



Emerging Analytical Methods for Quantitative Determination of Biofuel-Petroleum Fuel Blends Composition

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ABSTRACT

Bioethanol blending with petroleum fuels is being practiced all over the world to cut down on fuel prices and in-order to curb vehicular emissions. However, variations from the stipulated amount of bioethanol in petroleum fuels can be caused intentionally or unintentionally and is detrimental to engine life and performance. In recent times, research has progressed to introducing portable devices that are capable of sensitively and rapid analyzing real samples without prior pre-treatment. The focus of this review will be the emerging trends in the field of blended fuel analysis. Application of techniques such as electrochemical, spectroscopic and those based on physical and electrical parameters will be discussed in the review.

Keywords: Bioethanol; Petroleum; Pre-treatment; Blended fuel; Electrical parameters

INTRODUCTION

Blending petroleum fuels with bio-alternatives has become a global need, and use of bioethanol blended fuels is steadily increasing throughout the world [1]. The unsustainable use of petroleum fuels, rising emission levels leading to global warming, price-hikes, and ever-increasing demands have called for immediate and rational solutions such as bioethanol blending [2]. Blending bioethanol with petroleum fuel keeps a check on soaring fuel prices and is desirable from numerous perspectives [3]. Bioethanol increases the oxygen content in fuel, resulting in cleaner and complete combustion. Thus, reducing the emission of hydrocarbon particulate matter and carbon monoxide is a primary reason for adopting bioethanol-blended fuels [4,5]. Bioethanol blending up to an optimal composition of 10%-15% would require no modification of existing Internal Combustion (IC) engines [6] and is a pragmatic switch for the commoner. Furthermore, bioethanol improves octane rating, a higher octane correlates with increased compression ratio and power output [7,8]. The addition of bioethanol enhances heat release rate, and volumetric efficiency and leads to greater torque output [9-11]. The break specific fuel consumption decreases while using blends, thus giving improved Brake Thermal Efficiency (BTE) [12].

On the other hand, the Net Heating Value (NHV) of bioethanol is 33% less than petrol. This translates into increased fuel consumption of blends compared to pure petroleum fuel [13]. Bioethanol has lower vapour pressure than petroleum fuels, making starting cold engines problematic [14]. Bioethanol production from food crops threatens food security, as arable land and resources set aside for feeding the population are used up. This issue can only be solved if we shift to second-generation and gradually to third generation bioethanol [15]. Bioethanol is a hygroscopic substance; hence moisture in the fuel tank can cause phase separation of oil-bioethanol and corrode metallic parts of the engine and fuel tank [16]. Since bioethanol is more economical than petroleum fuels, governments usually advocate for obligatory blending to avert the price inflammation of petroleum oils [17]. Retailers can take advantage of the situation and indulge in malpractices involving addition of excessive bioethanol to raise their profit margins [18]. As a consumer, this is distasteful as continual usage of higher percentages of bioethanol in the fuel may cause current IC engines to wear prematurely. Hence, there is a need for retail petrol outlets to undergo regular quality checks to ensure that the vendors adhere to the stipulated standards.

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While chromatographic techniques are the earliest reported and have been adopted into standard procedures, the rising use of bioethanol blends all over the world has interested researchers in finding rapid, low cost and portable analytical tools. The emergence of innovative technologies to assess the fuel blend composition has motivated a mini-review in this domain. The analytical challenges, emerging trends, and future possibilities will be discussed in this review.

LITERATURE REVIEW

Analytical challenges

Petroleum fuels are highly complex mixtures, mainly consisting of hydrocarbons (paraffin, naphthenes, polyaromatic hydrocarbons). However, their composition may vary according to the source of crude oil and the refining process [19,20]. Besides hydrocarbon components, petroleum oil constitutes remnants of biogenic species such as porphyrin, hematin, and anthocyanins [21]. Hence the following challenges arise:

- PAHs and plant derived species absorb strongly and lend to highly complex spectral characteristics.
- Co-elution of hydrocarbons in bioethanol makes the separation process difficult (chromatographic techniques).

