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Fuel Quality Monitoring by Color Detection

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Abstract

The quality of automotive fuels—gasoline, diesel, biodiesel, and ethanol—is discussed in the light of their specifications in different countries and regions and in terms of their adulteration, which has such a prejudicial effect on the production chain, distribution chain, tax revenues, the environment, and end consumers. Different ways of adulterating automotive fuels are analyzed, as are the procedures for their detection. Several analytical methods for monitoring quality and detecting adulteration have been addressed in the literature, emphasizing the determination of properties such as density, distillation curve, octane rating, vapor pressure, etc., by means of physicochemical methods and chromatographic and spectrographic techniques, to the detriment of colorimetric methods. This chapter looks at colorimetric techniques designed for quality monitoring and the detection of adulteration in fuels, especially simple, quick, low-cost procedures with potential to be used in the field.

Keywords: quality, adulteration, gasoline, diesel, biodiesel, ethanol, methanol, glycerin, water, colorimetric tests, hydroxamic acid test, Schiff's reagent, solvatochromic effect, field test

1. Introduction

The quality of a fuel is associated with its fitness for use, the minimum requirements for which are given by its specifications, defined as a set of characteristics and their respective limits, which are required to ensure its good performance in engines. A comparison of the specifications for gasoline, ethanol, diesel, and biodiesel in different countries and regions is provided in the **Supplementary Material** to this chapter.

The failure of a fuel to meet any of its specifications is referred to as a nonconformity, which means the fuel is not fit for use. Nonconformity is not always due to adulteration, which is the deliberate and illegal addition of lower-cost substances to a fuel, usually with tax evasion, all with the purpose of increasing the profit margin by illicit means, resulting in reduced tax revenues, unfair competition, harm to the environment, and increased wear and tear of vehicle engines [1–5]. In fact, a fuel may be adulterated and yet stay within its specifications, in which case the only detrimental effect is on tax revenues [6]. It is a challenge to detect the adulteration of fuels because adulterants usually include compounds that are already present in the fuels themselves [2, 6].

The illegal practice of fuel adulteration may impair the fuel's quality while also resulting in increased environmental contamination by polluting gases and

particulate matter because the combustion process is affected, leading to higher emissions of pollutants and compounds that cause acid rain, like NOx and SOx, as well as CO, which is highly asphyxiating [4, 7, 8].

The biggest detrimental effect of fuel adulteration is on the performance of the vehicle. In 2006, around 95% of vehicle repairs in São Paulo city, Brazil, were directly or indirectly attributable to poor fuel quality. Indeed, it has been estimated that fuel adulteration cost Brazil over 1 billion dollars that year, including 400 million dollars in lost tax revenues, affecting both local and federal budgets [9]. According to the Brazilian newspaper *Estadão*, a study done in 2017 by the Getúlio Vargas Foundation found that 4.8 billion reais is lost in the fuel sector every year to money laundering and tax evasion, with serious knock-on effects on the economy as a whole [10].

According to ANP, the agency responsible for monitoring fuel quality in the country, gasoline can be adulterated in multiple ways, such as by the addition of ethanol over the maximum permitted limit or the illicit addition of light and heavy aliphatic and aromatic solvents, which are themselves constituents of gasoline [6].

Gasoline and ethanol are both adulterated with methanol in Brazil, which is not allowed to exceed 0.5% v/v due to its toxicity, but whose low price makes it an attractive adulterant [11]. Meanwhile, the main nonconformity found in diesel in Brazil is a failure to comply with the correct quantity of biodiesel, which is set by ANP at 10% v/v [12]. Petroleum products like fuels are extremely important inputs for economies, industries, and basic everyday activities all around the world. Their importance to governments—whether for geopolitical reasons or because of armed conflicts or economic factors—means they tend to be taxed heavily, which raises their cost to consumers. As a result, adulteration has become a common practice in regions as diverse as South America and South Asia [13].

In India, kerosene is subsidized, which makes it particularly popular for adulterating gasoline, along with other products like naphtha, rubber solvents, aromatics, ethanol, light and heavy aliphatic solvents, and lubricants [2, 14, 15]. In 2018, the Petroleum Institute of East Africa announced that up to 75% of the 33 million liters of kerosene consumed every month ends up contaminating diesel and gasoline: only 5 million liters is actually used every month for lighting and cooking [16].

Cases of gasoline adulteration with acetone and sec-butyl acetate were reported in Vietnam and China in 2016, although this practice is less widespread in Vietnam now with the introduction of new limits for ketones in its gasoline specifications. In China, gasoline is often adulterated with substances like naphtha, ethanol, methanol, and even silicon oil or waste chemicals containing silicon [17].

In France, the most common form of adulteration consists of the addition of soybean oil or used cooking oil to diesel. In the last 5 years, the European Commission has invested heavily in preventing fuel adulteration [18].

According to Mani et al. (2017), the parameters that affect which adulterants are used in fuels—including considerations such as profitability, availability, and chemical compatibility—vary from place to place. The main adulteration methods are blending small quantities of middle distillate fuels like diesel and kerosene in gasoline; blending waste lubricants in gasoline and diesel, because the lubricants are expensive to dispose of in compliance with environmental standards; and adding small quantities of heavier fuel oils to diesel [3].

In Australia, the Department of the Environment and Energy regulates the Fuel Quality Standards Act 2000, which legislates and provides the standards on fuel quality in the country. In Europe, mandatory quality requirements for automotive gasoline and diesel are laid down by Directive 98/70/EC.

In the United States, ASTM International publishes standards on each type of fuel. Responsibility for setting the standards for fuel quality lies with

the Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants. Meanwhile, in Japan there are two standards for fuels: the mandatory standards set by the Central Environment Council, under the Ministry of the Environment, and the Japanese Industry Standards. The former are statutory requirements and regulate the Act on Quality Control for Gasoline and Other Fuels, which has been enforced since April 1996 [19]. **Tables 1–4** showing the gasoline, diesel, ethanol, and biodiesel specifications for each country or region are included in the **Supplementary Material**.

PROPERTY	AUSTRALIA	EUROPE		USA	JAPAN		SOUTH KOREA	BRAZIL
Spec Name/ Year	Fuel Quality Standards Act 2000 (2008)	Dir. 98/70/EC as amended (2009)	EN 228:2012 (2013)	EN 228:2012 (2013)	ASTM D 4814 (2014)	JIS K 2202 (2012)	JIS K 2202 (2012)	Petroleum and Alternative Fuels Business Act (2009)	Resolution ANP #40 (2013)
Source	Department of Environment	Dir. 98/70/EC as amended	EN 228:2012	EN 228:2012	ASTM International	Japanese Standards Association	Japanese Standards Association	Korea Petroleum Quality & Distribution Authority	ANP
Grade	ULP / PULP	Petrol	Unleaded Petrol	Unleaded Petrol E10	Unleaded	Regular / Premium	Regular (E) / Premium (E)	Regular / Premium	Regular (Type C) / Premium (Type C)
RON, min	91 / 95	95[1]	95[1]	95[1]		89 / 96	89 / 96	91 / 94	
MON, min	81 / 85	85	85	85					82 /
Antiknock index, calculated, min					[2]				87.0 / 91.0
Sulfur, ppm, max	150 / 50	10	10	10	80[3]	10	10	10	50
Lead, g/l, max	0.005	0.005	0.005	0.005	0.013[4]			0.013	
Manganese, g/l, max		2	2	2					
Benzene, vol%, max	1	1	1	1		1	1	0.7	1
Aromatics, vol%, max	42% pool average over 6 months with a cap of 45%	35	35	35		24[5]			35
Olefins, vol%, max	18	18	18	18				16(27)	25 (34)(35)
RVP à 37.8°C, kPa, min-max		60 max[6][7][8]	45-60 (class A) - 70-100 (class F1)[9]	45-60 (class A) - 70-100 (class F1)[9]	103 max[10]	44-65 (s) / 44-93 (w)	44 (s) / 55 (w)[11]	44-82[12]	69.0 max[13]
Density à 15°C, kg/m³, min-max			720-775	720-775		783 max	783 max		Note at 20°C
Distillation, T10, °C, max					70[14]	70	70	70	65
Distillation, T50, °C, min-max					77-121[14][15][16]	75-110	70-105 (s) / 65-105(w)	125 max	80
Distillation, T90, °C, min-max					190[14]	180 max	180 max	170 max	190
Distillation, E70, vol%, min-max			20-48 (class A) 22-50 (class F1)[9]	22-50 (class A) 24-52(class F1)[9]					
Distillation, E100, vol%, min-max		46 min	46-71	46-72					
Distillation, E150, vol%, min		75	75	75					
Distillation, FBP, °C, max	210		210	210	225	220	220	225	215
Distillation, Residue, vol%, max			2	2	2	2	2	2	2
Oxygen, wt%, min-max	2.7 max (no ethanol) 3.9 max (with ethanol)	3.7 max[17]	2.7 max	3.7 max		1.3 max	1.3-3.7	2.3 max[18]	
Methanol, vol%, max		3[19]	3	3				0.1 wt%	0.5
Ethanol, vol%, max	10	10[19]	5	10		3	10		[20]
Iso-propyl alcohol, vol%, max		12	[21]	12					
Iso-butyl alcohol, vol%, max		15	[21]	15					
Tert-butyl alcohol, vol%, max	0.5	15	[21]	15					
Ethers (5 or more C atoms), vol%, max	1 DIPE; 1 MTBE	22	[21]	22		7 MTBE	7 MTBE		
Phosphorus, g/l, max	0.0013	0[22]	0[22]		0.0013[4]			0.0013	
Induction period, minutes, min	360		360	360	240	240	240	480	360
Water and sediment, vol%, max								0.01	
Existent gum (solvent washed), mg/100ml, max	5		5	5	5	5	5	5	5
Copper corrosion, 3hr at 50°C, merit (class), max	1		1	1	1	1	1	1	1
Silver corrosion, merit (class), max					1				
Color						Orange	Orange	Yellow / Green	[23]
Appearance			Clear & bright	Clear & bright					LII[24]

