuels comprises of high indices in absorption with the wave length of $0.4 \mu\text{m}$ and unleaded petrol in the range $0.66\text{-}1.215 \mu\text{m}$. Diesel fuel contains various types or classes of compounds, including paraffin's, naphthenic, olefins, and aromatics. The aromatics are cyclic hydrocarbon compounds, planar compounds and the chemical behavior which comprises of benzene, toluene, ethyl-benzene and xylene isomers. The carbon atoms are alternately double bonded with one another, e.g. benzene. The alkyl-substituted benzene compounds such as polycyclic aromatic compounds

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(PAC) and heterocyclic hydrocarbons contain PAC's, phenols, acids and alcohols [34, 35]. The compounds that contain hetero atoms such as sulfur, nitrogen, and oxygen are also present. Aromatics necessitate discussion because (i) they have a consequence on the combustion quality of the fuel, (ii) Typically, they are the only hydrocarbon type listed in diesel fuel specifications and (iii) Increased amounts of aromatics can have a negative impact on vehicle emissions. It is well known that an increase in the total aromatics content of diesel fuel have an adverse effect on the ignition quality, i.e., CN of the fuel [20, 36].

From the analysis, the peaks were sorted first by percent of the total peak area, calculated to identify the most common compounds for each fuel. At this point, identified compounds give the number of peaks and the percent of total peak area calculated. In this instance, the mixture was relatively easy to be defined by an upper and lower retention time, so these compounds were included in the analysis. In the TLC separations, the mobile phase is relatively non-polar. However, the polar compounds will strongly retained on the plate and non-polar compounds will move with the mobile phase. Solvents in general are chosen with the opposite polarity to the stationary phase, whereas the relative retentions can be easily predicted. Based on the relative polarity of compounds between stationary and mobile phases, they will be retained on TLC plates. More the polar compound, more it strongly retains on the stationary phase [37]. Retention factor (Rf) refers to the spot of the analytic band on the TLC plate. i.e. distance of the analytic band from initial spot with respect to the distance to the solvent. Absorbance Unit (AU) refers to the mathematical representation for the loss of incident radiant energy intensity (e.g., ultraviolet, visible, infrared) as it leave behind the sample. It relates the concentration solution of an analyte by its Beer's law: $A = \epsilon bC$, where ϵ is the absorptivity of analyte, b is the cell path, and C is the concentration of analyte [38].

The important parameters which influences the chromatographic separation within the mixture are partition coefficient, retention factor and capacity factor (the ratio of the retention time of the substance in the stationary phase to that in the mobile phase) of the individual constituent on the plate. The selection of mobile and stationary phase in the solutes and plate height decides the separation efficiency in addition to the individual constituent within a mixture [39]. The detection of chromatogram peaks using HPTLC scanner for different fuel blends is presented in Figure 3. In the experimental analysis of diesel fuel, the major peak identified was saturates. The retention factor for the same was found lying between 0.79 and 0.99. The peak height and peak areas for saturates were 536.6 AU and 35531 AU respectively. Polar compounds in the diesel resolved as 145.8 AU peak height and peak area 1383 AU. In case of ethanol, the Rf lies between 0.03 and 0.98 and the same for DBE, it was found lying between 0.05 and 0.97. The resolved peak areas corresponding to the polar, aromatics and saturate constituents for the different tri-fuel blends were determined. The diesel percentage decreased in various fuel blends resulted with the proportionate decrease in the corresponding peak heights and peak areas as depicted in Figure 4 (a-d) and Figure 5 (a-d) as compared with diesel.