The evolution of analytical techniques

Analysis of bioethanol in petroleum fuel blends has evolved over the years and is based on a wide range of physical and chemical characteristics of the blends. Techniques based on physical parameters include those based on density measurements [22]. The earliest analytical procedures were based on chromatographic separation of components, followed by spectroscopic detection. Gas Chromatography (GC) solves the issue of the co-elution of hydrocarbons with the low molecular weight alcohol additives through three main approaches [23,24].

- Use of multiple columns for the separation step.
- Using an extraction step prior to chromatographic analysis [25,26].
- Use of a selective detector for oxygenates in the blend such as chemical ionisation mass spectrometry [27], Flame Ionisation Detection (FID) [28-31], Atomic Emission Detection (AED) [32,33].

Liquid Chromatography (LC) techniques are similar to GC but use a liquid mobile phase. Reversed-phase LC technique and reverse-phase HPLC have been described in literature [34,35].

The standard techniques recommended by organizations such as The American Society for Testing and Materials (ASTM international) and Brazilian association still utilize chromatographic methods. ASTM recommends employing D5501, which describes the usage of GC. This method can be used when bioethanol content is more significant than 20%, and standard tests like D5599 and D4815 are required to measure lower ethanolic percentage [36]. Brazilian Association

Technical Standard recommends NBR 13992, which relies on a liquid-liquid extraction procedure [37]. Using multiple columns or selective detectors for oxygen containing compounds requires modifications to existing instruments. Employing an extraction step is also time-consuming and laborious. Besides, chromatographic techniques such as GC and LC require sophisticated and expensive instrumentation and technical knowledge to handle the samples and instruments. These methods cannot be adopted outside a laboratory setup.

A new era of emerging analytical trends

The analytical perspective has shifted, with more countries adopting blended fuels and fuel quality control becoming a pressing issue. The emerging trend focuses on techniques that can be adapted for real time on-site analysis and can eventually be available for the layman (Figure 1).

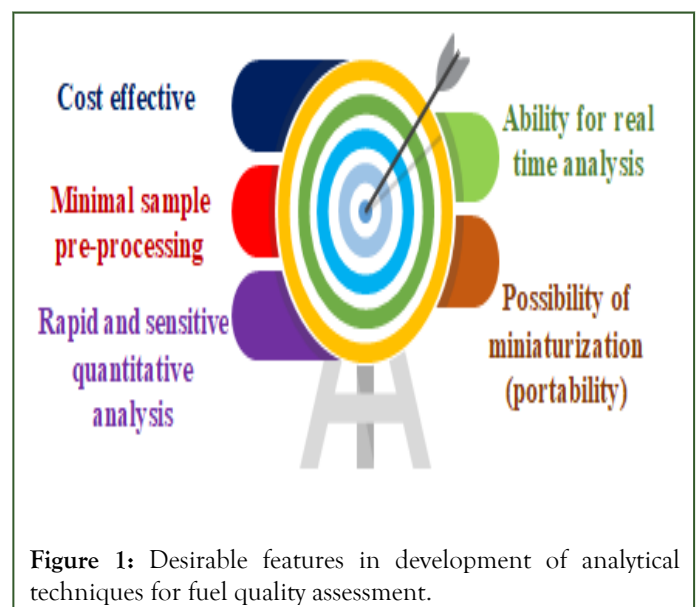


Figure 1: Desirable features in development of analytical techniques for fuel quality assessment.

Optical spectroscopic techniques, certain electrochemical and electrical methods show potential to satisfy these criteria.

Electroanalytical methods

Electroanalytical tools are used to investigate analytes by measuring potential or current in an electrochemical cell carrying the sample [38].

Pereira et al., electrochemically measured bioethanol composition using Batch Injection Analysis (BIA) cell system in combination with multiple pulse amperometric detection. The sample undergoes an aqueous extraction procedure, after which it is directly injected into a gold working electrode. The system was proposed for fast on-site analysis, and the Limit of Detection (LOD) and Limit of Quantification (LOQ) for bioethanol were $1.1 \times 10^{-3}\%$ and $3.63 \times 10^{-3}\%$, respectively [39].