(1)   Member States may decide to continue to permit the marketing of gasoline with a minimum MON of 81 and a minimum RON of 91.

(2)   Octane limits are set and regulated at the state level; the industry (R+M)/2 standard is generally 87/89/91+ for regular, midgrade and premium. Certification and posting of octane ratings regulated by Federal Trade Commission under 16 Code of Federal Regulations (CFR) 306.

(3)   Per-gallon cap per EPA regulation (65 FR 6698; 2/10/00). The refinery average is 30 ppm.

(4)   Leaded gasoline has been banned in the U.S. by EPA since 1996. Per EPA regulation (59 FR 7716; 2/16/94), no intentional addition of heavy metals allowed. While ASTM has no limit, EPA limits the phosphorus content of gasoline to a maximum of 0.0013 g/L. The regulations do not prohibit lead additives in aircraft, racing cars, and off-road farm & marine engines.

(5)   Either aromatics 24 vol% max and olefins 16 vol% max, or aromatics 21 vol% max and olefins 19 vol% max.

(6)   Vapor pressure determined for summer period.

(7)   The summer period shall begin no later than May 1, and shall not end before Sept. 30. For Member States with low ambient summer temperatures the summer period shall begin no later than June 1 and shall not end before Aug 31.

(8)   In the case of Member States with low ambient summer temperatures, where the derogation from 60 kPa, after the assessment and permission of the European Commission, is in effect, the maximum vapor pressure shall be 70 kPa. In the case of Member States with no low ambient summer temperatures, vapor pressure shall be 60 kPa plus the waiver specified in the Directive (0-8 kPa).

(9)   Depends on volatility classes determined by the country's seasonal and geographical conditions. To relevant countries, volatility class A shall apply during summer starting no later than May 1 and ending not before Sept. 30. In countries with arctic conditions class B shall apply during summer, starting no later than June 1 and ending not before Aug. 31.

(10) ASTM advises to consult EPA for approved test methods for compliance with vapor pressure regulations. RVP varies by season and region. See EPA regulation (54 FR 11868; 3/22/89).

(11) If the ambient temperature is below -10°C, RVP min becomes 60 kPa.

(12) Hot climate (June - August): 60 kPa; Cold climate (October - March): 96 kPa.

(13) For the states of Rio Grande do Sul, Santa Catarina, Paraná, São Paulo, Rio de Janeiro, Espírito Santo, Minas Gerais, Mato Grosso, Mato Grosso do Sul, Goiás, and Tocantins, and for the Federal District, up to 7.0 kPa higher vapor pressure is permitted between April and November.

(14) Volatility requirements vary by season and region.

(15) Gasolines that may be blended with 1 to 10 vol% ethanol or all other gasolines whose disposition with ethanol blending is not known shall meet a minimum T50 of 77°C (170°F) prior to blending with ethanol. Gasolines that contain 1 to 10 vol% ethanol shall meet a minimum T50 of 66°C (150°F) after blending.

(16) Gasolines known from the origin to retail that will not be blended with ethanol may meet a minimum T50 of 66°C (150°F) for volatility classes D and E only. Gasolines meeting these limits are not suitable for blending with ethanol.

(17) Member States shall require suppliers to ensure the placing on the market of gasoline with a maximum oxygen content of 2.7% and a maximum ethanol content of 5% until 2013 and may require placing on the market of such gasoline for a longer period if they consider it necessary.

(18) Oxygen contained in MTBE, ETBE and Bio-ethanol.

(19) Stabilizing agents may be added.

(20) The level of anhydrous ethanol to be blended with regular gasoline to produce the gasoline-ethanol blend must comply with the existing regulations. At the time of writing, it stands at 27% vol.

(21) Volume blending restricted to 2.7 % (m/m) maximum oxygen content.

(22) In order to protect automotive catalyst systems, phosphorus containing compounds shall not be included in unleaded gasoline.

(23) From colorless to yellow if it does not contain a dye, although a dye can be added (up to 50 ppm), which can be any color but blue, which is reserved for aviation fuel.

(24) Clear and free of suspended matter.

Table 1.
Gasoline specification.

PROPERTY	AUSTRALIA	EUROPE		USA	JAPAN	SOUTH KOREA	BRAZIL
Spec Name / Year	Fuel Standard (Automotive Diesel)	Dir. 98/70/EC as amended (1) (2009)	EN 590 (2013)	ASTM D 975 (2014)	JIS K 2204 (2007)	Petroleum and Alternative Fuels Business Act	Resolution ANP #50 (2013)
Source	Department of the Environment	Dir. 98/70/EC as amended	EN 590:2013	ASTM International	Japanese Standards Association	Korea Petroleum Quality & Distribution Authority	ANP
Grade		Diesel	Diesel	N° 1 - D S15 / N° 2 - D S15	Class Special 1 / Class 1 / Class 2 / Class 3 / Class Special 3	Automotive Diesel	S10 / S500
Cetane number, min	51.0	51	51 (temperate) / 47-49 (arctic & severe winter)(1)	40	50 / 50 / 45 / 45 / 45(2)	52(3)	48 / 42(4)
Cetane index, min	46.0		46 (temperate) / 43-46 (arctic & severe winter)(1)	40(11)	50 / 50 / 45 / 45 / 45(2)	52(3)	
Sulfur, ppm, max	10	10	10	15(5)	10	10	10 / 500
Polyaromatics, wt%, max	11	8	8			2-5	11 /
Density à 15°C, kg/m³, min-max	820 - 850		820-845 (temperate) / 800-840 (arctic & severe winter)(1)		860	815-835	815.0-850.0 à 20°C (22) / 815.0-865.0 à 20°C
Viscosity at 40°C, cSt, min-max	2.0 - 4.5		2.0-4.5 (temperate) / 1.2-4.0(arctic & severe winter)(1)		2.7 / 2.7 / 2.5 / 2 / 1.7	1.9-5.5	2.0-4.5 (mm²/s) / 2-4.5 (mm²/s)
Distillation, T10, °C, min - max							180 /
Distillation, T50, °C, min - max							245-295 / 245-310
Distillation , T85, °C, min - max							/ 360
Distillation, T90, °C, min - max				282-338(6)	360 / 360 / 350 / 330(7) / 330	360	
Distillation, T95, °C, max	360	360	360				370 /
Distillation, E180, vol%, max				10			
Distillation, E250, vol%, max				<65			
Distillation, E340, vol%, min				95(8)			
Distillation, E350, vol%, min				85			
Flash Point, °C, min	61.5		55	52(6)	50 / 50 / 50 / 45 / 45	40	38
Carbon residue 10%, wt%, max	0.2		0.3	0.35	0.1	0,15	0.25
Cold Filter Plugging Point, °C, max			+5 (class A temperate) to -44(arctic & severe winter)(1)		/ -1 / -5 / -12 / -19	-18	(9)
Cloud Point (CF), °C, max				-10 to -34(6)			
Pour Point (PP), °C, max					5, -2.5, -7.5, -20, -30	-23.0 (w) / 0.0 (s)	
Water and sediment, vol%, max	0.05			0.05		0.02	0.05
Water, mg.kg⁻¹, max			200				200 / 500
Ash, wt%, max	0.01		0.01	0.01		0.02	0.010
Lubricity, HFRR wear scar diam à 60°C, micron, max	0.460		460	520		400	
Copper corrosion, 3hr at 50°C, merit (class), max	1		1	3		1	1
Oxidation stability, mg/100ml, max	25		5				2.5 /
FAME content, vol%, max	5.0	7(10)	7	5		5	10(11)
Conductivity at ambient temp, pS/m, min	50			25			25

(1) Depends on climate rating.
(2) Cetane number or cetane index may be used.
(3) Winter (Nov. 15 - Feb. 18): 48.
(4) Alternatively, the determination of the cetane number using the method described in Brazilian standard NBR 14759 (ASTM D4737) is permitted when the product does not contain a cetane improver, with a minimum limit of 45. In cases of nonconformity, cetane testing should be done. The producer and importer must include information on any use of a cetane improver in the quality certificate. Note that the cetane number does not translate into the quality of ignition of diesel containing biodiesel and/or cetane booster.
(5) Other limits may apply to selected areas.
(6) When a cloud point is less than -12°C is specified, it is permitted and normal blending practice to combine Grades No.1-D and No.2-D to meet the low temperature requirements. In that case, the minimum flash point shall be 38°C, the minimum viscosity at 40°C shall be 1.77 cSt, and the minimum 90% recovered temperature shall be waived.
(7) T90 should be 350°C max if viscosity is 4.7 cSt max.
(8) Only applicable to countries with arctic or severe winter conditions.
(9) Only applicable to countries with arctic or severe winter conditions.
(10) Either the specification for minimum cetane index or that for maximum total aromatics must be met.
(11) Only applicable for a diesel-biodiesel blend.

