A review on the Chromatographic Analysis of Biodiesel

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ABSTRACT
Chromatographic analysis have been used in many ways in quantifying and identifying individual components in biodiesel samples, such as the identification of contaminants and Fatty acids methyl esters. Chromatography is vital in modern quality control analysis of biodiesel hence, its wide application in the study of biodiesel composition. These relevant studies have contributed immensely to the rapid growth of biodiesel production and analysis, with modern techniques providing better results. In this paper, several past research work on chromatographic analysis of Biodiesel from different oils have been reviewed.

Keywords: Chromatography, Biodiesel, transesterification, acidic catalyst, Base catalyst, Fatty acids methyl esters, Biofuel.

1.0 Introduction

1.1 Biodiesel and its synthesis

Biodiesel has become more attractive because of its benefits and with increase in petroleum fuel prices and concern for petroleum availability, there are so many renewed interests in using various vegetable based oils for the production of biodiesels. Biodiesel was by far the most abundant fuel in Europe and represent 82% of the biofuel produced in 2003 (European Biodiesel Board [EBB], 2007).

The term biodiesel refers to fatty acids mono alkyl esters which are produced from renewable feed stock, such as vegetable oils with glycerin as the by product. Biodiesel production involves the transesterification of triglycerides with methanol (Canakci and Sanli, 2008. Ma and milford, 1999). Transesterification reduces the high viscosity of the oils to a value closer to that of petrol diesel. Biodiesel can be used in its pure state alone (B100), or more commonly as (B5) or (B20) blend with petroleum diesel. The advantage of biodiesel is the biodegradability, renewability, improved nontoxic emission from exhaust and high lubricating properties of engine parts which it possesses (Lotero, 2005). Biodiesel can be produced from inorganic acids, such as: (HCL or H_2SO_4) (Liu, 2007. Ataya, 2007), alkali (NaOH and KOH) (Leung and Guo, 2006. Dias, Maria and Manuel,

2008) and free/immobilized lipase (Dizge and Keshkinler, 2009). Biodiesel production from alkali catalyst such as sodium hydroxide and potassium hydroxide require anhydrous condition because the presence of water leads to the formation of soap, which reduces the productivity and causes difficulty during the separation of product at the end of the process (Ma and Milford, 1999). The above problem can be prevented by the use of acidic catalyst such as sulfuric acids and hydrochloric acid. In recent times, the use of particularly immobilized lipase as catalyst for alcoholysis of oils was investigated. However, enzymes that are used as catalyst are not abundant in the production of biodiesel because enzymes are expensive and the regeneration of enzymes is limited (Salis, Pinna, Monduzzi and Solinos, 2005. Wu, Du, Zeng and Liu, 2004). Various oils serve as raw materials for biodiesel production and they include rapeseed, soya bean, palm, sunflower oil etc. (Demirbas, 2003. Jothiramalingam and Wang 2009).

1.2 Chromatography

Chromatography is the study of the separation of mixtures and is often used to identify unknown components in a mixture. In chromatography, the components in a mixture move along a stationary phase. Each component in a mixture retains its own properties and thus moves at a rate determined by its characteristics. Separation of the individual component in a mixture is achieved by passing the mixture to be separated into the mobile phase through the stationary phase, whereby the rate of migration is used for the separation. The flow rate (RF) is the rate of flow of the mobile phase across the separation medium, measured in ml/min or µl/min (Still, Khan and Mitra, 1978).

There are different types of chromatographic techniques, but the most known are; Column Planer Chromatography, Gas Chromatography (GC), High performance liquid chromatography (HPLC), Ion exchange chromatography, Super critical fluid chromatography, Size exclusion chromatography (SEC). There are other chromatographic methods that have been used, but those outlined above were the most commonly used techniques. Others are: Reverse phase column chromatography, Two-dimensional chromatography, Simulated moving bed chromatography, Pyrolysis gas chromatography etc.

2.0 Literature Review

Sagiroglu, Sebnem, Hakki, Hatice and Neslihan (2010), researched on the comparison of biodiesel production from different vegetable oil using acidic catalysis. The productivity percentages were determined based on the ratio of ester to oil content (W/W). The productivities for all the oils were found to be about 80% and about 90% at 25^{o}C and 100^{o}C respectively. The result they collected shows that biodiesel yield is dependent on temperature for some oils, but no significant difference was found among all of the oils types on biodiesel productivities. They performed a qualitative analysis of biodiesel yield by thin layer chromatography. For the quantitative analysis of methyl esters in biodiesel, they performed a gas chromatographic analysis. From their results, they observed that hazelnut, olive and canola oil contained higher percentages (78.0, 74.0 and 63.05 respectively) of oleic acids when compared to the others, and the safflower, waste sunflower, sunflower, corn and soya bean oil contained higher percentages (72.3,59.6,58.5, 58.4 and 56.2

respectively) of linoleic acid. The fatty acid content of the analyzed oils were generally unsaturated (18.1 and 18.2) fatty acids rich according to GC analysis (Sagiroglu et al, 2010). Figure 1 illustrates the result of their thin layer chromatography of biodiesels from various vegetable oils.