In addition, the boiling point of components of the sample also plays a role in determining the retention time. Solvent system of n-hexane and n-butyl ethyl acetate with a volume ratio of 92:8 (v/v) was found to be resulting in detectable changes between various tri-fuel combinations tried in this study. Polarity is not a simple property, but rather a composite of different physical properties. Scanning UV detector allows the possibility of identifying chromatographic peaks either from complete spectra or absorbance ratios at several wavelengths. The number of separated peaks in a random chromatogram is a function of the total peak capacity per unit time. Therefore, extremely high values of the peak capacity are required for the separation of complex samples. The most important influence on the retention of compounds will be their polarity relative to the stationary and mobile phases. The more polar a compound is, the more strongly it will be retained by the stationary phase [40, 41]. Saturates resolved as the prominent peak in all the chromatograms for tri-fuel blends with diesel proportion ranging from D20 BE80 to D90 BE10. Gradual decrease in diesel quantity in various tri-fuel blends leads to corresponding decrease in peak heights and peak areas of saturates in the tri-fuel blend peak profiles. The decrease in peak area was more prominent between D50 BE50 and D40 BE60. As the diesel proportion decreased for various tri-fuel blends, there was a decrease in peak areas of aromatics and polar too, but the same remain less prominent, when compared with the drop in peak area of saturates between different tri-fuel blends. It was noticed that the corresponding polar compounds attained slight prominence by its peak height and peak area found to be the same for the last three blends (D40 BE60 to D20 BE80). Addition of DBE and ethanol in increasing proportion could have added to the steady state of polar fractions in the last three fuel blends as indicated by the peak areas. Table 1 indicates the combination of tri-fuel blends and its peak area quantification. The peak area of saturates varies between 85.68 to 33.53% for different fuel blends. As the diesel proportion in the tri-fuel blends decreases, it is found that saturates present in the fuel blend decreases up to be 60.77%. The peak area percentage of polar is 3.32% for diesel and attains the maximum of 23.19% for D20 BE80 blend. Whereas there is an increase in 87.7% polar and 76% for aromatics as compared to diesel.

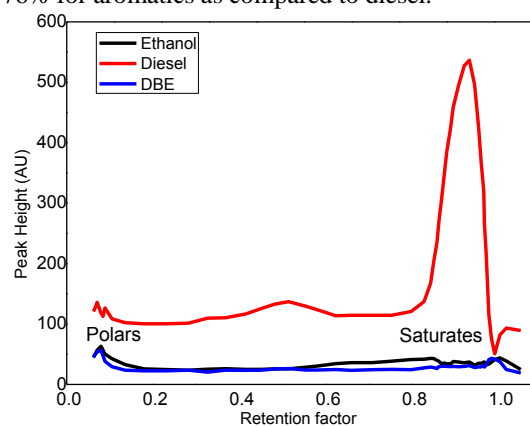


Fig.3 Chromatogram of diesel, ethanol and dibutyl ether.

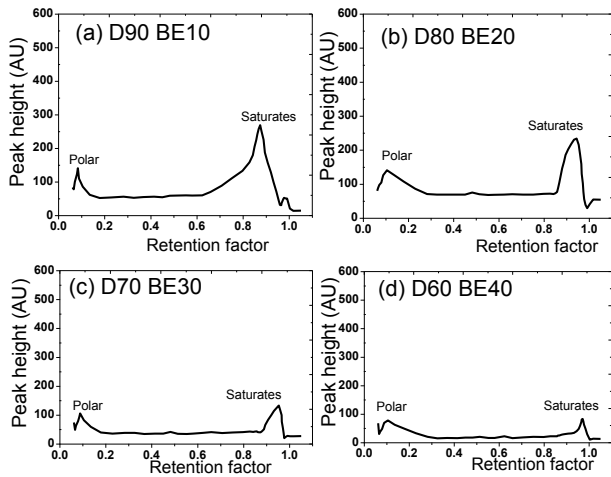


Fig. 4 Chromatogram of D90 BE10 to D60 BE40 fuel blends.

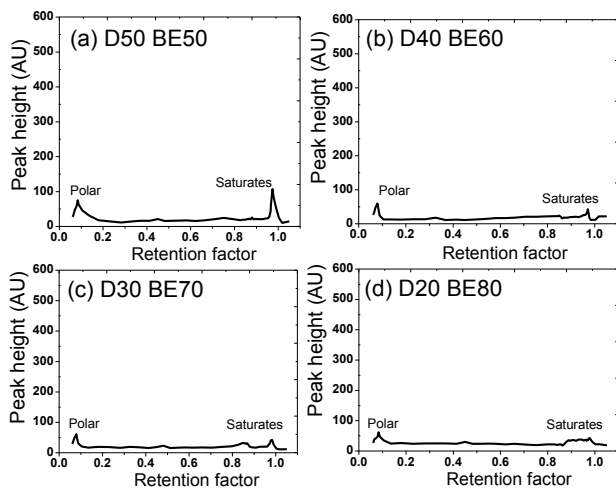


Fig. 5 Chromatogram of D50 BE50 to D20 BE80 fuel blends.

Table 1 Combination of tri-fuel blends and its peak area quantification.