Table 2.
Diesel fuel specification.

PROPERTY	AUSTRALIA	EUROPE	USA	BRAZIL
Spec Name / Year	Fuel Standard (Ethanol E85) Determination (2012)	CEN/TS 15293 (2011)	ASTM D 5798 (2013)	Resolution ANP #19 (2015)
Source	Department of the Environment	CEN/TS 15293	ASTM International	ANP
Grade	E85	E85	E85-Class 1 E85-Class 2 E85-Class 3 E85-Class 4	EAC (Anhydrous Ethanol)/ EHC (Hydrous Ethanol)
RON, min	100	104(1)		
MON, min	87	88(1)		
Sulfur, ppm, max	70	10	80	Note
Lead, g/l, max	0.005		(2)	
Benzene, vol%, max	0.35			
RVP à 37.8°C (100°F), kPa, min-max	38-65	35-60 (s) / 50-80 (w)(2)	38-62 / 48-65 59-83 / 66-103	
Density at 15°C, kg/m³, min-max		760-800		791.5 máx (11) à 20°C / 805.2-811.0(11) à 20°C
Distillation, FBP, °C, max	210			
Methanol, vol%, max	0.5	1.0	0.5	0.5
Ethanol, vol%, min-max	70-85	70-85 (s) / 50-75 (w)(2)	51-83	98 / 94.5
Ethers (5 or more C atoms), vol%, max	1	11		
C3-C5 alcohols, ppm, max	2 vol%(4)	6	2 vol%(4)	
Phosphorus, g/l, max	0.0013	0.00015	(5)	
Oxidation stability, minutes, min	360	360		
Water, vol%, max	1 wt%	0.4	1 wt%	0.7 (wt%) / 7.5 (wt%)
Existent gum (solvent washed), mg/100ml, max	5	5	5	
Existent gum (solvent unwashed), mg/100ml, max			20	
Chloride, inorganic, ppm, max	1	1.2		1
Copper, ppm, max	0.1	0.1	0.07	0.07
Copper corrosion, 3h, 50°C, merit (class), max		1		
Color			Clear & bright	(6) / (7)
pH, min-max	6.5-9.0	6.5-9.0	6.5-9.0	/ 6.0 a 8.0
Acidity, wt%, max	0.006	0.005(8)	0.005(8)	
Electrical Conductivity, µS/m, max		1.5		300
Sulfate, ppm, max	4	4		4
Appearance		Clear and bright	Clear and bright	LII(9)
Total acidity, Max, mg/L				30
Alcohol content, %wt				99.3 min / 92.5-94.6
Residue by evaporation, mg/100 mL, max.				5
Hydrocarbon content, %vol, max				3
Iron content, max. (mg/Kg)				5
Sodium content, max. (mg/Kg)				2

* Until 2004, the main use of ethanol in Japan was for beverage production (Buainain AM. Cadeia Produtiva de Agroenergia. 2007. p. 32).
** At the time of writing, South Korea uses around 140 million gallons of ethanol a year, but just for beverages and industrial uses. (https://grains.org/south-korean-trade-team-focuses-on-fuel-ethanol-potential/).
(1) Recommended value.
(2) Lead is not permitted to be added, according to Federal Regulations; the lead limit for gasoline is 0.013 g/L.
(3) Summer: Class A May 1 - Sept. 30, Winter: CEN notes that each country must choose which climate classes to use for other periods of the year.
(4) C3-C8.
(5) Phosphorus may not be added, according to federal regulations; the phosphorus limit in gasoline is 0.0013 g/L.
(6) Orange after the addition of the dye specified in Table VII of these technical regulations.
(7) May not be orange or blue, which are for anhydrous ethanol and aviation fuel, respectively.
(8) As acetic acid.
(9) Clear and free of suspended matter

Table 3.
Ethanol fuel specification.

PROPERTY	ÁUSTRIA	CZECH REPUBLIC	FRANCE	GERMANY	ITÁLY	USA	EUROPE	COLÔMBIA	BRAZIL
Spec Name	ON	CSN	Journal Oficial	DIN	UNI	ASTM	EN 14214	ICONTEC	
Appearance									LII[1]
Total Contamination, max. mg Kg⁻¹		24		20			24	24	24
Free Glycerin, max. wt%	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Monoglycerides, max. wt%			0.8	0.8	0.8		0.8	0.8	0.8
Diglycerides, max. wt%			0.2	0.4	0.2		0.2	0.2	0.2
Triglycerides, max. wt%			0.2	0.4	0.1		0.2	0.2	0.2
Total Glycerin, max. wt%	0.24	0.24	0.25	0.25		0.24	0.25	0.25	0.25
Carbon Residue, max. wt%	0.05	0.05		0.05		0.05	0.3²		0.05⁽²⁾
Fatty Acid Methyl Esters, min. wt%			96.5		98		96.5	96.5	96.5
Flash Point, min. ºC		100	110	100	110	130	120	120	100
Methanol or ethanol, max. wt%	0.2		0.1	0.3	0.2		0.2	0.2	0.2
Sulfated Ash, max. wt%	0.02	0.02		0.02			0.02	0.02	0.02
Sodium + Potassion, max. mg.Kg⁻¹							5		5
Density at 15ºC, min-max. Kg m⁻³	850-890	870-890	870-900	870-900	860-900		860-900	860-900	850-900⁽³⁾
Viscosity at 40ºC, min-max. mm² s⁻¹	3.5-5.0	3.5-5.0	3.5-5.0	3.5-5.0	3.5-5.0	1.9-6.0	3.5-5.0	1.9-6.0	3.0-6.0
Iodine, max. g I2 100g⁻¹	120		115		115		120		Note
Distillation T90, max. ºC			360		360	360		360	
Cetane Number, min-max.	49	48	49	49		47	51	47	Note
Clould Point, ºC					Anotar				
Cold Filter Plugging Point, min-max. ºC	0/-15	-5		0/-20			Por região		By region
Poor Point, min-max. ºC			-10		0/-5		Por região	3	

(1) Clear and free of suspended matter
(2) Determination of carbon residue on 10 % (volume) distillation residues
(3) Specification 20ºC;

Table 4.
Biodiesel fuel specification.

Analytical methods for monitoring gasoline and diesel adulteration were the target of a recent review [2], emphasizing the determination of their different properties, such as density, distillation curve, octane rating, vapor pressure, etc., using physicochemical methods and chromatographic and spectroscopic techniques. Nondestructive analytical methods for identifying off-spec levels of biodiesel in diesel-biodiesel blends and adulteration of the blend have also been covered in a recent review [20], focusing on first-order multivariate calibration models. In this chapter, different colorimetric techniques that can be used in fuel quality control are addressed, especially simple, rapid, low-cost methods that have the potential capacity to detect fuel adulteration in the field.

2. Colorimetric methods for monitoring fuel quality in laboratories

The colorimetric assays used on a routine basis in fuel quality control laboratories in Brazil are visual color, ASTM color, and the copper strip corrosion test.

In Brazil, hydrous ethanol should be colorless, while anhydrous ethanol has an orange dye added to it. This difference is designed to prevent the kind of fraud known as "wet ethanol," whereby fraudsters acquire anhydrous ethanol directly from the plants that produce it, evading taxes, then mix it with water, and sell it on as hydrous ethanol. Regular gasoline, additized gasoline, and premium gasoline can be told apart visually by their color: regular gasoline ranges from colorless to yellow, while the other two are colored with a dye, which may be of any color but blue (which is reserved for aviation fuel), but which is normally green for additized and purple for premium [11, 21]. All the dye does is enable the two products to be distinguished from one another; it has no effect on their specifications. Meanwhile, diesel S10 (containing 10 mg kg⁻¹ sulfur) is naturally yellow in color, while S500 (500 mg kg⁻¹ sulfur) is dyed red to prevent incorrect refueling with this diesel, whose high sulfur level means it could cause damage to vehicles with more sophisticated engine technologies like selective catalytic reduction or exhaust gas recirculation systems.