Eberlin, Patricia, Alan, Gilberto, Romeu, Vanderlea, and Marcos (2009), in their worked on analysis of biodiesel and biodiesel-petrol-diesel blends by high performance thin layer chromatography, combined high performance thin layer chromatography with on-spot detection and characterization through easy ambient sonic spray ionization mass spectrometry (EASI-MS) for the analysis of biodiesel (B100) and biodiesel petrol-diesel blends. High performance thin layer chromatography provides chromatographic resolution of the major components in fuels while the easy ambient sonic spray mass spectrometry allows on spot characterization which was performed directly on surface at ambient conditions. Constituents (M) are detected by EASI-MS as a one component one ion fashion as either $[M+Na]^+$ or $\{M+H]^+$. For both B100 and biodiesel blend samples typical profile of fatty acid methyl ester detected as $[FAME+Na]^+$ ions allow biodiesels typification. The spectrum of the petrol-diesel spots displays a homologous series of protonated alkyl pyridine which were characteristics for petrol fuel (natural markers), the spectrum for residual or admixture oil spot was characterized by sodiated triglycerides $[TAG+Na]^+$ (Eberlin et al, 2009). Their results showing the application of HPTLC to analyze B100 and biodiesel blend samples and its combination with EASI-Ms for on spot characterization and quality control is figures 2 and 3.

Furthermore, Fontana, Zagonel, Vochiatto, Costa, Laurindo and Pelison (2009), studied on the simple TLC-screening of Acylglycerol level in biodiesel as an alternative to gas chromatography determination, they achieved this by staining thin layer chromatography with hot acidic p-anisaldehyde which was a fast and low cost technique to monitor main lipid contaminants such as triacylglycerols, diacylglycerol and monoacylglycerol in biodiesels (Fontana et al, 2009). The acylglycerols were detected by the proposed planer chromatographic analysis method and thin layer chromatography was confirmed with data from gas chromatography of methyl esters of soya oil. The result of their work is given in figures 4 and 5

Ragonese,Tranchida, Sciarrone and Mondello (2009), worked on the conventional and fast chromatographic analysis of biodiesel blend using ionic liquid stationary phase concentrated on the gas chromatographic determination of fatty acids methyl esters in diesel blend by an ionic liquid stationary phase (Ragonese et al, 2009). The result they collected from soya beans biodiesel (B20) carried out on an SLB-IL 100 convectional column were compared with polyethyleneglycol column of equivalent dimension. Figures 6-8 show the chromatograms of soya beans biodiesel blends they obtained.

Seeley, Libby and Mc Curry (2007), performed an analysis of biodiesel and petrol-diesel blends with comprehensive two-dimensional gas chromatography. They found that petroleum hydrocarbon chromatograms intensities are lower than that of the fatty acids methyl ester chromatograms. This allows fatty acids methyl esters to be quantified by integration, the method used was calibrated by analyzing soybean biodiesel standard mixture in petroleum diesel with different concentrations from 1 to 20% v/v. The resulting calibration curve produced a perfect linear curve, which was used to

determine the concentration of biodiesel/petroleum diesel blend obtained from a retailer in which excellent precision and accuracy were obtained (Seeley et al, 2007).

Tiyapongpattana, Wilairat and Marriott (2008), studied the development of a comprehensive 2-D gas chromatography flame ionization detection method for biodiesel fuels for the analysis of fatty acid methyl esters in both biodiesel and biodiesel blend. Separation of the fatty acids methyl esters was based on the individual boiling point of the components in the first dimension and polarity in the second dimension by using a BPX5/BP20 column set to provide a measure of 'orthogonality' in the 2-D space and the final method contains eight cryotrap temperature settings. The developed two dimensional gas chromatography method was able to characterize and identify both biodiesel B100 and B5 fatty acid methyl esters components in vegetable oils with high precision, the fatty acids methyl esters were able to be analyzed with carbon numbers C4-C24 which was used to characterize various types of biodiesel, making it possible to differentiate the type and origin of fatty acid methyl esters used in the biodiesel samples (Tiyapongpattana et al, 2008).

Further work by Ferreira, Santos, Souza and Polito (2008), in their paper on analysis on the emission of volatile organic compounds from the compression ignition engine fueled by diesel biodiesel blends and diesel oil using gas chromatography, illustrated the procedure of the analysis of pollutant gases as volatile organic compounds such as; benzene, toluene, ethyl-benzene, *o*-xylene, *m*-xylene and *p*-xylene emitted by diesel engines. They also reported a comprehensive two-dimensional gas chromatography method that was developed and used for quantitation of fatty acid esters in middle distillates matrices and figure 9-11 illustrate their results.