Sl. No.	Fuel blend	Tri-fuel blends in volume percentage	Peak area percentage	
			Polar	Saturates
1.	D	Base diesel	3.32	85.48
2.	D90 BE10	Diesel 90 with di-butyl ether 7.5 and ethanol 2.5	2.84	83.92
3.	D80 BE20	Diesel 80 with di-butyl ether 15 and ethanol 5	3.32	79.82
4.	D70 BE30	Diesel 70 with di-butyl ether 22.5 and ethanol 7.5	3.32	77.96
5.	D60 BE40	Diesel 60 with di-butyl ether 30 and ethanol 10	3.73	77.66
6.	D50 BE50	Diesel 50 with di-butyl ether 37.5 and ethanol 12.5	6.11	76.29
7.	D40	Diesel 40 with	13.67	42.05

	BE60	di-butyl ether 45 and ethanol 15		
8.	D30 BE70	Diesel 30 with di-butyl ether 52.5 and ethanol 17.5	19.78	39.52
9.	D20 BE80	Diesel 20 with di-butyl ether 60 and ethanol 20	23.19	33.53

D - Base diesel, B - Di-butyl ether, E - Ethanol

3.1.1. Statistical Analysis

The Statistical Package for Social Science (SPSS) software package was used for HPTLC data analysis with version 13.0 to determine whether the peak height in terms of absorption units for ten different fuel and its blends were statistically different from each other. Quantification experiments of each HPTLC test were also viewed as representing the performance and an alternative instrumental technique for the considered samples. The analyte quantification method employed by performing an appropriate statistical analysis. A one-way analysis of variance (ANOVA) is the most efficient parametric method available for the analysis of data from experiments. The one-way ANOVA test was performed to check the formulated null and alternate hypothesis since the normal distribution of treatment group means and homogeneity of variances between means were satisfied [42]. The descriptive statistics of peak height for various fuel blends such as mean, standard deviation and co-efficient of variance were computed and compared with diesel for its performance measure is shown in Table 2. Similarly, by using the fuel compounds as independent variables in identifying the potential significant differences of polar, aromatics and saturate constituents between the fuel blends. The diesel chromatogram peak height attains the mean value of 201.40 AU, standard deviation of 138.42 AU and 0.69 AU as co-efficient of variance. Ethanol and di-butyl ether resulted in festering on the mean, standard deviation and co-efficient of variance as compared with diesel. The averages of mean, standard deviation and co-efficient of variance values of different fuel and its blends were 60.77, 73.07 and 1.2 respectively. Diesel shows the maximum value among the tested blends. From the analysis, the mean and standard deviation of D90 BE10 blend had been reduced up to 50% for diesel. However, it had significant reduction for ethanol, di-butyl ether and different blends when compared with standard diesel. The mean value for peak height in terms of absorption unit is found declining when the percentage of di-butyl ether in the blend was increased. Similarly for the standard deviation follows the same trend.

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Table 2 Descriptive Statistics of peak height for various fuel blends

Fuel blend	Mean	Standard deviation	Co-efficient of variance
D	201.40	138.42	0.69
D90 BE10	99.35	70.14	0.71
D80 BE20	104.07	52.88	0.51
D70 BE30	55.12	29.10	0.53
D60 BE40	35.74	21.05	0.59
D50 BE50	31.22	22.96	0.74
D40 BE60	21.10	10.02	0.47
D30 BE70	23.90	10.00	0.42
D20 BE80	29.58	9.19	0.31
DBE	30.53	8.63	0.28
Ethanol	36.43	8.77	0.24
Total	60.77	73.07	1.20

3.1.2 Level of Significance

The chromatogram resulted from the HPTLC scanned results were analyzed for its significance. A one-way ANOVA test was performed to determine the chromatograph peaks in terms of absorption units. The preferred level of significance is identified as 5% and the confidence level is 95%. "F" statistics was used as a test statistics for the suggested analysis. The précis of one way ANOVA resulted with sum of squares, degrees of freedom, mean square, F test and P value is shown in Table 3. The values show a dispersion or distribution about the mean, and these distributions need to be characterized within the range of acceptable control values. The source consists of treatment and error values, in which the mean square values were 150422 and 2648. The one way ANOVA results of the peak height in absorption unit as a testing variable, gave evidence to the results for the various blends as a factor. The significance level found to be less than 0.05 and the significant difference between the groups with a confidence level is 95%. Therefore, the rejection of null hypothesis exits and accepts the alternate hypothesis. This result clearly states that at least one of the blends is significantly different from the other blend. In order to explore further to reveal which were the blends significantly different from each other, Tukey simultaneous comparison t-values and probability values were calculated. The differences exist among the mean. However, the one-way Analysis of variance (ANOVA) procedure provides multiple

comparisons of mean in order to identify the dissimilarity. The mean value of each peak height with a 0.05 significance level for different fuel and its blends were compared by one-way ANOVA and post hoc Tukey's multiple comparison tests. A significant p-value results from a one way ANOVA test conclude that the differences considered to be significant, if $p < 0.05$. Consequently, the alternate hypothesis has been accepted.