Paixao et al., modified a copper disc microelectrode as the amperometric sensor. The method requires prior ethanol extraction onto an aqueous phase of 1 molL⁻¹ NaOH solution; this amperometric method showed repeatability of 3.4% and LOD of 0.01% (v/v) [40].

A biosensor combines a biological species with a physicochemical detector. Campanella et al., designed an Organic Phase Enzyme Electrode (OPEE) consisting of catalase enzyme coupled to an amperometric gaseous diffusion Clark-type oxygen electrode [41].

Electrochemical sensors are great for fieldable applications due to their inherent simplicity and portability. However, the selectivity of such techniques for solvents such as ethanol can be unreliable.

Table 1: Summary of electroanalytical techniques for bioethanol quantification in fuel blends.

Technique	Description	Advantages	Limitations	LOD (%)	LOQ (%)	RMSEP (%)	RSD (%)	Reference
Amperometric sensor	Copper micro-electrode polarised at 0.6 V vs. Ag/AgCl is used as the sensor	Inexpensive and fast	Formation of the Cu ₂ O ₃ can impede sensitivity/poor selectivity towards ethanol in presence of methanol.	0.01*				Griffiths PR, et al.
Electrochemical biosensor	Organic phase catalase enzyme electrode is coupled to a gaseous diffusion Clark-type oxygen electrode.	Portable, pre-treatment of samples not required.	Short life-time (about 7 days) of biosensor, poor selectivity towards ethanol in presence of methanol.				7.8	Battiste DR, et al.
Amperometric sensor with BIA system	Multiple-pulse amperometric detection using a gold electrode and alkaline electrolyte (NaOH)	Rapid, sensitive and on-site analysis possible.	Requires extra accessories such as the BIA system.	0.0011	0.0036		0.4	Campanella L, et al.

Spectroscopic techniques

Infrared spectroscopy: Absorption of infrared light causes transitions between quantized vibrational states of a molecule. The frequency of IR radiation absorbed is characteristic of the nature of the bond (bond strength and bond length) and atomic size [42].

Battiste et al., chose 880 cm⁻¹ absorbances to determine bioethanol in gasoline selectively. The study eliminated the gasoline signals by subtraction method [43]. Prasad and co-workers illustrated the use of ethanol's -OH functional group peak at 3354 cm⁻¹ (free from hydrocarbon peaks of petrol) to quantify bioethanol in petrol [44].

Multivariate technique of PCA-LDA (Principal Component Analysis-Linear Discrimination Analysis) has been applied to FTIR spectroscopy to detect adulteration and type of adulterant in gasoline. Although the method showed 93% efficiency in identifying the type of adulterant (solvent), the study could not provide quantitative information about the adulterant concentration [45].

Corsetti et al., employed two approaches to quantify ethanol up to 10%:

- Application of an algorithm that allowed the identification of features in the absorption spectrum that can be quantified using Beer-Lamberts law.
- A ratiometric approach involving analysis of areas of -OH and -CH absorption peaks [46].

NMR spectroscopy: NMR spectroscopy can provide structural information about analytes under question based on the interaction of nuclear spins with radiofrequency electromagnetic radiation [47].

Renzone et al., employed a ^1H NMR technique to quantify alcohols by integrating the chemical shift region around 3.5 δ ppm where carbinolic protons of alcohols resonate (region free of petroleum resonance) [48]. Meusinger used ^1H -NMR spectra that were ^{13}C decoupled to quantify oxygenates in fuel blends and further employed two-dimensional ^{13}C correlated NMR for the assignment of ^1H NMR signals [49]. Sarpal et al., used ^{13}C NMR to quantify oxygenates in petrol, bioethanol determination relied on the ethanolic signal at 57.8 ppm [50]. Researchers have also demonstrated the application of ^{17}O NMR to quantify bioethanol in gasoline in the range of 1%-20% [51].

Time domain NMR is the latest NMR technique used for quantifying blends. It utilizes the changes in transverse relaxation time of commercial petrol (2.03-2.05 s) and bioethanol (1.6 s) [52].