Shang, Zhen, Chen, Ching-Yuan and Rung (2012), presented a new method for characterizing the composition of a biodiesel that was composed of fatty acid methyl esters through high-performance liquid chromatography. The chromatograms of methyl palmitate and methyl oleate which are the main fatty acid methyl esters usually overlap chromatographically in the high performance liquid chromatographic analysis. A mathematical method was developed to estimate the individual masses of methyl palmitate and methyl oleate from their overlapping chromatograms in the high performance liquid chromatogram with refractive index and ultraviolet detectors. The individual masses of methyl palmitate and methyl oleate in the artificial mixtures was quantified. Moreover, fatty acid methyl esters composition and the yield of the biodiesel that was obtained from the transesterification of soya bean oil were quantified for verification in the study. Figure 12 illustrates the results they obtained (Shang et al, 2012).

3.0 Summary and Suggestions

Most of the works we have reviewed in this paper include comparison of biodiesel productivities of different vegetable oils by acidic catalysis, analysis of biodiesel and petrol-diesel blends by high performance liquid chromatography combined with easy ambient sonic-spray ionization mass spectrometry. Simple thin layer chromatography screening of acylglycerol level in biodiesel as an alternative to gas chromatography was reviewed as well as conventional and fast chromatography

analysis of biodiesel blend using ionic liquid stationary phase. Furthermore, we studied the discovery of the two-dimensional chromatography equipped with a flame ionization detector that was used to quantify, identify and confirm the component as well as the purity of biodiesels. Despite extensive work reported, much research is still on ground on how to improve the chromatographic techniques to the present world status, such as to improve the chromatography view to 3D view and advancement of current methods.

