

# Development of laboratory protocols for the analysis of biodiesel quality parameters

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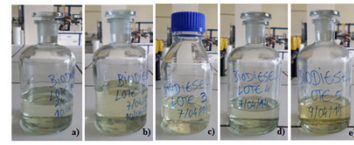
## Introduction/Objectives

- ✓ Production of Biodiesel by the classic base-catalyzed transesterification process of commercial oils;
- ✓ EN 14214 specifies the properties, the proper quality limits, and the respective characterization methods, for commercial biodiesel;
- ✓ Development of experimental protocols for the characterization of produced biodiesel, based on selected procedures established by the European Standard EN 14214.

## European Standard EN 14214

Property	Unit	Limits		Test method
		Minimum	Maximum	
FAME Content	% (m/m)	96,5	-	EN 14103
Density at 15°C	kg/m <sup>3</sup>	860	900	EN ISO 3675
Viscosity at 40°C	mm <sup>2</sup> /s	3,50	5,00	EN ISO 3104
Flash Point	°C	101	-	EN ISO 2719
Sulfur content	mg/kg	-	10,0	EN ISO 20846
Carbon residues (in 10% of distilled residue)	% (m/m)	-	0,30	EN ISO 10370
Cetane number	-	51,0	-	EN ISO 5165
Sulfated ash content	% (m/m)	-	0,02	ISO 3987
Water content	mg/kg	-	500	EN ISO 12937
Total contamination	mg/kg	-	24	EN 12662
Copper band corrosion (3 h at 50°C)	Rating	Class 1	-	EN ISO 2160
Oxidation stability, 110°C	hours	6,0	-	EN 15751
Acid value	mg KOH/g	-	0,50	EN 14104
Iodine value	g I <sub>2</sub> /100 g	-	120	EN 14111
Linolenic acid methyl ester (≥ 4 double bonds)	% (m/m)	-	12,0	EN 14103
Polysaturated methyl ester	% (m/m)	-	1	EN 14103
Methanol content	% (m/m)	-	0,20	EN 14110
Monoglyceride content	% (m/m)	-	0,80	EN 14105

- Batch 1** → Sunflower oil WB1
- Batch 2** → Peanut oil
- Batch 3** → Sunflower oil CB
- Batch 4** → Sunflower oil WB2
- Batch 5** → Soybean oil



a) batch 1; b) batch 2; c) batch 3; d) batch 4; e) batch 5

	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5
mass NaOH/250 mL oil (g)	1,4250	1,4125	1,3913	1,4000	1,3913
FFA content	0,84%	0,80%	0,73%	0,76%	0,73%
Biodiesel volume (mL)	192	188	206	212	224
Reaction yield	76,8%	75,2%	82,4%	84,8%	89,6%

- ✓ Methanol ratio of 20% (v/v) added to 250 mL batches of pre-heated oil at 55 °C, for 1 hour, under normal pressure;
- ✓ Base catalyst NaOH used at a ratio of 5% (g/L) plus the necessary amount to neutralize the free fatty acids (FFAs) content in a oil batch, previously measured by non-aqueous volumetric titration;
- ✓ Biodiesel volume obtained after several washing cycles and a drying procedure.

## 1. Density

- ✓ Density determined with a pycnometer of 5 mL using a procedure based on Portuguese standard NP 938 (1998);
- ✓ The density values of all biodiesel batches are very similar and are in the range allowed for commercial biodiesel;
- ✓ Batch 2 exhibits slightly lower density in relation to the other batches, on the other hand batch 1 shows the highest value measured.