Raman spectroscopy: Raman spectroscopy studies the vibrational modes of a molecular system using UV-Visible light. Unlike the IR technique that relies on absorption data, Raman spectroscopy is based on the process of light scattering of light [53].

Ye and coworkers introduced a simple technique using Raman spectroscopy, where authors used unique Raman signals associated with petrol and bioethanol for ratiometrically determining the bioethanol proportion [54].

Fortunato et al., used Raman spectroscopy to quantify bioethanol composition in bioethanol petrol blends. The method proposed combines Liquid-Liquid Extraction (LLE), Flow Analysis (FA), and Standard Dilution Analysis (SDA) prior to Raman analysis. The study was carried out using portable 785 nm laser Raman systems. The RSD, LOD and LOQ values for the method were found to be 2%, 0.5% and 1.8% (v/v), respectively [55].

NIR spectroscopy: Near-infrared spectroscopy is a quick-analytical technique for recording the spectra of samples without demanding any prior manipulation. It uses near-IR radiation with wavelengths ranging from 780 nm to 2500 nm and is essentially a vibrational spectroscopy [56].

Fernandes et al., illustrated the use of near-infrared spectroscopy in simultaneously quantifying ethanol and methanol in petrol based on spectra collected in the range 1105 nm-1683 nm. Quantitative models were constructed using Partial Least Squares (PLS) regression. The obtained Root Mean Square Error of Prediction (RMSEP) value was 0.28% (v/v) for ethanol (both PLS models) and 0.83% (v/v) for commercial samples [57]. Researchers have also developed a modified NIR spectrometer equipped with an InGaAs diode array detector that could determine the percentage of bioethanol in petrol with a LOD of 0.68% (w/w) and a LOQ of 2.04% (w/w). They utilized a computational technique (vibrational self-consistent field second order perturbative treatment (PT2-VSCF)) to assign NIR bands

[58]. Later, Correia and coworkers reported using a portable MicroNIR™ miniature pro 1700 model instrument for fuel quality control based on PLS calibration model. An RMSEP value of 3.81, LOD of 0.75 wt% and LOQ of 2.50 wt% was reported [59].

Fluorescence spectroscopy: An excited state molecule can relax *via* radiative and non-radiative processes. The radiative decay from the S1V0 level to the ground state is called fluorescence. Fluorimetry measures emitted radiation to produce an emission spectrum [60]. Emission spectrum is dependent on the properties of the analytical system, and the spectrum's shift or intensity changes can be monitored for analytical purposes (Figure 2).

Kumar et al., employed Principal Component Regression (PCR) and PLS calibration models with synchronous fluorescence spectroscopy and an excitation-emission matrix fluorescence spectroscopy coupled with multiway Partial Least Square regression (N-PLS) and unfolded PLS for monitoring fuel quality. This procedure allowed for the analysis of samples without a pre-treatment step and has RMSEC and RMSEP values of <2% [61].

The bioethanol-fuel blends show a gradual shift in the fluorescence emission to the higher energy region (hypsochromic shift) with increasing bioethanol content. Prakash and Mishra quantified the fuel-biofuel blends satisfactorily using a combination of White Light Excitation Fluorescence (WLEF) and multivariate methods such as PCR and PLSR. R^2 values >0.998 and RMSEP values <1% are achieved in this method. A fibre-optic portable fluorimeter capable of WLEF measurements is proposed that contains the following components: White light source, collimator, sample cell, synchronizer, PMT detector (Figure 2c). The device could be connected to a personal computer/laptop for data processing [62].

Kumar and Mishra developed a fluorescence spectroscopic method based on solvatochromism of Reichardt's dye. With the increase in the bioethanol concentration in petrol-bioethanol blends, Reichardt's dye shows a blue shift of the absorbance maxima due to solvent relaxation. A calibration model was developed for the batch-independent quantification of bioethanol in petrol-bioethanol blends by studying the variation of transition energy of Reichardt's dye as a function of bioethanol concentration. The RMSEP value attained was less than 2% [63]. Gotor and co-workers used a similar approach to develop test strips coated with a solvatochromic polarity probe to detect bioethanol in fuel blends. They designed a smartphone-based measurement system for on-site monitoring. The measurements require two accessories- an excitation source and a 3-D printed dark chamber. The smartphone's back camera is used in place of the detector in combination with a filter to record the response from the test-strip. An LOD value of 0.5% was obtained. (Figure 2a) [64].