Figures

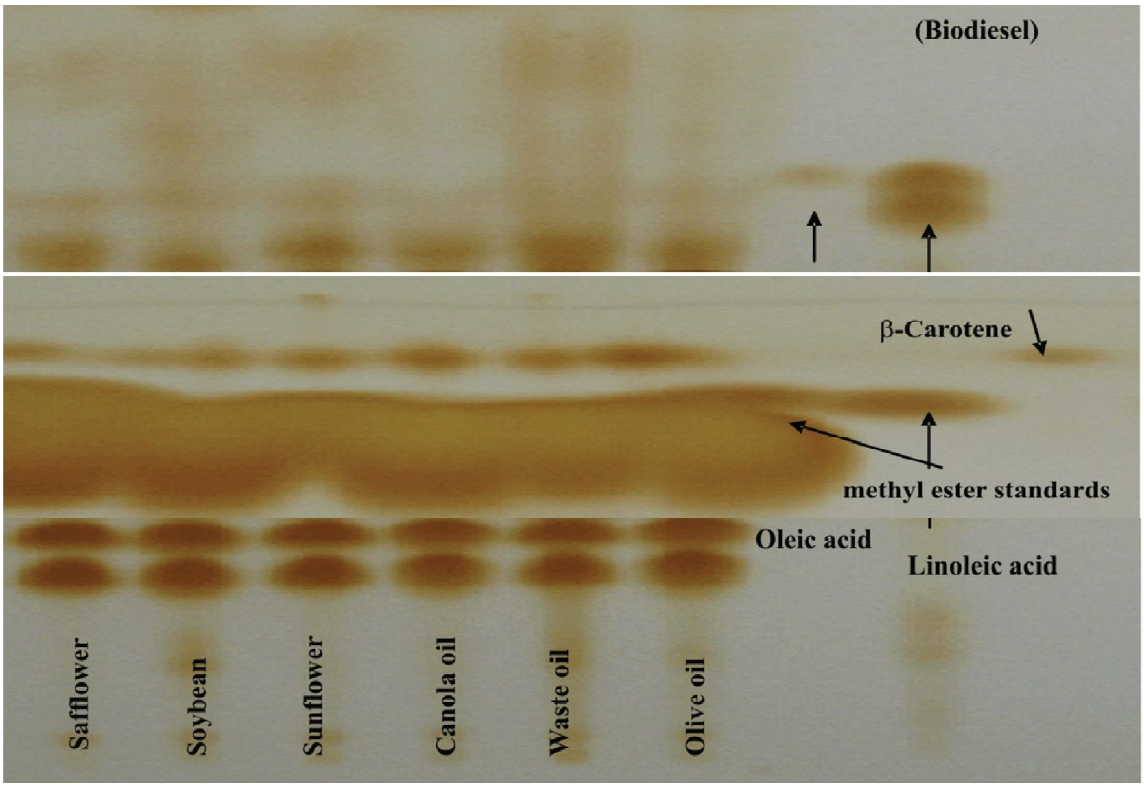

Fig.1 Thin layer chromatography of biodiesels and standards by acidic catalysis

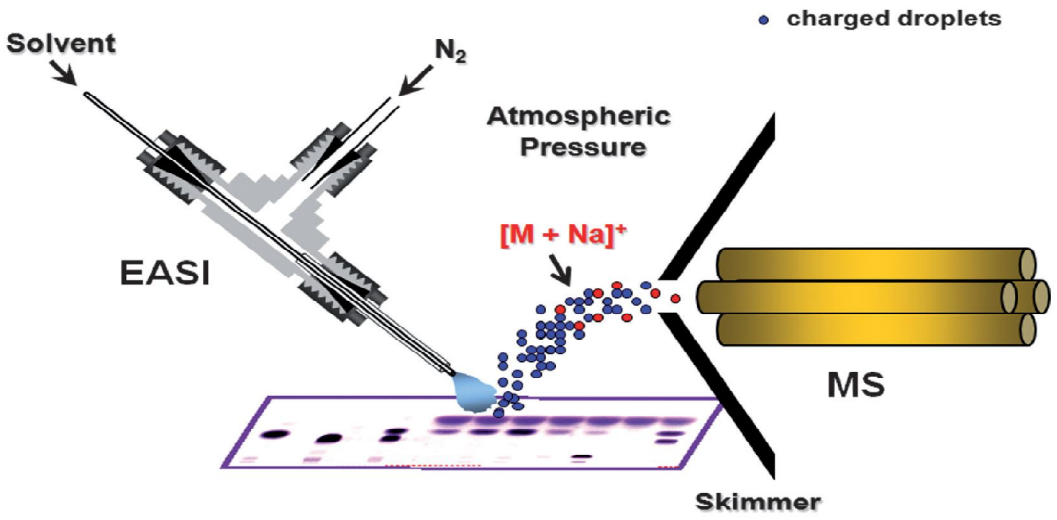

Fig. 2 On-spot EASI-MS characterization of HPTLC runs of biodiesel and biodiesel blends

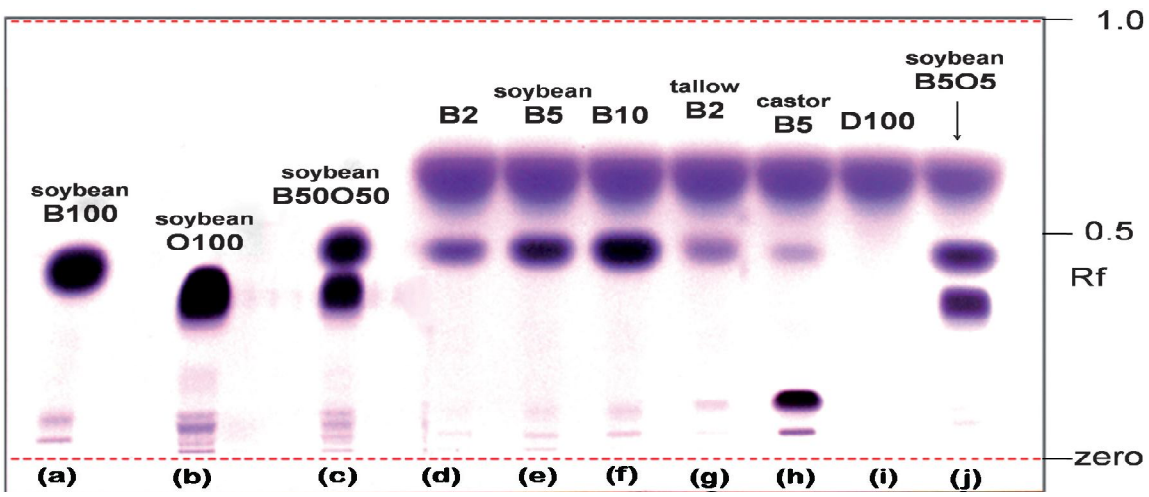

Fig.3 HPTLC of (a) soybean biodiesel (B100); (b) soybean oil (O100);(c) soybean B50O50 blend; (d) soybean B2 blend; (e) soybean B5 blend;(f) soybean B10 blend; (g) tallow B2 blend; (h) castor B5 blend; (i) petroldiesel (D100), (j) soybean biodiesel/oil/petroldiesel B5O5 blend.