Table 3 One way analysis

Source	Sum of squares	Degrees of freedom	Mean square	F test	P value
Treatment	1,504,219	10	150,422	56.81	9.19E-78
Error	1,427,250	539	2,648	-	-
Total	2,931,470	549	-	-	-

Null Hypothesis (H0): The absorption units of various blends formed using diesel, ethanol, di-butyl ether are not significantly different.

Null Hypothesis (H1): The absorption units of various blends formed using diesel, ethanol, di-butyl ether are significantly different.

In addition, the Tukey's honest significant difference (HSD) post hoc similarity technique be employed for the analysis of significant differences between mean and the principal component analysis (PCA) which resulted in association of elemental components [43, 44]. This result leads to the further analysis of Tukey simultaneous comparison Test. To eliminate the ambiguity of the test results, it was necessary to compute the Tukey's HSD to conduct post hoc tests. The studentized - range values was below and there was no difference at a 5% level of significance in their respective absorption unit. As a result, the null hypothesis rejects and accepts the alternative hypothesis. However, the one way ANOVA analysis with 5% significance level does not affect the absorption unit and also indicates the statistical differences between the pair of groups. Post Hoc test determines the specific pair/pairs, which express the discrepancy. From the test results of Tukey's simultaneous comparison probability of t-value as shown in Table 4, the statistical significance for diesel, ethanol, di-butyl ether and various fuel combinations were analyzed. There was a significant effect on peak height in AU and the results were $F(10,539) = 56.81$, $MSE = 2648$ and $p = 9.19E-78$. Subsequent analysis using Tukey's HSD indicated that the absorption units were significantly different. From the analysis, it is clear that the diesel resulted as the major dominant factor for the fuel blends D90 BE10, D80 BE20 and D70 BE30. In addition, the blends of D60 BE40 to D20 BE80 resulted with ethanol as the dominated factor. The blend D90 BE10 to D20 BE80 also had no statistical significance difference except D70 BE30 among the test blends.

Table 4 Tukey’s simultaneous comparison probability of t-value

Blend	Mean Value	D40 BE60	D30 BE70	D20 BE80	DBE	D50 BE50	D60 BE40	Ethano l	D70 BE30	D90 BE10	D80 BE20
D40 BE60	21.10										
D30 BE70	23.90	0.27 0.785									
D20 BE80	29.58	0.82 0.410	0.55 0.581								
DBE	30.53	0.92 0.359	0.64 0.519	0.09 0.926							
D50 BE50	31.22	0.98 0.326	0.71 0.477	0.16 0.874	0.07 0.946						
D60 BE40	35.74	1.42 0.155	1.15 0.250	0.60 0.550	0.51 0.613	0.440 0.660					
Ethano l	36.43	1.49 0.136	1.22 0.224	0.67 0.506	0.57 0.566	0.51 0.612	0.07 0.946				
D70 BE30	55.12	3.31 0.001	3.03 0.002	2.48 0.013	2.39 0.017	2.32 0.020	1.88 0.060	1.820 0.070			
D90 BE10	99.35	7.60 1.29 E-13	7.33 8.42 E-13	6.78 3.19 E-11	6.69 5.71 E-11	6.62 8.68 E-11	6.18 1.26 E-09	6.11 1.87 E-09	4.30 2.04 E-05		
D80 BE20	104.0	8.06 4.88 E-15	7.79 3.48 E-14	7.24 1.58 E-12	7.15 2.93 E-12	7.08 4.55 E-12	6.64 7.69 E-11	6.57 1.17 E-10	4.76 2.53 E-06	0.46 0.646	
Diesel	201.4	17.52 1.01 E-54	17.25 2.11 E-53	16.69 9.68 E-51	16.6 2.67 E-50	16.54 5.56 E-50	16.10 6.85 E-48	16.0 1.43E-47	14.213 61 E-39	9.92 2.12 E-21	9.46 9.68 E-20