Panigrahi and Mishra, the authors, considered petroleum blends' intrinsic inner filter effect for mapping bioethanol constitution. A redshift is induced in the fluorescence emission spectra due to the inner filter effect, whose extent is a function

of the inner filter effect. Based on this phenomenon, they built PLS calibration models, and an RMSEP value of 4.7333 was obtained [65].

Electronic spectroscopy: Electronic or UV-Visible absorption spectroscopy operates in the UV-Visible region (190 nm-800 nm) and affects electronic transitions in a molecule [66]. Colorimetric techniques make use of UV-Visible spectroscopy for detection purposes.

Alhadeff and co-workers used a bi-enzymatic (alcohol oxidase and horseradish peroxidase enzymes) biosensor integrated with flow injection analysis to detect bioethanol. The colorimetric detection was based on a biochemical reaction yielding coloured product. The technique was plagued with short lifetime of the enzymes and inactivation of enzymes at higher temperature [67]. Muncharoen et al., proposed the application of Membrane-Less Gas Diffusion (MBL-GD) along with an aqueous extraction step for sample pre-treatment. Further, a color developing reagent was used for spectrophotometric detection to determine bioethanol in gasohol with LOD of up to 1%. The MBL-GD set-up was contained in a micro-unit and has the potential for on-site use [68].

Recently, Vijayan and Prakash described the use of a common dye to analyze blended fuels without any pre-processing. The unique molar absorption coefficient values of the probe molecule in petrol and ethanol media is taken into advantage. The study describes a hyperchromic shift-based model and a ratiometric model with LOD and LOQ values of 0.02%, 0.080% and 0.01%, 0.04% respectively. The RMSEP values were found to be less than 2%. Biodegradable hydrogel pellets are proposed for probe delivery. Furthermore, a portable LED spectrophotometer-‘ethanometer’ with low-cost components such LED light source, sample cell and PMT detector was proposed.

This device could easily be converted into a hand held device and used for quantitative in-field analysis (Figure 2a-2c and Table 2).