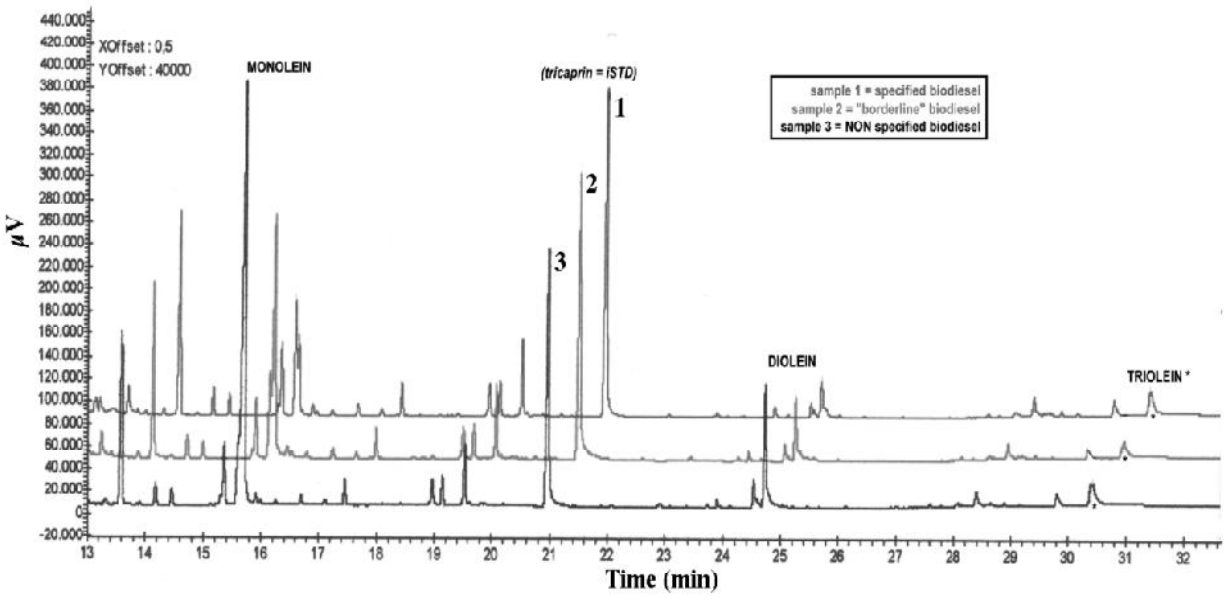

Fig. 4. Combined analysis of gas chromatography of specified biodiesel (upper chromatogram), "borderline" biodiesel (middle chromatogram), and non-specified biodiesel (lower chromatogram).

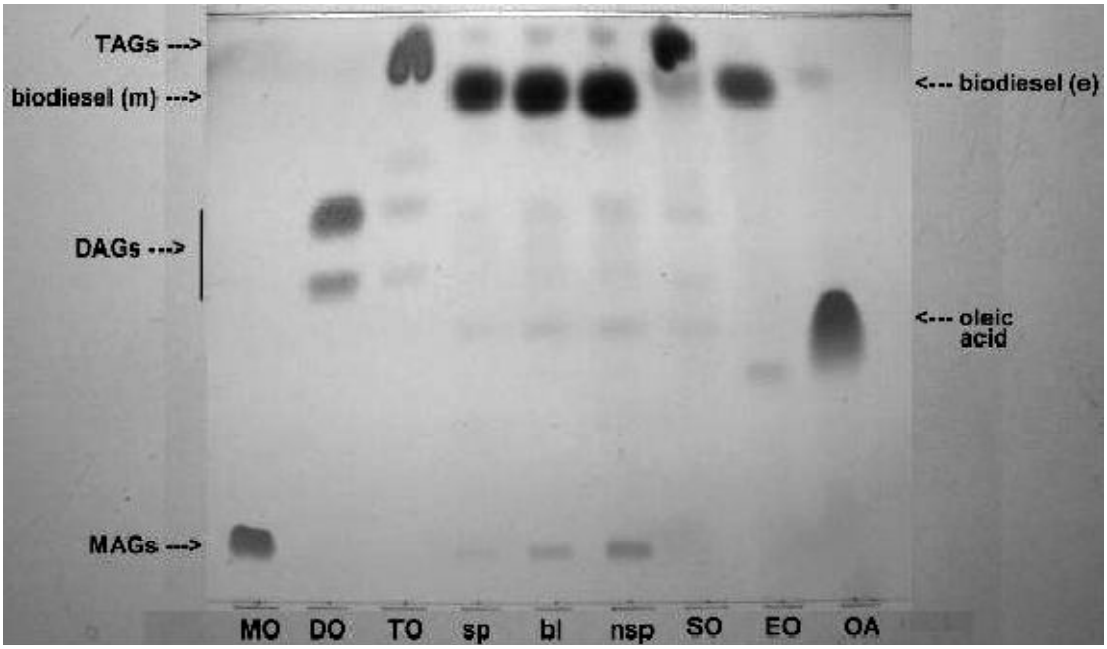

Fig. 5. TLC of reference lipids and biodiesel samples with p-anisaldehyde as the detection reagent. Toluene -chloroform–acetone (7:2:1, v/v/v) was utilized as mobile phase. MO = monoolein (MAG); DO =dioleins (DAGs); TO = triolein (TAG); sp = specified soy biodiesel; bl ="borderline" soy biodiesel; nsp = non-specified soy biodiesel; SO = soy oil; EO = ethyl oleate; OA = oleic acid.