The box and whisker distribution plot for various combinations of fuel blend is shown in Fig. 6 and Fig. 7. From the distribution plot, it was evident that the blend D90BE10, D80BE20 were not significantly different from each other but they were different from diesel. However, diesel was considered as the reference fuel and the blends were evaluated. From the box and whisker plot distribution for D70 BE30 to D20 BE80 fuel blends, it was clear that the di-butyl ether was significantly different from ethanol and obviously ethanol was different from D20BE80, D40BE60, D30BE70, BE60, D50BE50, D60BE40, D70BE30 blend. Moreover, di-butyl ether was significantly different from D40BE60, D30BE70, D50BE50, D70BE30 and it was not significantly different from D20BE80, D60BE40 blend. The peak profile comparison for various fuel blends were plotted in the Fig. 8 and the overall mean value in terms of absorption unit was found to be 60.77. The blend D90 BE10 and D80 BE20’s mean values were more than the grand mean value and other blend’s mean values were less than the grand mean. The Post hoc analysis was carried out for further analysis and the resulted Tukey simultaneous comparison probabilities for pair wise t-tests values were also tabulated. The Tukey simultaneous comparison t-values, in which the mean peak height absorption unit values were distributed in the ascending order from 21.10 AU (D40BE60) to 104 AU (D80BE20) with reference to

diesel fuel. The critical values for experimental wise error rate lies between 3.28 for the significance value of 5% to 3.80 for significance value of 1%. The mean values compared between various fuel blends ranges between 0.09 (DBE and D20 BE80) to 17.52 (diesel and D40BE60) and the consequences for the various fuel blends were tabulated.

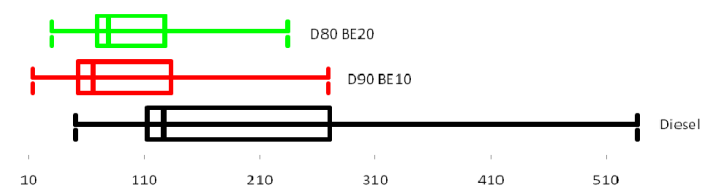


Fig. 6 – Box and whisker plot distribution of D90BE10 to D80BE20 fuel blends.

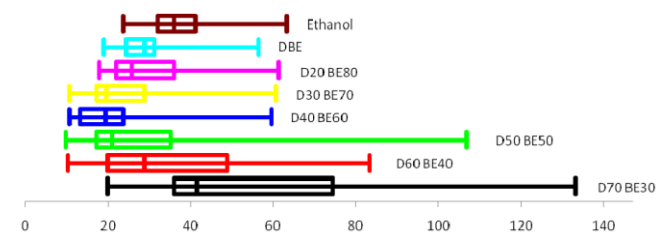


Fig. 7 Box-and-whisker plot distribution of D70 BE30 to D20 BE80 fuel blends.