The standard test method for the ASTM color of petroleum products (ASTM 1500:2012) is used on samples of diesel S10 (which contains no dye). The test involves transferring a sample of the product to a test tube and comparing its color with the color of standard colored glass disks, which represent a range of values from 0.5 to 8.0. A standard light source is used in this test [22]. Corgozinho et al. have developed a method using partial least squared regression with molecular absorption spectrophotometry to determine the ASTM color of diesel in the 0–6.5 range, offering greater precision than the standard colorimetry test [23].

Corrosiveness is determined using the copper strip test in Brazil (ABNT NBR 14359), the USA (ASTM D130), and Europe (EN ISO 2160). It consists of immersing a standard copper strip in a sample of biodiesel in a corrosion bath for 3 hours at 50°C. The strip is then rinsed in solvent and compared with an ASTM copper strip corrosion standard, which has different colors that correspond to different levels of corrosion, classified from 1 to 4 [24–26].

3. Colorimetric methods for monitoring fuel quality with potential for use in the field

3.1 Biodiesel

3.1.1 In a diesel-biodiesel blend

The level of biodiesel in a diesel-biodiesel blend is determined in a laboratory by observing the mid-infrared absorption of the $C=O$ bond present in the fatty acid methyl esters (FAMEs) that constitute the biodiesel. Although this test gives satisfactory results, it cannot be used in the field, which is a major drawback, as fuel distributors need to test the fuel when they are adding biodiesel to diesel on a commercial scale. Furthermore, the accuracy of the results will be compromised if the biodiesel itself is adulterated with vegetable oil or animal fat, whose constituent triglycerides also have $C=O$ bonds.

The conversion of esters into hydroxamates by their reaction with hydroxylamine [27–29], forming complexes of a red to violet color caused by the reaction with Fe^{3+}, has been used to confirm esters in organic analysis procedures. **Figure 1** shows the reaction by which this complex is formed.

Figure 1.
Chemical reactions involved in the test for esters known as the hydroxamic acid test, used to test for the presence of biodiesel in fossil diesel. Adapted from Silva et al. [29].

Silva et al. used this test to develop a new spectrophotometric method to determine biodiesel levels in diesel-biodiesel blends ranging from B0 (pure fossil diesel) to B5 (fossil diesel containing 5% biodiesel), in which the esters from the biodiesel present in the mixtures react with hydroxylamine chlorhydrate in an alkaline solution, forming alkaline salts from the hydroxamic acid, followed by acidification, to form hydroxamic acid, followed by a reaction with Fe^{3+} ions. The complex formed, the intensity of whose color is proportional to the biodiesel content, is extracted with *n*-hexane/*n*-heptane, forming an upper phase with a yellow, orange, or red color, depending on the biodiesel concentration, as shown in **Figure 2**. Absorbance can be measured using spectrophotometry at 420–440 nm. The linearity, limit of detection, limit of quantification, accuracy, selectivity, and specificity results indicate that the proposed method is adequate for analyses of biodiesel in diesel-biodiesel blends. A simplified method was proposed for qualitative analyses for use at filling stations [29, 31].
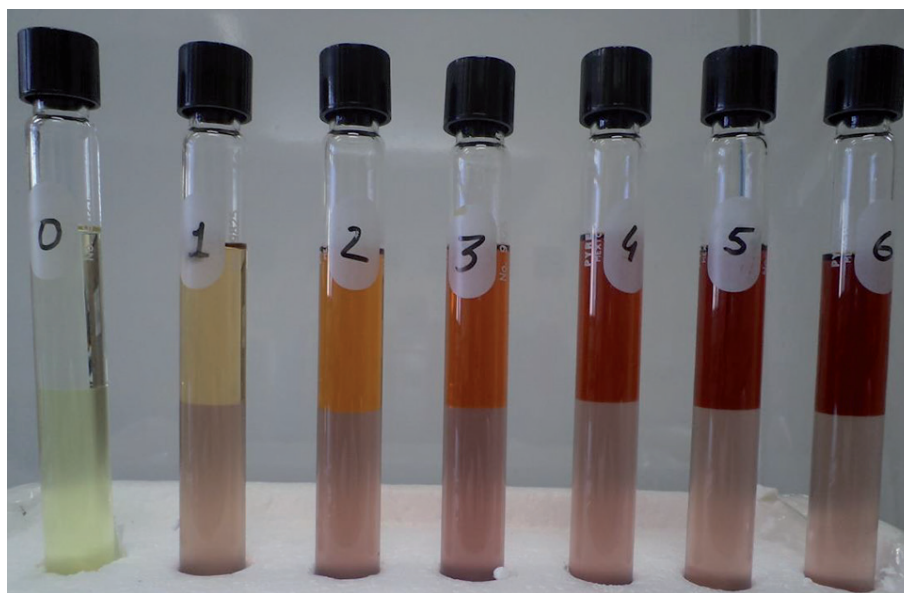
Figure 2.
Color scale of samples of fossil diesel containing biodiesel at 0–6% v/v, showing intensities proportional to the concentrations of biodiesel in the diesel, for semiquantitative analysis observable by the naked eye. Source: Santos [30].

Using the same reaction, Santos developed a simple, practical, rapid method that could be used in the field for semiquantitative identification by the naked eye of biodiesel in diesel-biodiesel blends ranging from 0% to 6% v/v biodiesel [30]. A similar method was developed by Leite and Fernandes for the 0–7% range [32]. What sets these methods apart from their predecessors is the separation of the biodiesel from the blend before the hydroxamic acid test. To do this, solid-phase extraction is conducted using a chromatographic column adapted from a 3mL disposable plastic syringe into which around 0.4 g silica gel is inserted, supported by a cotton plug (see **Figure 3a**). The diesel-biodiesel blend is introduced as if in frontal chromatography, pushed by a plunger, generating a less polar diesel fraction (F1) followed by a more polar fraction containing biodiesel (F2), displaced by the addition of ethanol (see **Figure 3b**).

By using seven reference samples of the diesel-biodiesel blend containing 0, 1, 2, 3, 4, 5, and 6% (v/v) biodiesel, the concentrations of which were confirmed by the laboratory reference method [33], a standard table of colors was prepared that could be used for the semiquantitative analysis of the percentage of biodiesel, as in **Figure 2**, since the intensity of the color formed by the ferric hydroxamate complex is proportional to the level of biodiesel present in the sample. By comparing the observed colors with the standard color table, it was possible to determine the
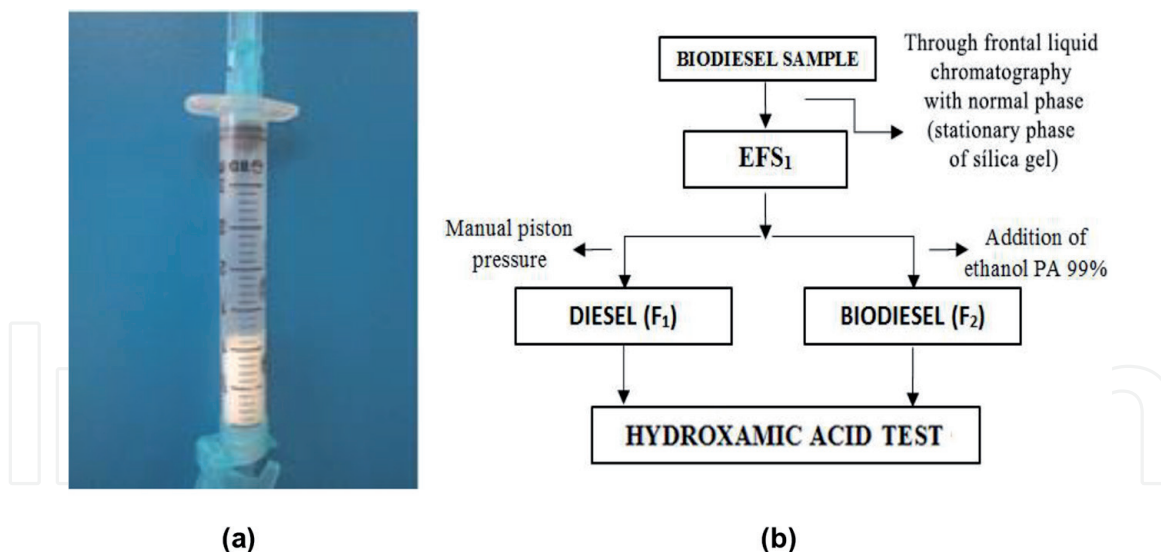
Figure 3.
(a) Chromatographic column adapted from a disposable plastic syringe; (b) solid-phase extraction of the biodiesel from the diesel-biodiesel blend before undergoing the hydroxamic acid test.

biodiesel concentration semiquantitatively with the naked eye, with a relative error of around 1%. This could be done in the field to find out whether samples are off spec. The proposed method was used on 33 samples of diesel containing different biodiesel concentrations and was found to be equivalent to the laboratory reference method (EN14078) by Student's t-test, with 95% confidence [30].