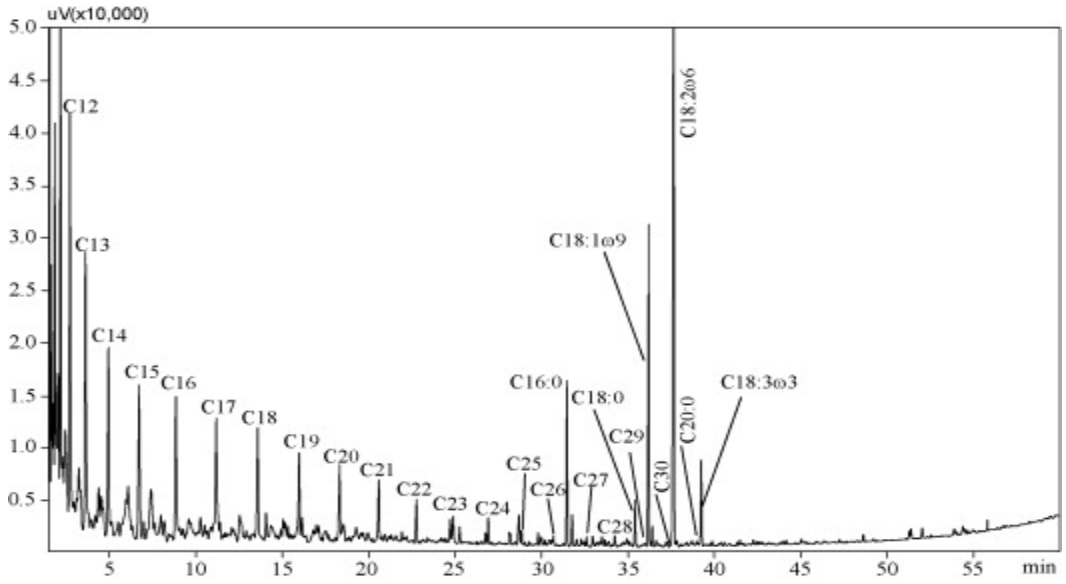

Fig.6. Biodiesel blend (B20) of soybean on SLB-IL100 30m column.

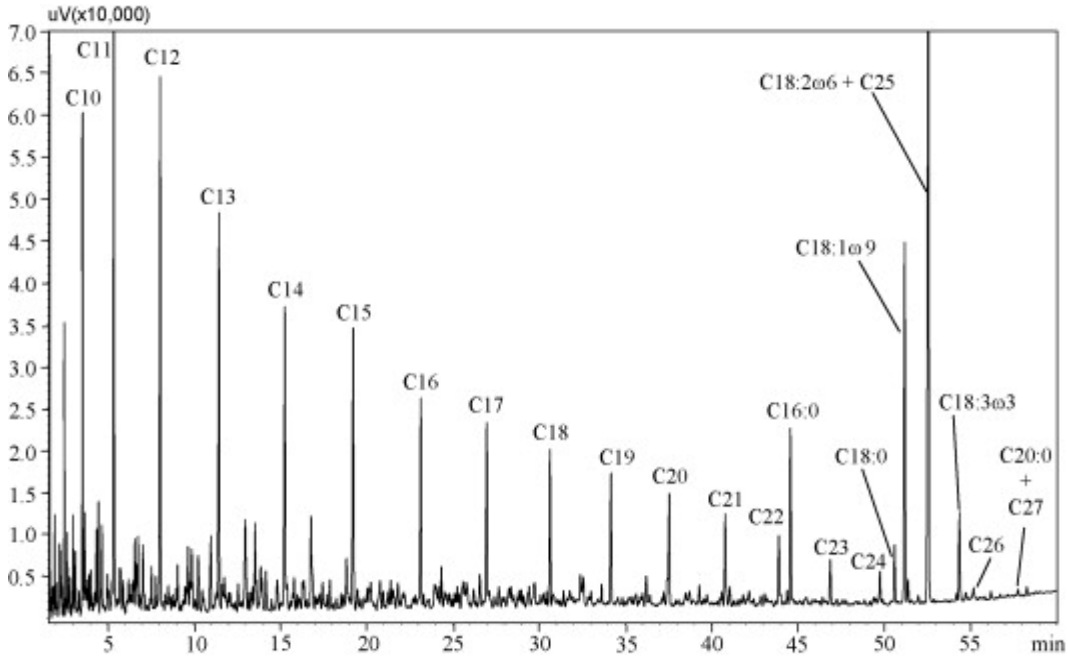

Fig. 7. Biodiesel blend (B20) of soybean on Supelcowax-10 30 m columns.