STUDY OF DIESEL WITH OXYGENATED FUEL BLENDS FOR ITS PROMINENCE USING HIGH PERFORMANCE THIN LAYER CHROMATOGRAPHY

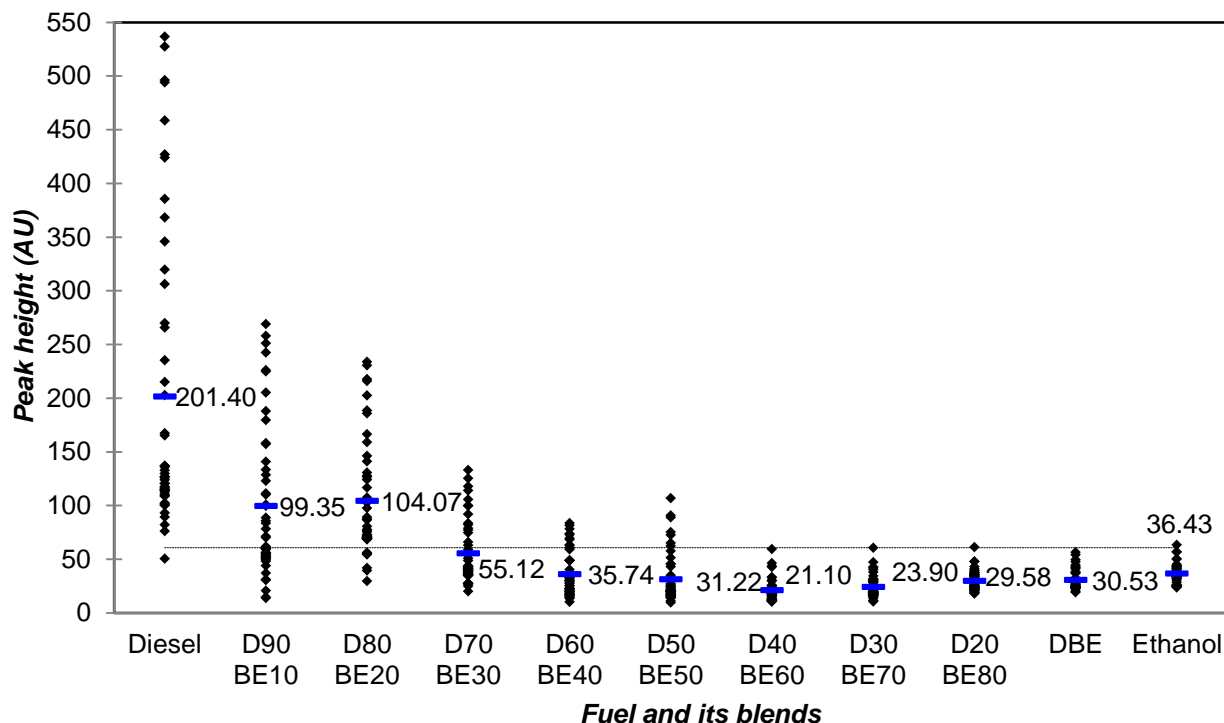


Fig. 8 Peak profile comparison for various fuel blends.

4.0 CONCLUSION

The HPTLC method was a rapid and precise technique for determining the fundamental analysis of a substance with its qualitative chromatographic behavior. The tri-fuel blends of diesel, di-butyl ether and ethanol were analyzed for the peak homogeneity through identification of chromatographic peaks. From the qualitative analysis, the compounds such as polar, aromatics and saturate presented in various tri-fuel blends represented as the diverse retention times, absorption units, peak heights and peak areas were resolved and compared with that of the diesel. The reference diesel resulted with maximum $R_f = 0.90$, peak height 536.6 AU and peak area 35531 AU for saturates and peak height 145.8 AU and peak area 1383 AU for polar compounds. Further, the mean and standard deviation were computed for the performance measure and a one-way ANOVA test determines the chromatograph peaks in terms of absorption unit for different fuel blends as compared with diesel fuel. The comparison of experimental as well as one-way ANOVA test results has proven precisely in separation of multifaceted mixtures which challenges the separation inadequacies.

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REFERENCES

1. Siamak, A.; Hamid, O.; Dong-Shik K., A review on synthesis of alkoxy methyl furfural, a biofuel candidate. *Renewable and Sustainable Energy Reviews*, 2015; 71: 908–26.
2. Agarwal, D.; Agarwal, A.K., Performance and emissions characteristics of Jatropha oil (preheated and blends) in a direct injection compression ignition engine. *Applied Thermal Engineering*, 2007; 27 (13): 2314-23.
3. Subramaniam, D.; Murugesan, A.; Avinash, A.; Kumaravel, A., Bio-diesel production and its engine characteristics—An

expatiate view. *Renewable Sustainable Energy Reviews*, 2013; 22: 361–70.