	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5
Biodiesel density (kg/m <sup>3</sup> )	894	882	889	885	889

## 2. Water content

	Water content (mg H <sub>2</sub> O/kg biodiesel)	Average water content (mg H <sub>2</sub> O/kg biodiesel)
Batch 1	1st test: 439 2nd test: 488 3rd test: 442	456
Batch 2	1st test: 459 2nd test: 347 3rd test: 433	413
Batch 3	1st test: 503 2nd test: 412 3rd test: 505	473
Batch 4	1st test: 1319 2nd test: 1278 3rd test: 1320	1306
Batch 5	1st test: 1197 2nd test: 1106 3rd test: 1144	1149

- ✓ Water content analysis was performed using an automatic Karl Fisher Titrator, procedure based on ISO 12937 standard;
- ✓ Batches 1, 2 and 3 show water contents which do not exceed the maximum limit;
- ✓ Batches 4 and 5 display very high water contents, which could only be explained by a deficient (too short) heating cycle for the final drying.

## 3. Acid value

- ✓ Measurement of acid value was carried out according to the standard EN 14104;
- ✓ All acid values for every biodiesel batch are very similar and way below the maximum limit;
- ✓ Soybean oil biodiesel exhibits the higher acidity.

	Acid value (mg KOH/g)	Average acid value (mg KOH/g)
Batch 1	1st test: 0,14 2nd test: 0,13	0,13
Batch 2	1st test: 0,14 2nd test: 0,14	0,14
Batch 3	1st test: 0,14 2nd test: 0,15	0,14
Batch 4	1st test: 0,15 2nd test: 0,15	0,15
Batch 5	1st test: 0,17 2nd test: 0,16	0,16

## 4. Iodine value

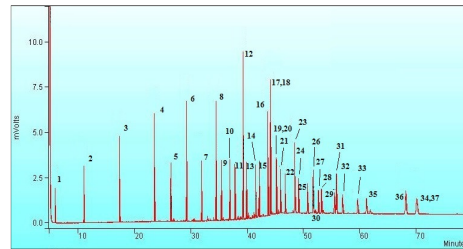
	Iodine value (g I <sub>2</sub> /100 g)	Average iodine value (g I <sub>2</sub> /100 g)
Batch 1	1st test: 157 2nd test: 158	158
Batch 2	1st test: 124 2nd test: 121	123
Batch 3	1st test: 160 2nd test: 160	160
Batch 4	1st test: 163 2nd test: 163	163
Batch 5	1st test: 163	163

- ✓ Iodine index measurement has been carried out according to standard EN 14111;
- ✓ Iodine index is a stability measure for biodiesel, a greater iodine index means a least stable, more unsaturated, biodiesel.
- ✓ Batch 2 is more stable than the other batches, because it shows greater content in the monounsaturated oleic acid (C18:1) and lower content in the polyunsaturated linoleic acid (C18:2).

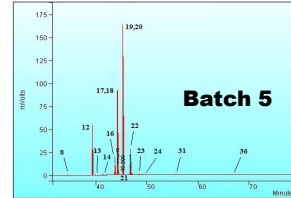
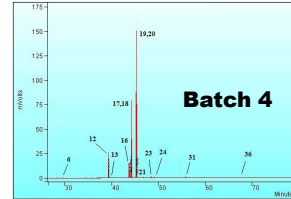
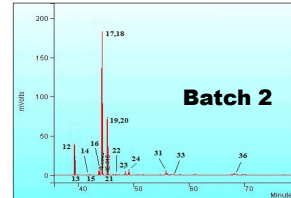
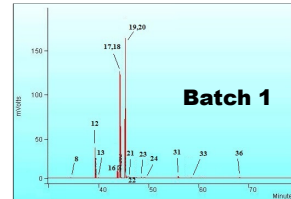
## Conclusions

- ✓ The application of a selected set of protocols provides a wide variety of analytical methods, ranging from volumetric to instrumental procedures, suitable for intensive chemistry laboratory training;
- ✓ Conjugation of a simple chemical reaction setup using widely available reactants and relatively mild conditions, with a flexible battery of analytical procedures, for the quality assessment of a well-known biofuel.