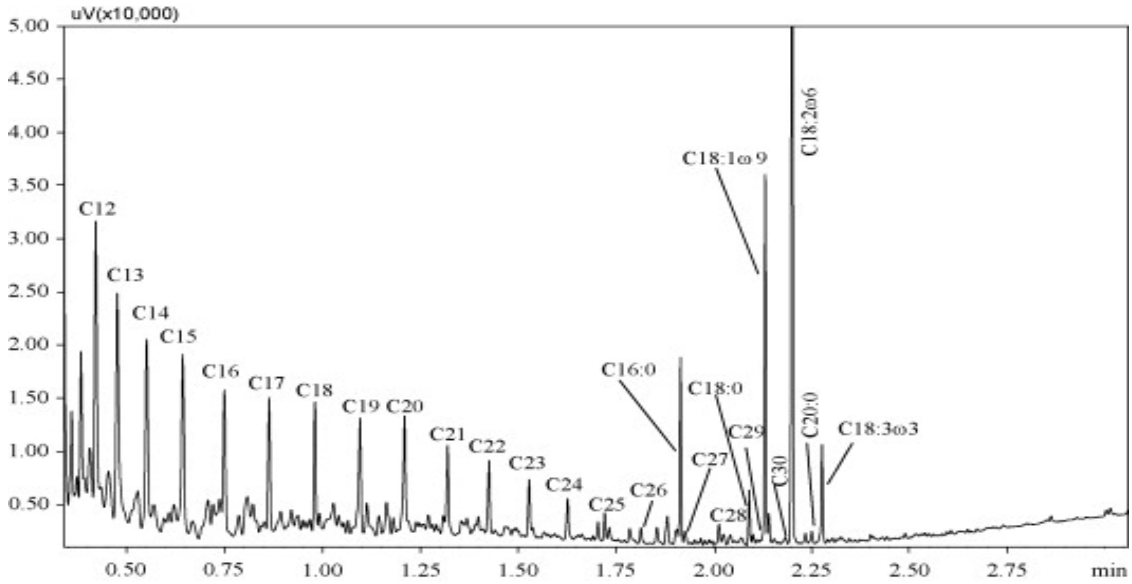

Fig. 8. Analysis of biodiesel blend (B20) of soybean on SLB-IL100 12m column.

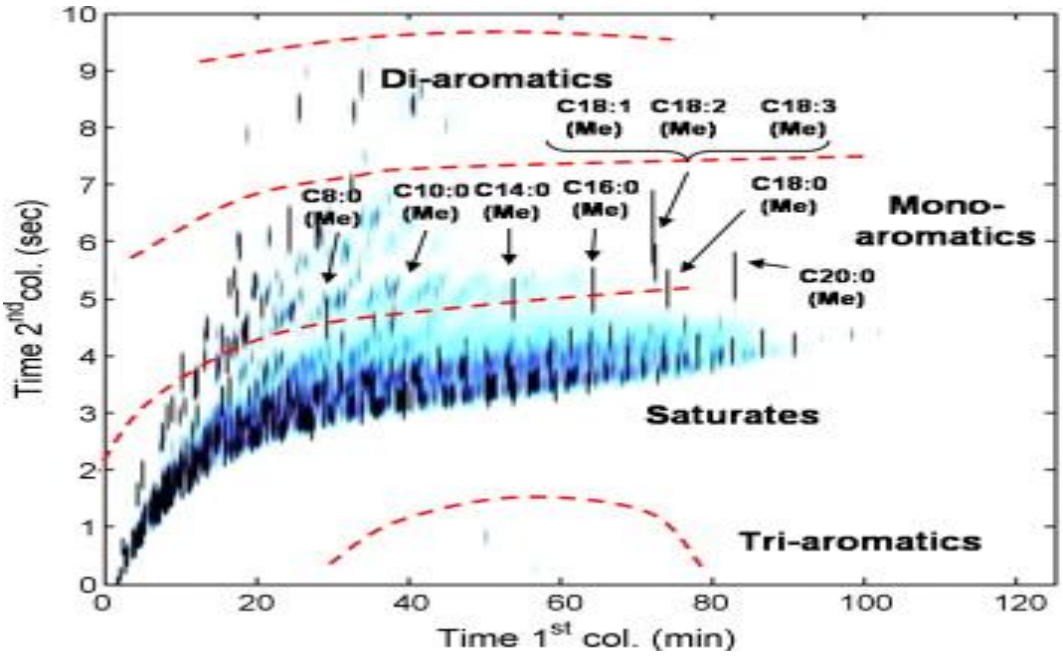

Fig.9. Two-dimensional chromatogram of sample STD2 using conventional chromatographic conditions,which was applied to the analysis of two blends of commercial petroleum diesel sample and transesterified coprah oil or rapeseed oil.

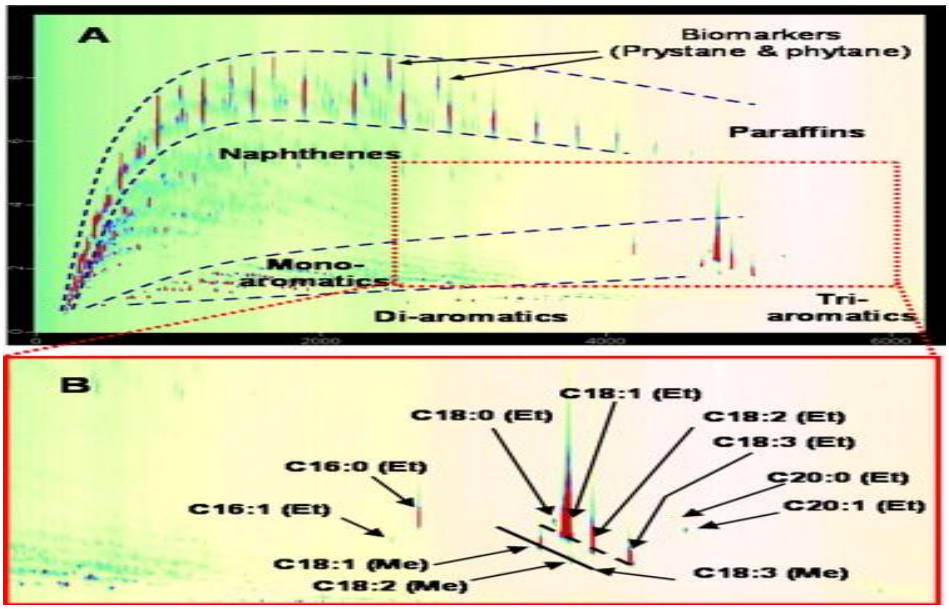

Fig. 10. Two dimensional gas chromatography of a polar × non-polar approach for the separation of fatty acid esters occurring in esterified coprah oil and hydrocarbons in synthetic B5 diesel samples.