Another method—also adaptable for use in the field—has been developed for determining biodiesel in a diesel-biodiesel blend and for identifying the presence of vegetable oil in this blend. After solid-phase extraction using a silica stationary phase (EFS_1), the fraction composed of biodiesel and potentially vegetable oil is then put through another solid-phase extraction with an aminopropyl stationary phase (EFS_2) to separate the biodiesel from any vegetable oil (**Figure 4a**). For use in the field, the stages involving a manifold for solid-phase extraction and nitrogen-supported solvent evaporation are replaced by the manual use of plungers in the solid-phase extraction cartridges, which has yielded viable preliminary results. **Figure 4b** illustrates the procedures that can be done in the field to obtain the complexes. **Figure 5** also illustrates the use of the hydroxamic acid test on both fractions to confirm the presence of esters, which has also proven satisfactory for indicating adulteration with 1% or more vegetable oil in diesel containing 5% biodiesel [32].

Any sample identified in the field as potentially adulterated with vegetable oil could be sent to a laboratory for confirmation via more precise analytical techniques, like high-performance liquid chromatography. As such, both methods (semiquantitative identification of the percentage of biodiesel in diesel and the identification of any vegetable oil in the blend) are potentially effective for field analyses not only for their ease of use but also for their speed. Furthermore, the fact that the methods use low-cost, low-toxicity materials and reagents makes them even more attractive.

The sequence of operations for the hydroxamic acid test, illustrated in **Figure 5**, is easily adapted for field analysis.

Costa has also developed an alternative method for determining the level of biodiesel in fossil diesel using the hydroxamic acid test in association with image processing and a colorimeter and compared it with the standard method (EN 14078). After the hydroxamic acid test, the images were photographed, and the
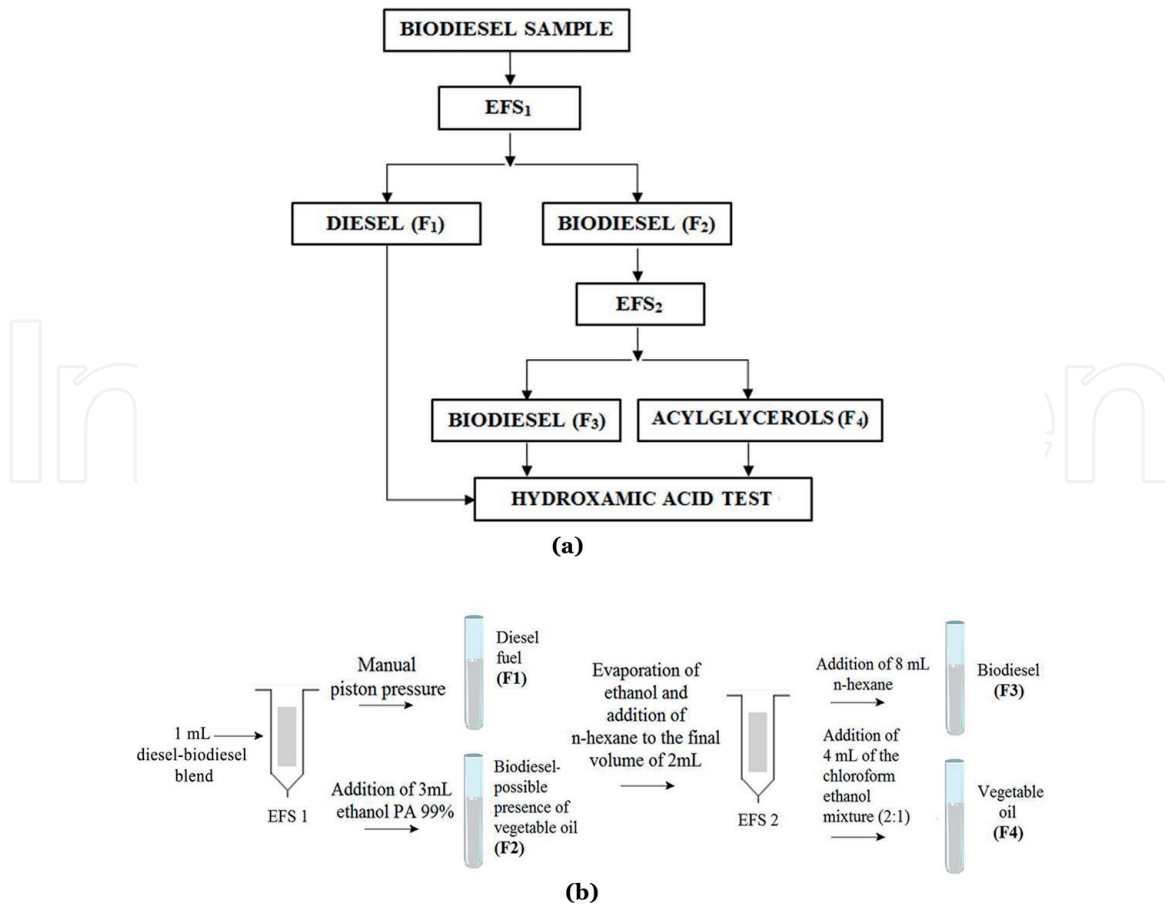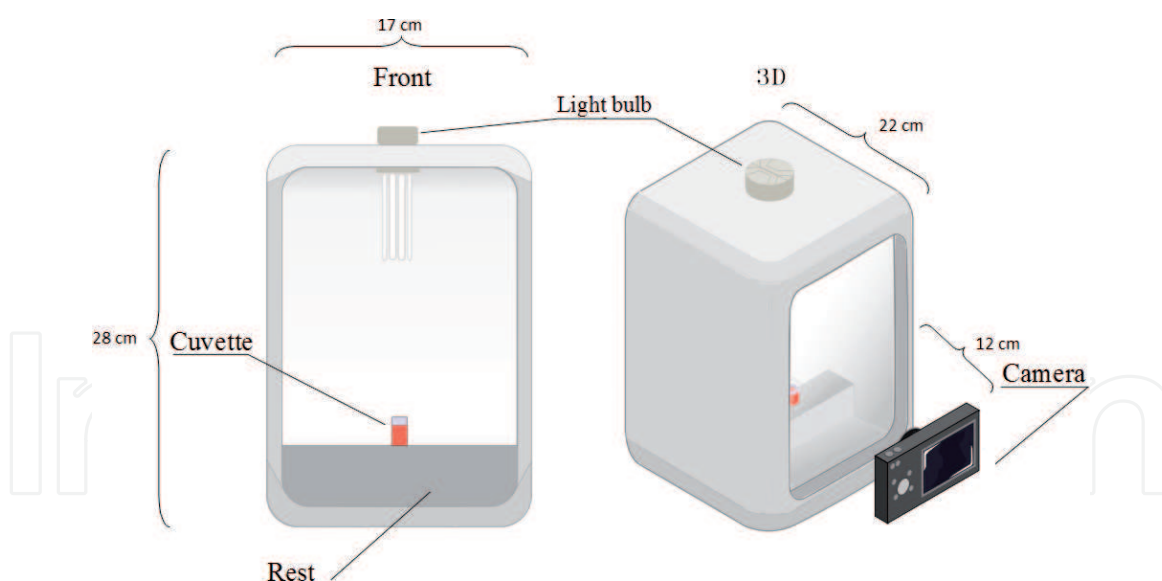
Figure 4.
(a) Sequence of operations for solid-phase extraction to separate biodiesel from diesel-biodiesel blends in a silica column (EFS₁) and to separate any vegetable oil or animal fat contaminating the biodiesel in an aminopropyl column (EFS₂). (b) Field test made up of solid-phase extraction followed by hydroxamic acid test.
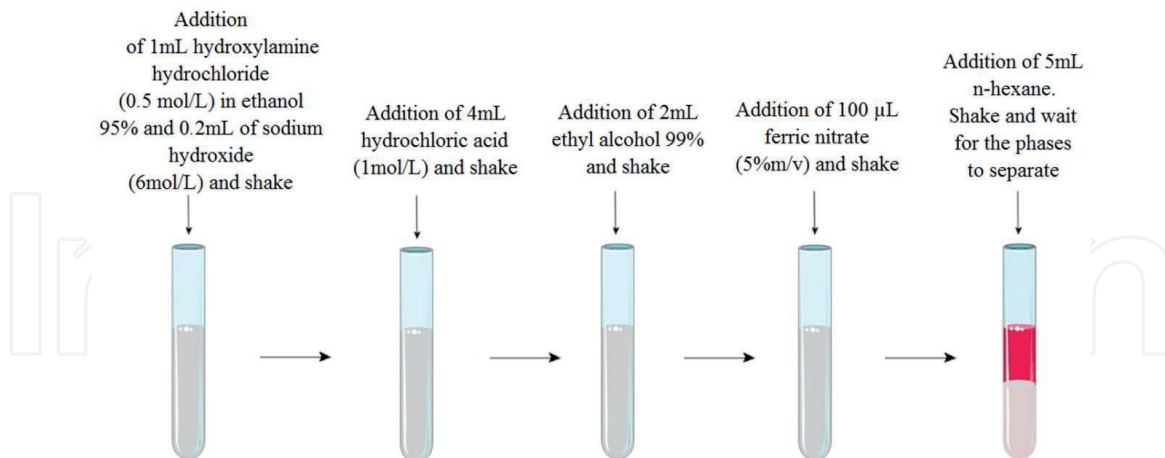
Figure 5.
*Schematic representation of hydroxamic acid colorimetric test. Adapted from Costa [34].*