4. Chikwe, T.N.; Osuji L.C.; Ogali R.E.; Okoye, I.P., Effects of Petroleum Condensate/ Diesel Mixture on Diesel Engines Research. *Journal of Recent Sciences*, 2013; 2 (1):1-8.
5. Sunil, K.M., Opportunities, recent trends and challenges of integrated bio-refinery: Part I. *Renewable and Sustainable Energy Reviews*, 2015; 43: 1427–45.
6. Rahiman, M.K.; Venkatachalam, R.; Nedunchezian, N., Experimental investigation on thermal barrier coated diesel engine fueled with diesel-biodiesel-ethanol-diethyl ether blends. *Journal Renewable Sustainable Energy*, 2013; 5 : 033114.
7. Yoon, S.H., Park, S.H., Kim, M.Y.; Lee, C.S., Experimental investigation on the fuel properties of biodiesel and its blends at various temperatures. *Energy and Fuels*, 2008; 27: 56 - 65.
8. Nigam, P.S.; Singh, A., Production of liquid bio-fuels from renewable resources. *Progressive Energy Combustion Science*, 2011; 37 (1): 52 - 68.
9. Agarwal, A.K., Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. *Progressive Energy Combustion Science*, 2007; 33 (3) : 233 - 71.
10. Li, Z.; Smith, K.H.; Stevens, G.W., The use of environmentally sustainable bio-derived solvents in solvent extraction applications – a review. *Chinese Journal of Chemical Engineering*, 2016; 24, (2): 215-20.
11. Zhang, Z.; Hu, S.; Chen, D.; Zhu, B, An analysis of an ethanol-based, whole-crop refinery system in China. *Chinese Journal of Chemical Engineering*, 2016; 24 (11) :1609-18.
12. Calero, J.; Luna, D.; Sancho, E.D.; Luna, C.; Bautista, F.M.; Romero, A.A.; Posadillo, A.; Berbel, J.; Escamilla, C.V., An overview on glycerol-free processes for the production of renewable liquid biofuels, applicable in diesel engines. *Renewable and Sustainable Energy Reviews*, 2015; 42: 1437–52.
13. Wang, Y.; Genbao, L.; Zhu, W.; Zhou, L., Study on the application of DME/diesel blends in a diesel engine. *Fuel Processing Technology*, 2008; 89 (12): 1272-80.
14. Ribeiro, N.M.; Pinto, A.C.; Quintella, C.M.; Rocha, G.O.; Teixeira, L.S.G.; Guarieiro, L.L. N.; Rangel, M. D. C.; Veloso, M.C.C.; Rezende, M.J.C.; Cruz, R.S.D.; Oliveira, A.M.D.; Torres, E.A.; Andrade, J.B.D., The role of additives for diesel and diesel blended (ethanol or biodiesel) fuels: A review. *Energy and Fuels*, 2007; 21 (4) : 2433 - 45.