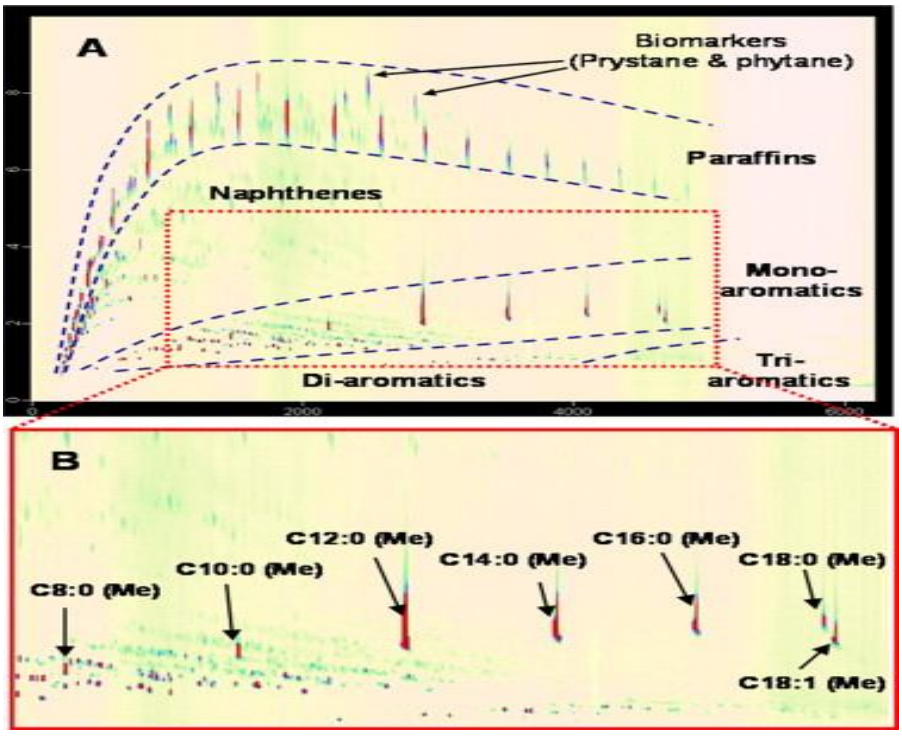

Fig.11. Illustration of a polar × non-polar approach for the separation of fatty acid esters occurring in esterified rapeseed oil and hydrocarbons in synthetic B5 diesel samples.

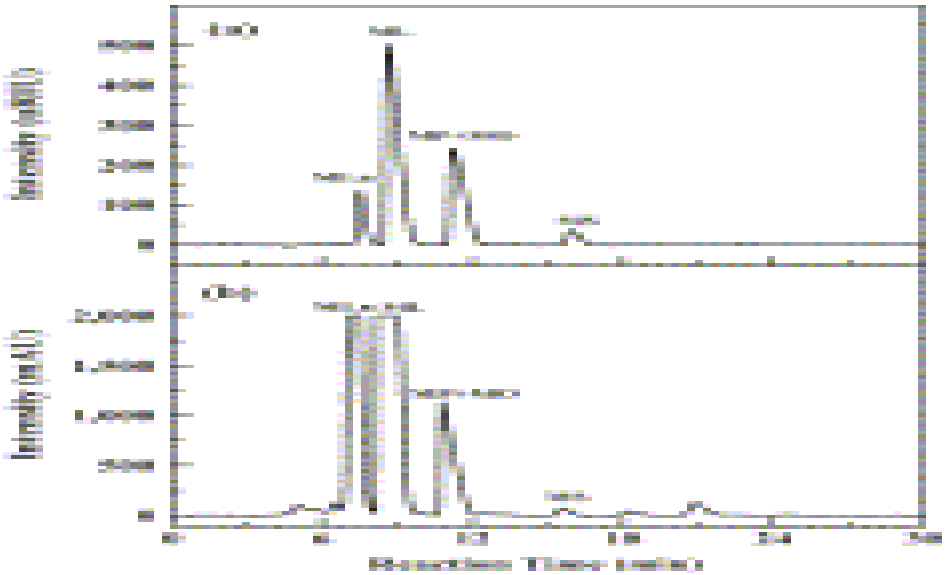

Fig. 12. High performance liquid chromatography separation of soya bean biodiesel by refractive index and ultraviolet detection.

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