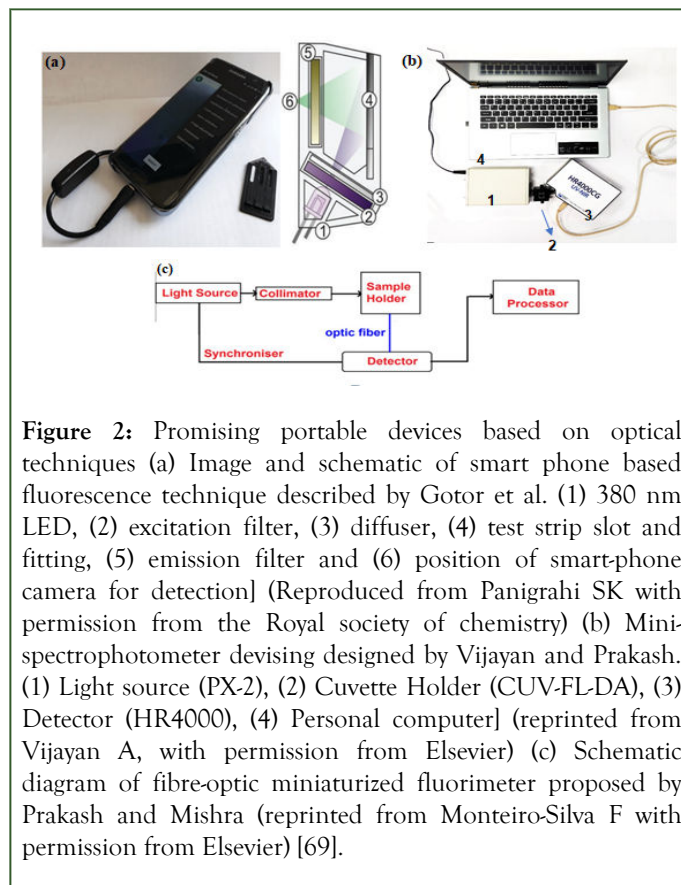


Figure 2: Promising portable devices based on optical techniques (a) Image and schematic of smart phone based fluorescence technique described by Gotor et al. (1) 380 nm LED, (2) excitation filter, (3) diffuser, (4) test strip slot and fitting, (5) emission filter and (6) position of smart-phone camera for detection] (Reproduced from Panigrahi SK with permission from the Royal society of chemistry) (b) Mini-spectrophotometer devised by Vijayan and Prakash. (1) Light source (PX-2), (2) Cuvette Holder (CUV-FL-DA), (3) Detector (HR4000), (4) Personal computer] (reprinted from Vijayan A, with permission from Elsevier) (c) Schematic diagram of fibre-optic miniaturized fluorimeter proposed by Prakash and Mishra (reprinted from Monteiro-Silva F with permission from Elsevier) [69].

Table 2: Summary of spectroscopic techniques for bioethanol quantification in fuel blends.

Technique	Description	Advantages	Limitations	LOD (%)	LOQ (%)	RMSEP (%)	RSD (%)	Reference
Infra-Red spectroscopy								
IR spectroscopy	IR band at 880 cm ⁻¹ is used to determine bioethanol percentage. Petroleum signals are subtracted from overall spectra	Simple and straightforward technique	The variation in petroleum signatures from one batch to another is not considered					Pereira RCC, et al.
FTIR spectroscopy with multi-variate analysis	Spectroscopic data is calibrated using PCA-LDA	Works well as a preliminary inspection tool	Quantitative analysis not possible					Keeler J, et al.

FTIR spectroscopy	-OH functional group peak is chosen for bioethanol quantification	Direct analysis without prior separation possible	Percentage relative error can go up to $\pm 2\%$	1	0.064	Corsetti S, et al.
FTIR and excess FTIR spectroscopy	Two approaches, including one ratiometric approach have been suggested	Helps understand blending at molecular level	Compromises between sensitivity and accuracy have to be made			Renzoni GE, et al.
NMR spectroscopy						
^1H NMR spectroscopy	chemical shift region of carbinolic proton of alcohols is chosen for quantitative analysis	Direct sample analysis possible	High instrument acquisition costs and non-portable device	0.007		Sarpal AS, et al.
^1H and ^{13}C NMR spectroscopy	^1H NMR spectra that are ^{13}C decoupled were used in combination with 2-D ^{13}C NMR for peak assignment	Selective determination of ethanol in presence of other oxygenates possible				Lonnon DG, et al.
^{13}C NMR spectroscopy	Measurement based on the ethanolic signal at 57.8 ppm	Low sample consumption, no pre-treatment required and	High Instrument acquisition costs and non-portable device			Romanel SA, et al.
^{17}O NMR spectroscopy	Internal standard and calibration curve QNMR methods are used for simultaneous quantification of multiple oxygenates	Quantification is independent of petroleum signals		0.1	1	Long DA.
TD-NMR spectroscopy	Differences in transverse relaxation time of petrol and ethanol is used for quantification	Sensitive measurement over a large range of ethanol proportion (0%-50%)				Ye Q.
Raman spectroscopy						