Colorsys program was used to create calibration curves based on color vs. biodiesel concentration, enabling the color determination of biodiesel content by the intensity of the color. It was found that the hydroxamic acid test associated with image processing was adequate for detecting and quantifying the biodiesel content of diesel-biodiesel blends because the results given by the method were statistically similar to those given by the reference method using infrared spectroscopy (EN 14078). Furthermore, it is easily adapted for field analysis (**Figure 6**) [34].

Figure 6.
Schematic representation of procedure for taking pictures of samples (front and perspective views). Source: Costa [34].

Solvatochromism is the term used to describe the phenomenon of color change of a solute when it is dissolved in different solvents, resulting in a change in the position of absorption or emission of its spectroscopic band. When these changes of position occur in the visible range, they exhibit different colors that can be detected by the naked eye and can be used as sensors to determine the composition of mixtures [59–61].

Fong and Xue have developed an optical sensor to detect biodiesel in diesel-biodiesel blends based on the solvatochromic behavior of the dye called Nile Blue chloride, which turns blue when dissolved in ethanol or methanol and pink when in contact with biodiesel. **Figure 7** illustrates the change in color, enabling the direct, rapid detection of variations from 0.5 ppm to 20% v/v biodiesel in diesel-biodiesel blends [35].
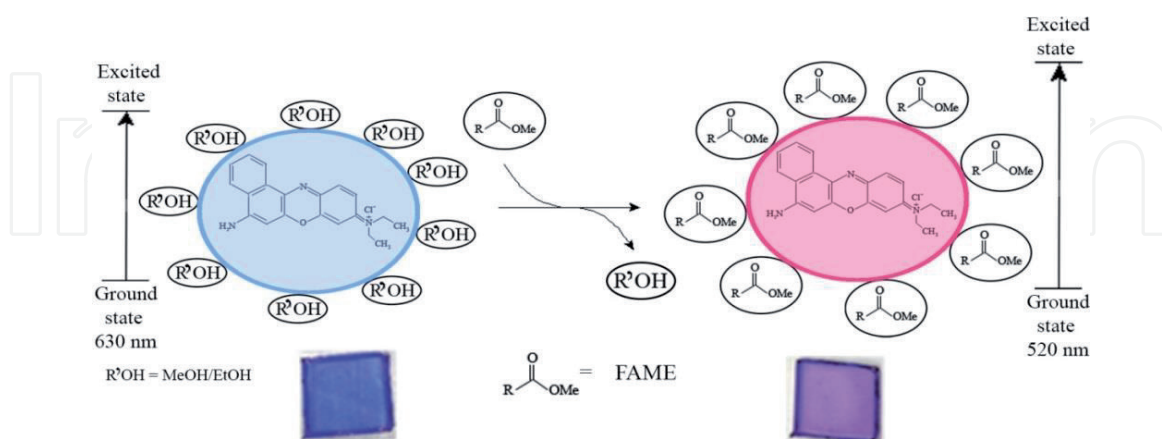
Figure 7.
Change in color of Nile Blue chloride from blue (without diesel) to pink (exposed to biodiesel), due to solvatochromic effects. Adapted from Fong and Xue [35].

As Nile Blue chloride is not soluble in nonpolar solvents, like diesel, it was encapsulated in an ethyl cellulose polymer, dissolved in methanol or ethanol in the form of a fine film that turns blue in alcohols, with absorbance at 610 nm, and pink when

in contact with biodiesel, with absorbance at around 520 nm. Exposing the sensor containing the Nile Blue chloride to diesel resulted in no change in color or change in its stability. When it was exposed to biodiesel, it changed from blue to pink, which can be attributed to the alcohols surrounding the sensor being replaced by FAMEs from the biodiesel, resulting in a solvatochromic effect. The sensor provides a quick, direct method compared with methods involving gas chromatography or infrared spectrophotometry, presenting a linear response between color intensity and biodiesel concentration for low concentrations, between 0.5 and 30 mg kg^{-1}. For high concentrations of biodiesel (up to 20% v/v), absorbance may be linearly adjusted by a logarithmic function [35].

3.1.2 Free and total glycerin

Free or total glycerin in biodiesel can be determined by spectrophotometry, since the reactions shown in **Figure 8** result in a colored compound, as initially described by Greenhill [37]. Several publications have used similar methods, taking advantage of kits used to analyze triglycerides in blood [36, 38–40]. In the presence of adenosine-5'-triphosphate (ATP) and the enzyme glycerol kinase (GK), glycerol produces diphosphate adenosine-5'diphosphate (ADP) and glycerol-3-phosphate (G-3-P; reaction 1), which, in the presence of glycerol phosphate oxidase (GPO) and oxygen, produces dihydroxyacetone phosphate (DAP) and hydrogen peroxide (H_2O_2; reaction 2). Then, in the presence of a peroxidase, an oxygen acceptor (OA), and 4-aminoantipyrine (4-AAP), water and a colored compound (CC) are formed (reaction 3):

$$\text{Glycerol} + \rightarrow \text{G-3-P} + \text{ADP (in the presence of GK)} \qquad \textbf{(Reaction 1)}$$
$$\text{G-3-P} + \text{O2} \rightarrow \text{ATP DAP} + \text{H2O2 (in the presence of GPO)} \qquad \textbf{(Reaction 2)}$$
$$\text{H2O2} + \text{4-AAP} + \text{OA} \rightarrow \text{CC} + \text{H2O (in the presence of peroxidase)} \qquad \textbf{(Reaction 3)}$$
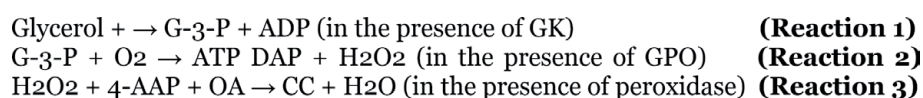
Figure 8.
Glycerol reactions generating a colored compound analyzable by spectrophotometry. Adapted from Muniz et al. [36].

To determine total glycerin, it is necessary to use solid-phase extraction in an aminopropyl cartridge to separate the biodiesel (FAMEs) from the fraction containing the free glycerin (FG), monoacylglycerols (MAGs), diacylglycerols (DAGs), triacylglycerols (TAGs), and combined glycerin, as shown in **Figure 9a** [36]. To determine free glycerin, the biodiesel (FAME) is separated and isolated from the fraction containing the free glycerin (FG) by solid-phase extraction in a silica cartridge (see **Figure 9b**).