15. Kravanja, P.; Modarresi, A.; Fried, A., Heat integration of biochemical ethanol production from straw -A case study, *Applied Energy*, 2013; 102 (1): 32-43.
16. Souza, S.P.; Seabra, J.E.A., Environmental benefits of the integrated production of ethanol and biodiesel, *Applied Energy*, 2013; 102 (1): 5-12.
17. Arteconi, A.; Mazzarini, A.; Nicola, G.D., Emissions from ethers and organic carbonate fuel additives: A Review. *Water Air Soil Pollution*, 2011; 221: 405-23.
18. William, B.S.; Keith J. P.; Kevin, E.P., Matthew. S.L., Determination of polycyclic aromatic hydrocarbons, ibenzothiophene, and alkylated homologs in the lichen *Hypogymnia physodes* by gas Chromatography using single quadrupole mass spectrometry and time-of-flight mass spectrometry, *Journal of Chromatography A*, 2017; 1492: 106–16.
19. <http://www.epa.gov/ttn/chief/trends/index.htm>.
20. Totten, G.E.; Westbrook, S.R.; Shah R.J., *Fuels and Lubricants Handbook : Technology, Properties, Performance, and Testing*, ASTM International, West Conshohocken 2003.
21. Furong, L.; Yurong W.; Junhao C.; Wang S.; Jingsong, Z.; Zhongyang L., Characterization of Pyrolytic Lignins with different activities obtained from bio-oil. *Chinese Journal of Chemical Engineering*, 2017; 25 (3): 324-29.
22. Butler, H.T.; Coddens, M.E.; Khalil, S.; Poole C.F., Determination of polycyclic aromatic hydrocarbons in environmental samples by high performance thin layer chromatography and fluorescence scanning densitometry. *Journal of Chromatograph Science*, 1965; 23: 200-07.
23. Wang, H.; Chen, L.; Tang, X.; Jia, Y.; Li, G.; Sun. X.; Wen. A., Synthesis and characterization of novel polar-embedded silica stationary phases for use in reversed-phase high-performance liquid chromatography. *Journal of Chromatography A*, 2013; 1271 (1): 153-62.
24. Chattopadhyay, S.; Das. S.; Sen. R., Rapid and precise estimation of biodiesel by high performance thin layer chromatography. *Applied Energy*, 2011; 88 (12): 5188 - 92.
25. Eberlin, L.S.; Abdelnur, P.V.; Passero, A.; Desa, G.F.; Daroda, R.J.; Desouza, V., *Analyst*, 2009; 134: 1652 - 57.
26. Kwanchareon, P.; Luengnaruemitchai, A.; Samai. J., Solubility of a diesel–biodiesel – ethanol blend, its fuel properties, and its emission characteristics from diesel engine. *Fuel*, 2007; 86 (7–8): 1053–61.
27. Vicente, L.C.; Vela, J.; Luis, M.; Ana, C.F., Suitability of Thin-Layer Chromatography-Flame Ionization Detection with Regard to Quantitative Characterization of Different Fossil Fuel Products. I. FID Performances and Response of Pure Compounds Related to Fossil Fuel Products. *Journal of Chromatographic Science*, 1998; 36: 479-86.
28. Knothe, G., Analytical methods used in the production and fuel quality assessment of biodiesel. *American Society Agricultural Engineers*, 2001; 44 (1): 193 - 200.
29. Livia, S. E.; Patricia, V.A.; Alan, P.; Gilberto F. de Sa.; Romeu, J. D.; Vanderlea de Souza and Marcos, N.E., Analysis of biodiesel and biodiesel–petro diesel blends by high performance thin layer chromatography combined with easy ambient sonic-spray ionization mass spectrometry, *Analyst*, 2009; 134: 1652–57.
30. Barman, B.N., Hydrocarbon-Type Analysis of Base Oils and Other Heavy Distillates by Thin-Layer Chromatography with Flame-Ionization Detection and by the Clay–Gel Method, *Journal of Chromatography Science*, 1996; 34 (1): 219 - 25.
31. Barman, B.N.; Cebolla, V.L.; and Membrado, L., Chromatographic Techniques for Petroleum and Related Products. *Critical Reviews in Analytical Chemistry*, 2000; 30 (2-3): 75 - 120.
32. Yasin, G.; Bhangar, M.I.; Ansari, T.M.; Naqvi, S.M.S.R.; Talpur, F.N., Quality of commercial high speed diesel and its environmental impact. *Journal of Petroleum Technology and Alternative Fuels*, 2012; 3: 29-35.
33. Ioana, A.S.; Dorina, C.; Costel, S., High sensitive and selective HPTLC method assisted by digital image processing for simultaneous determination of catecholamines and related drugs, 2013.
34. Dombrovsky, L.A.; Sazhin, S.S.; Mikhalovsky, S.V.; Wood, R.; Heikal, M.R., Spectral properties of diesel fuel droplets. *Fuel*, 2003; 82: 15–22.
35. Agaev, S.G.; Yakovlev, N.S.; Gulyaev, S.V., ‘Improvement of low-temperature properties of diesel fuels’, *Chemistry of fossil fuels, Russian Journal of Applied Chemistry* 2007; 80: 488-95.
36. Speight, J.G., *Hand book of petroleum product analysis*. John Wiley & sons, Inc. 2002.
37. Dorina, C.; Ioana, A.S.; Costel, S., Thin-layer chromatography—an image-processing method for the determination of acidic catecholamine metabolites, 2014; 37: 2675–81.
38. Srivastava, M.M.; Variyar, P.S.; Chatterjee, S.; Sharma, A., High performance thin layer chromatography, Springer, New York, 2011.
39. Ioana, A.S.; Dorina, C.; Costel, S., High sensitive and selective HPTLC method assisted by digital image processing for simultaneous determination of catecholamines and related drugs, 2013.
40. Eberlin, L.S.; Abdelnur, P.V.; Passero, A.; Desa, G.F.; Daroda, R.J.; Desouza, V., Analysis of biodiesel and biodiesel–petrodiesel blends by high performance thin layer chromatography combined with easy ambient sonic-spray ionization mass spectrometry. *Analyst* 2009; 134: 1652 - 57.
41. Guido, C.; Beatrice, C.; Napolitano, P., Application of bioethanol/ RME/ diesel blend in a Euro5 automotive diesel engine: Potentiality of closed loop combustion control technology. *Applied Energy*, 2013; 102: 13–23.
42. Pedro, A.; Livar, F., Statistical power and analytical quantification *Journal of Chromatography B*, 2007; 847: 305–08.
43. Marian, K.; Joanna, G.; Tadeusz, G.; Rafal, K., Optimized conditions for hydrocarbon group type analysis of base oils by thin-layer chromatography-flame ionisation detection, *Journal of Chromatography A*, 2003; 991: 255–66.
44. Toussaint, B.; Grazia, P.; Bachisio, A.; Nathalie, C.; Pierpaolo, D.; Analysis and origins of volatile organic compounds smoke from ligno-cellulosic fuels. *Journal of Analytical and Applied Pyrolysis*, 2010; 89: 60–65.