Raman Spectroscopy	Ratiometric analysis of most intense fuel and bioethanol peaks	Simple and straightforward	Does not take into account varying nature of petroleum samples					Blanco M, et al
Raman spectroscopy with standard dilution analysis	Liquid-Liquid Extraction (LLE), flow analysis (FA), and Standard Dilution Analysis (SDA) is proposed with Raman spectroscopy for sample analysis	Takes into account matrix effect	Complex sample pre-treatment system	0.5*	1.8*		2*	Fernandes HL, et al.
NIR spectroscopy								
NIR spectroscopy	Ethanol and methanol are simultaneously determined and calibration models developed using PLS regression	Non-destructive and can selectively determine ethanol percentage	Laboratory-based technique, maybe affected by changes to petroleum matrix				0.28%*	Correia RM, et al.
NIR spectroscopy with modified InGaAS diode array detector	PLS regression model is applied to spectroscopic data and NIR band assignment is carried out using computational data	Mobile device	High cost of modifications required	0.68**	2.04**		0.21**	Lakowicz JRS, et al.
Micro-NIR spectroscopy	Calibration model based on	Portable, miniaturized device and no sample pre-treatment required	Bioethanol percentages below 25% was not considered while creating the calibration model	0.75**	2.50**	3.81**		Kumar K, et al.
Fluorescence spectroscopy								
Fluorescence spectroscopy	Based on solvatochromism of Reichardt's dye with increase in	Simple and rapid technique	Emission of window Reichardt's dye maybe influenced by				<2	Panigrahi SK, et al.

	solvent polarity		petroleum fluorescence			
Fluorescent solvatochromic test strips	Test-trips loaded with solvatochromic dye is immersed in fuel blend and smart-phone camera acts as detector and output interface	Smart-phone interface, layman-friendly	Error of prediction is high	0.5		Akash MSH, et al.
White Light Excitation Fluorescence (WLEF) with multivariate methods	WLEF is used for obtaining total fluorescence of the blends and calibration models are developed using PCR and PLSR	Good sensitivity, portable devising and no pre-treatment required	Complex spectral data		<1	Gotor R, et al.
Unconventional steady-state fluorescence techniques with multivariate methods	SFS and EEMF spectroscopic techniques are coupled with multiway Partial Least Square regression (N-PLS) and unfolded PLS	No pre-processing required	Portable devising is more complex compared to other fluorescence techniques		<2	Kumar K, et al.
Fluorescence spectroscopy	Inner filter effect induced red shift of petroleum samples is correlated with optical density for sample analysis	Direct analysis of fuel samples possible	Optical density of different petroleum batches may vary significantly		4.733	Alhadeff EM, et al.
Electronic spectroscopy						
Colorimetric sensing coupled with membrane less gas diffusion	Aqueous extraction of sample is followed by introduction into MLGD unit and colorimetric detection using colour	Micro-unit suitable for on-site applications	Direct analysis of samples <i>via</i> absorption spectroscopy is not possible			Monteiro-Silva F, et al.

		developing reagent					
Bienzymatic biosensor with colorimetric detection	Alcohol oxidase and horseradish peroxidase enzymes are used as biosensors in combination with flow injection analysis. Colorimetric detection is based on coloured product formed by biochemical reaction between biosensor and ethanol.	Good sensitivity	Short life time of enzymes and inactivation of enzymes at higher temperatures				Prakash J, et al.
Probe-based spectrophotometric detection	Hyperchromic shift of the probe is monitored using mini-LED spectrophotometer	Low-cost portable devising, good sensitivity and direct analysis of samples	Interference from petroleum absorption affects choice of probe	0.02 ^a 0.08 ^b	0.01 ^a 0.04 ^b	0.23 ^a 0.13 ^b	Vijayan A, et al.

Note: ^{*}v/v, ^{**}w/w, ^aHyperchromic-shift based model, ^bRatiometric analysis model

RESULTS AND DISCUSSION

Spectroscopic techniques offer huge advantages over other techniques as they rely on chemical information and are highly sensitive. However, techniques such as FTIR and NMR are difficult to miniaturize and are limited to laboratory analysis. In recent years, optical techniques such as Raman, NIR, fluorescence and electronic spectroscopy have shown tremendous potential as they can be effectively designed into portable devices without compromising sensitivity or selectivity.

Other methods

Sensors of cuprous oxide-coated LPFGs (Long-Period Fiber Gratings) were developed utilizing the dependence of spectral features of the grating on the surrounding medium's refractive index. A LOD of 1.63% and 2.1% (v/v) were calculated for wavelength and optical power modes, respectively.