3.2 Ethanol

Budag et al. have used four dyes as solvatochromic probes to study the effect of adding ethanol to pure gasoline. The dye 2,6-di(4-tert-butylphenyl)-4-[2,4,6-tri (4-tert-butylphenyl)pyridinium-1-yl]phenolate (t-Bu$_5$RB), for example, has a greenish blue color in gasoline, is violet in ethanol, and is bluish green in a mixture of 25% ethanol in gasoline, which means ethanol in gasoline can be detected by the naked eye. The development of analytical methods to determine fuel quality based on these promising probes has been discussed. Based on the spectroscopic determination of the maxima on the UV-visible spectra, the respective transition energy can be calculated, which is related to the composition of the fuel, opening up the potential for the development of an analytical method [41].
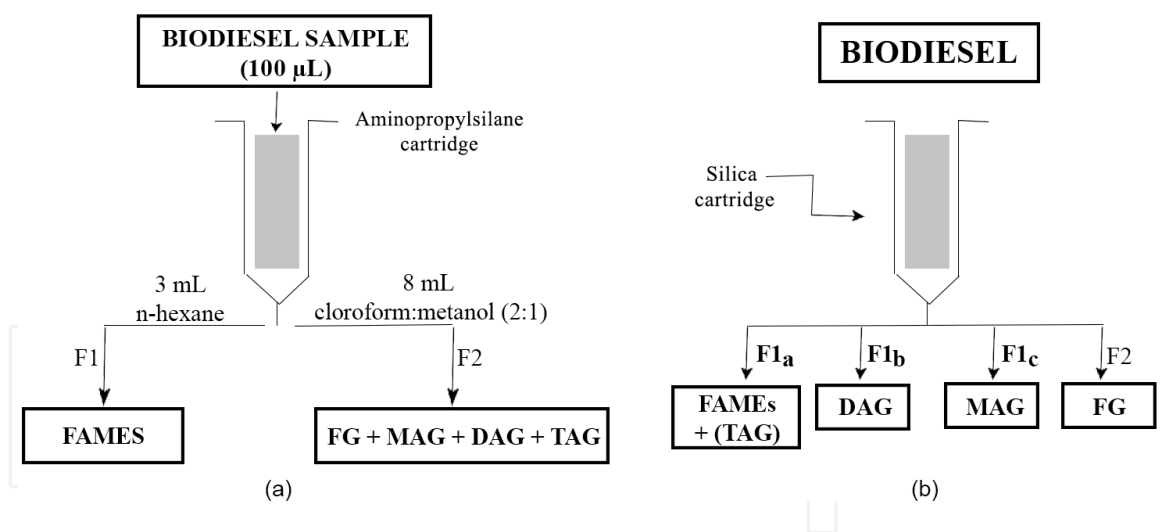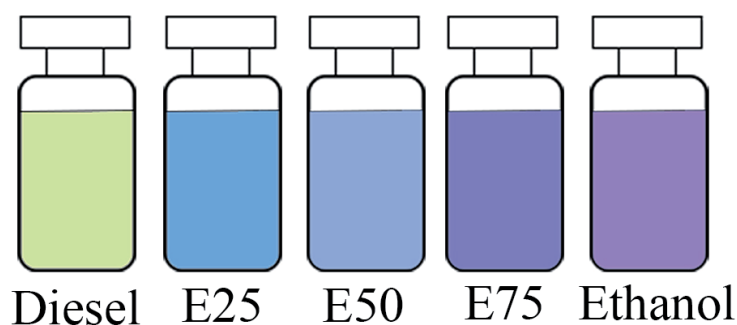
Figure 9.
(a) Solid-phase extraction in aminopropyl cartridge to separate and isolate total glycerin, made up of fractions of free glycerin (FG) and combined glycerin, monoacylglycerols (MAGs), diacylglycerols (DAGs), and triacylglycerols (TAGs). Source: Muniz et al. [36]. (b) Solid-phase extraction in silica cartridge to separate and isolate FG from the fractions containing FAME + TAGs, DAGs, and MAGs. For example, for 0.150 mL biodiesel, F_{1a} is eluted with 15 mL petroleum ether, (F_{1b}) with 40 mL of a mixture of 35% ethyl ether and 65% petroleum ether, (F_{1c}) with 40 mL ethyl ether, and (F_2) with 12 mL ethanol. Source: Serralvo Neto et al., 2018 (FR 1872032) [40].

El Seoud et al. have used the same dye in analytical chemical experiments for undergraduates, in the analysis of diesel-ethanol blends, also observing a solvato-chromic effect, with colors varying as the composition of the mixture changes, as shown in **Figure 10** [42].

Figure 10.
Color variation of solutions of t-Bu₅RB and pure diesel and ethanol and in solutions of ethanol (%v/v) in diesel. Adapted from El Seoud et al. [42].

Galgano et al. have also used the solvatochromic dye 2,6-bis[4-(tert-butyl) phenyl]-4-{2,4,6-tris[4-(tert-butyl)phenyl]-pyridinium-1-yl}phenolate (t-Bu)5RB) to make quantitative analyses of bioethanol and mixtures of bioethanol with gasoline and water in an experiment based on a constructivist approach for under-graduates in a chemistry class [43].

Solutions of the dye in ethanol-water and anhydrous ethanol-gasoline mixtures evidenced solvatochromic effects, with the color changing according to the composition of the mixture, as shown in **Figure 11**.

The results of using solvatochromic effects of different dyes in mixtures, especially involving additized or altered fuels, seem extremely promising for the development of alternative colorimetric methods with field applications.

3.2.1 Methanol

The maximum methanol content permitted in ethanol and gasoline in Brazil is 0.5% v/v, and the reference method for its detection uses gas chromatography [44].
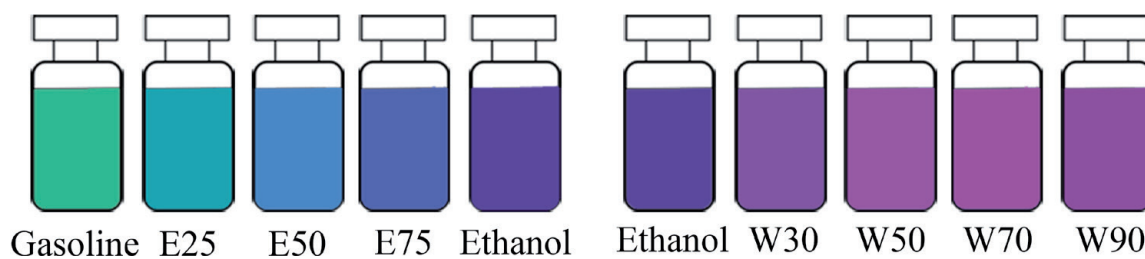
Figure 11.
Range of colors of solutions of the dye in binary mixtures of gasoline-ethanol (pure gasoline, E25, E50, E75, pure ethanol) and binary mixtures of ethanol-water (pure ethanol, W30, W50, W70, W90). Adapted from Galgano et al. [43].

In view of cases of ethanol adulteration with methanol identified in the country, a colorimetric kit has been designed for use in the field to identify this form of adulteration of anhydrous ethanol and hydrous ethanol and in gasoline with ethanol [45–47].

The procedure is based on visual detection of a violet blue color as a result of the reaction of aldehydes with Schiff's reagent used in qualitative organic analysis to identify functional aldehyde groups [48, 49]. The color is obtained using the aforementioned colorimetric kit by the following reactions:

1. Selective oxidation of the methanol adulterant to formaldehyde in the presence of potassium permanganate in an acid medium

2. Addition of oxalic acid in an acidic medium to reduce the excess of potassium permanganate, leaving the solution colorless

3. Formation of Schiff's reagent by the reaction of *p*-rosaniline with sodium metabisulfite in an acid medium

4. Addition of Schiff's reagent and observation of a violet blue color

The nonappearance of a color indicates the absence of methanol. When the solution turns violet blue, this is a qualitative indication of the presence of methanol in the fuel. A comparison of the intensity of the color with that of a reference solution containing 0.5% v/v methanol (the maximum permitted) enables conformity/non-conformity with specifications to be determined in the field.

Figure 12 shows the results of the samples of hydrous ethanol containing 0, 0.3, 0.5, and 1.0% methanol, showing the photos of the solutions after the test sequence. The higher the concentration of methanol in the sample, the stronger the blue of the solution. As expected, the blank, containing just ethanol, is colorless.
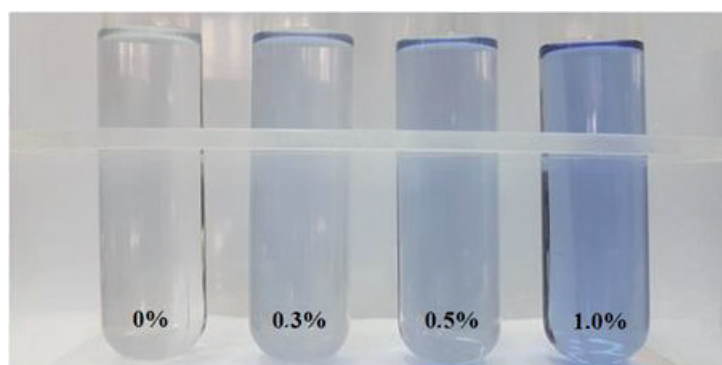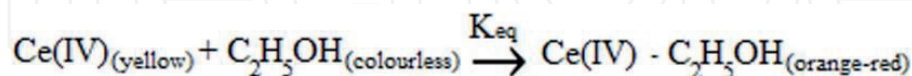

Figure 12.
Schiff test applied to samples of pure ethanol and ethanol contaminated with 0.3, 0.5, and 1.0% methanol.

3.2.2 Water

In Brazil, ANP Resolution #19, of 2015, states that hydrous ethanol fuel may contain up to 7.5% water [50]. Giordano et al. have developed a simple, rapid, portable, low-cost method that can be used in the field to indirectly determine water in ethanol fuel. The system is based on a colorimetric reaction between ethanol and ceric oxide (Ce(IV)), as shown in **Figure 13.** When a solution of ammonium cerium (IV) nitrate ($[(NH_4)_2Ce(NO_3)_6]$), which is yellow in color, is mixed with ethanol, an intense orangey-red color immediately appears because of the formation of Ce(IV)-ethanol (1:1) complexes [51].

$$Ce(IV)_{(yellow)} + C_2H_5OH_{(colourless)} \xrightarrow{K_{eq}} Ce(IV) - C_2H_5OH_{(orange-red)}$$

Figure 13.
Colorimetric reaction between the reagent Ce(IV) and ethanol. Adapted from Giordano et al. [51].