Distillation curves and a multivariate analytical method of Partial Least-Squares regression (PLS) were used to predict the alcoholic percentage in fuel blends.

Vaishali Rawat et al., proposed a device with a microstrip based metamaterial Complementary-Split-Ring-Resonator (CSRR) sensor operating in the microwave region to determine the composition of hybrid fuels by monitoring changes in permittivity values.

Santos determined the bioethanol content in fuel blends with an electronic system operating in the radio frequency range. The system inspects the changes in the dielectric constant of blends to indicate whether the level of bioethanol was above or below the approved standard [70-72].

Rocha et al., developed an impedance probe in which the transducer measures the bulk conductivity of samples and correlates the same to mass ratios of bioethanol and fuel blends. However, the technique's accuracy depended on maintaining a

constant operating temperature. Later, a contactless impedance probe was also developed by Opekar and co-workers.

The aforementioned techniques that utilize physical and electrical parameters can be easily converted into portable devices [73]. However, such techniques can be adversely affected by varying nature and composition of different fuel batches this

may affect their ability to quantitatively assess bioethanol composition in fuel blends. In comparison, optical techniques that rely of chemical information can be considered more reliable (Table 3).

Table 3: Summary of other techniques for bioethanol quantification in fuel blends.

Technique	Description	Advantages	Limitations	LOD (%)	LOQ (%)	RMSEP (%)	RSD (%)
Distillation curve method	distillation curves of fuel blends is used to build calibration model <i>via</i> PLSR method	Can provide different parameters in a single experiment	Normalizations are required for different petroleum batches, destructive technique			0.0009	
Optical fiber sensor	Dependence of spectral features of cuprous oxide coated LPFGs on surrounding medium's refractive index is monitored	Real-time measurement in flow configurations possible	Refractive index being a physical parameter may vary with type/source of petroleum oil	1.63 ^c , 2.1 ^d			
Complementary-Split-Ring-Resonator (CSRR) sensor	The metamaterial based CSRR sensor operates in microwave region and measures changes to permittivity value	Low-cost, compact and handy devising	Low precision				
Electronic system	Operates in the Radiofrequency region and is based on variations in dielectric constant of blends	Rapid <i>in situ</i> inspection possible without trained individuals	Qualitative in nature and recalibration required to monitor beyond or below a certain range				
Electric impedance sensor	Mass ratios of ethanol and petrol in blends are correlated to their bulk conductivity	Non-destructive, rapid	Temperature dependency			± 2	
Contactless impedance sensor	Based on difference in relative permittivity values of	Simple technique with possibility of miniaturization, no pre-treatment required	Recalibration maybe required for different fuel batches				<1.5

bioethanol and
petrol

Note: ^cWavelength shift mode ^dOptical power shift mode

CONCLUSION

Bioethanol blending with petroleum fuel is prevalent today and is considered an environmentally benign and cheaper alternative. Research in the recent times have yielded techniques that focus on minimal or no sample pre-processing and can be adopted for on-site analysis of fuel blends. This is a necessity as regular evaluation of fuel blends composition is required to ensure engine health and avoid malpractices. This review summarises the emerging techniques that can easily be miniaturized and can ensure rapid analysis. A number of electrochemical sensors, electrical and spectroscopic techniques show potential for *in-situ* and real-time assessment applications. Although techniques based on electrical, physical or electroanalytical parameters can be easily miniaturized, they often present issues with regards to selectivity and sensitivity. Optical techniques such as electronic absorption, fluorescence, NIR and Raman techniques has shown scope as they can be easily down sized and provide sensitive and accurate quantitative measurements. Portable optical devices capable of providing sensitive measurements is a promising opportunity. Currently, only a handful of spectrophotometric devices such LED-spectrophotometer, Micro-NIR and fluorescence based devices have been developed that are capable of on-site monitoring of blend composition.

The ultimate goal of on-going research in assessment of fuel blend quality involves addressing its benefits to the common man. Hence, future research should and will focus on portable tools that can be used by layman for the routine analysis of bioethanol blended fuel samples.

CONFLICT OF INTEREST

The authors have declared no conflict of interest.

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