The device is made up of mechanically connected layers of acrylic, a sample reservoir, a light source, and a detector. A solution containing the reagents is added to the reservoir, together with aqueous solutions of ethanol (standards or real samples) prepared at 0.2–5.0% v/v and transferred to the reservoir. The volume introduced is approximately 70 μL. As soon as the solutions are mixed, the reactions take place, as indicated by a change in color from yellow to orangey red.

Real samples of ethanol obtained from filling stations in Brazil were tested. The water concentrations were compared with those obtained by Karl Fischer titration (ASTM E203, reference method), and the data obtained by the two techniques were found to be statistically equivalent by Student's t-test, at a 95% confidence level [51, 52].

3.3 Gasoline

3.3.1 Methanol

The method for determining methanol in gasoline containing ethanol, applicable in the field, was described in 3.2.1.

3.3.2 Detergent-dispersant additives

Gasoline is additized with detergent-dispersant additives, which are designed to reduce the formation of deposits in engines and valves, enhance car engine efficiency, and ensure a cleaner combustion process, all of which has a positive impact on the environment. Although different types of additized gasoline have been available on the market for a long time, there is no reference method for analyzing the detergent-dispersant additives they contain.

Figure 14 illustrates the structure of some of the additives available on the market.

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Figure 14.
Structure of some types of additives available on the market. Source: Santos [53].

One factor that hampers the development of analytical methods for detergent-dispersant additives is that they are sold as packages, with the additives already dissolved in solvents compatible with the hydrocarbon composition of the fuel, without indicating their respective composition.

Santos et al. have developed two laboratory methods for analyzing detergent-dispersant additives in gasoline. One uses thermogravimetry to identify the type of additive in the gasoline, which is then quantified by size-exclusion chromatography with refraction index detector, while the other just uses thermogravimetry [53–55].

d'Avila and Souza have developed a method that can be used in the field for the qualitative and/or semiquantitative identification of detergent-dispersant additives in fuels and lubricating oils. It is based on differences in the chromatographic behavior, in nonpolar stationary phases like silica, of nonpolar fuels and oils that form the basis for lubricants, which, due to their hydrocarbon composition in nonpolar stationary phases like silica, are retained less than detergent-dispersant additives, which are polar. The basicity of amine groups in additives could be used to reveal their position in the chromatography column by the addition of different acid-base indicators, making the presence or absence of the additives in the fuels and lubricating oils unequivocal. The process could be used by customers, inspectors, producers, or even by distributors—i.e., by operators who are not necessarily technically qualified—because of the simplicity of the procedure and the interpretation of the results, as shown in **Figure 15**, for a gasoline additized with ethanol, as is commonplace in Brazil and in many other countries [56]. The stages are:

1. Extraction of the ethanol from the gasoline with a saline aqueous solution, as described in Brazilian standard NBR13992, which is available and executable at all fuel distribution stations to easily determine the ethanol content in the gasoline

2. Continuous introduction of gasoline without ethanol in the column made of a Pasteur pipette containing a polar adsorbent (e.g., silica), using a hypodermic syringe

3. Addition of an alcoholic solution of different acid-base indicators, followed by the addition of ethanol to remove any excess, revealing the presence of additive in the column due to the "turning" of the indicator and its change of color because of the change in pH caused by the presence of the additive in the column

When the fuel contains a detergent-dispersant additive, a colored ring is formed when the indicator changes color (in **Figure 15** exemplified by bromothymol blue), enabling qualitative identification by the naked eye. Semiquantitative identification may be possible, as the intensity of the color is proportional to the concentration of the additive in the fuel.
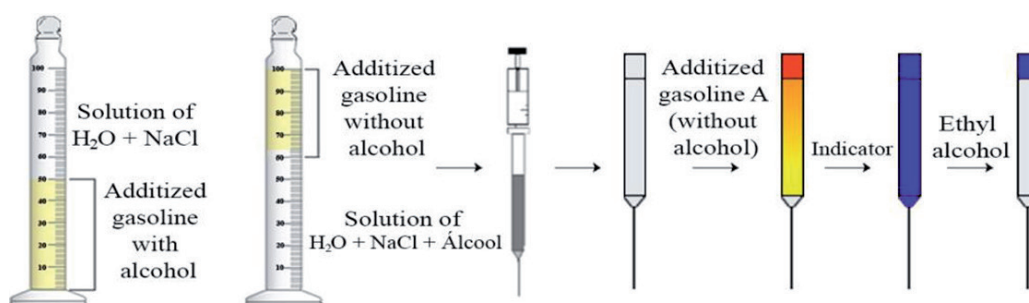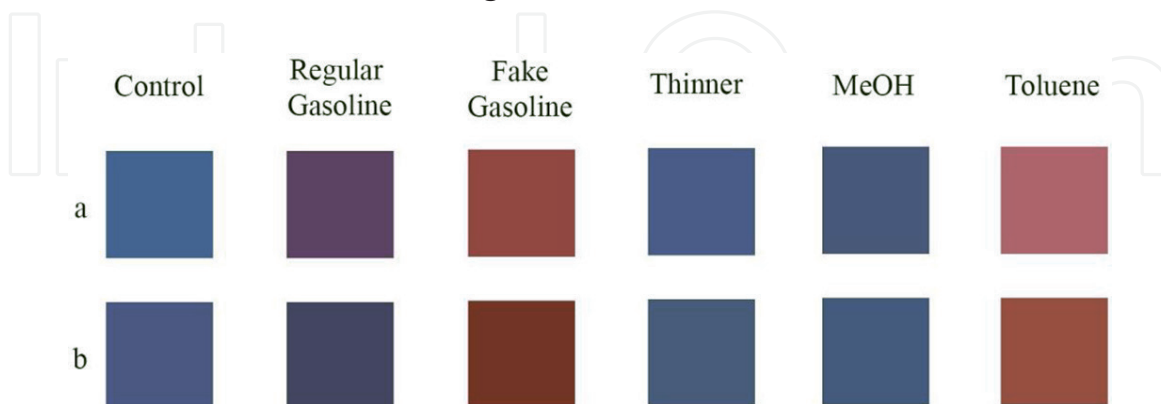

Figure 15.
Stages involved in the qualitative identification of detergent-dispersant additives in fuels, executable in the field. Source: d'Avila et al., 2012 (BR1020120292300/WO2014/075158A1) [56].

3.3.3 Adulteration

Lee et al. (2011) have developed a sensor to detect gasoline adulteration based on the solvatochromic behavior of a polydiacetylene (PDA) conjugated polymer embedded in matrix polymers of polystyrene and polyacrylic acid in the form of fibers. When exposed to pure and adulterated gasoline, they change to different colors and also change color in the presence of potential adulterants like paint thinner, methanol, and toluene (see **Figure 16**) [57].

Figure 16.
Photos after the exposure of the PDA fibers in polystyrene to commercial and adulterated gasoline, thinner, methanol, and toluene on glass (a) and on silica TLC plate (b). Adapted from Lee et al. [57].

4. Conclusions

The quality and adulteration of fuels have been the object of several publications, especially with the use of modern analytical techniques, such as chromatography, spectroscopy, and chemometric methods, but with very few examples of colorimetric techniques. Among the colorimetric techniques shown here, developed for fuel quality and adulteration monitoring, especially those that are based on simple, rapid, low-cost procedures with potential for application in the field, we highlight those traditionally used for the qualitative identification of functional groups in organic analysis. The colorimetric methods for detecting biodiesel and vegetable oil adulterants in diesel-biodiesel blends are based on the qualitative analysis of carboxylic esters using the hydroxamic acid test, which produces a colored ferric hydroxamate complex. The colorimetric detection of methanol in ethanol and in gasoline was also based on a reaction for identifying aldehydes by the reaction for the formation of a Schiff base, which is colored. These assays are based on spot tests developed and described by Fritz Feigl and colleagues, whose publications [27, 48, 58] describe an incommensurable archive of spot tests used in organic and inorganic analyses, which could serve as inspiration for the development of other colorimetric assays. Likewise, the solvatochromic effect of dyes and fibers, used as probes or sensors, has been used to detect biodiesel in diesel-biodiesel blends and water or ethanol in gasoline and even for detecting adulterants in gasoline. Publications that use solvatochromic effects for the analysis of fuels based on undergraduate experiments—showing their operational simplicity—are also highlighted [43]. The solvatochromic effect has been the target of several studies by Christian Reichardt and colleagues and also represents an opportunity for the development of new colorimetric techniques [59–61].

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