## 5. Fatty Acid Methyl Esters (FAME's) content - GC



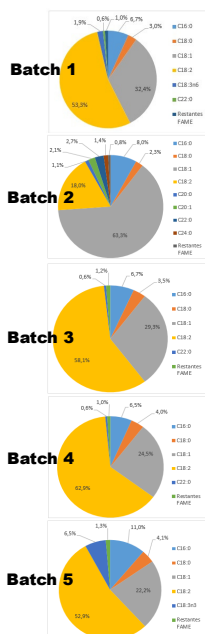
- ✓ FAME analysis with a gas chromatograph VARIAN, model 3800GC, with FID, and a Supelcowax 10 capillary column (30m x 0,25mm, 0,25µm)
- ✓ Method: gas - He (1 mL/min); injector - 250 °C; column - 50 °C (2 min), rise to 220 °C (at a 4 °C/min rate); detector - 250 °C; split ratio - 1:100; run time - 80 min
- ✓ Standard mix (47885-U SUPELCO) with 37 FAME's for quantification.



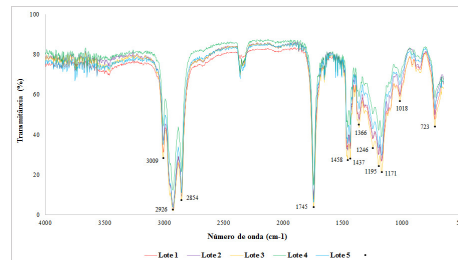
## Calibration

Order	Compound	N	Range (ppm)	y-intercept (µg/mL)	Slope (µg/mL)	R <sup>2</sup>	Detection limit (ppm)	Quantification limit (ppm)	CV (%) (1000 ppm)
1	C4:0	6	20-400	88,454837,39	9,7243,73	0,9289	140,56	468,52	31
2	C6:0	6	20-400	26,504151,73	18,7046,03	0,9489	61,97	393,04	32
3	C8:0	6	20-400	110,454178,72	31,2847,74	0,9862	90,56	303,88	24
4	C10:0	6	20-400	98,524589,05	41,1047,08	0,9848	63,07	210,22	21
5	C11:0	6	10-200	-38,813005,59	49,8748,96	0,9835	32,89	106,65	19
6	C12:0	6	20-400	-2,284780,06	48,8147,93	0,9865	59,50	198,32	15
7	C13:0	6	10-200	21,364833,76	49,5747,43	0,9886	27,33	91,10	13
8	C14:0	6	20-400	60,502048,77	50,5248,18	0,9867	58,89	196,31	9
9	C15:0	6	10-200	30,974819,20	52,6847,30	0,9901	25,37	84,57	11
10	C15:0	6	10-200	56,224923,55	53,7948,23	0,9880	28,01	93,36	6
11	C15:1	6	10-200	58,66444,27	49,3947,53	0,9881	27,89	92,96	9
12	C16:0	6	30-600	175,212626,56	50,3247,80	0,9878	85,13	285,75	7
13	C16:1	6	10-200	96,464817,17	51,0247,28	0,9895	26,13	87,10	10
14	C17:0	6	10-200	49,974844,86	50,1447,53	0,9884	27,49	91,63	7
15	C17:1	6	10-200	87,804009,91	52,1447,00	0,9847	31,61	105,38	7
16	C18:0	6	20-400	188,404178,92	47,3547,86	0,9866	92,23	197,42	6
17	C18:1	6	30-600	411,212999,32	50,5048,91	0,9841	96,89	322,96	7
18	C18:2	6	20-400	357,842726,82	52,5648,15	0,9727	85,12	283,75	6
21	C18:3	6	10-200	-21,40444,18	50,6247,53	0,9887	27,18	90,99	4
22	C18:3	6	10-200	139,354798,41	45,4747,12	0,9874	26,85	95,49	9
23	C20:0	6	10-200	187,814764,43	47,1547,86	0,9848	61,05	203,49	11
24	C20:1	6	10-200	54,654881,15	47,1547,86	0,9879	28,10	93,68	6
25	C20:2	6	10-200	97,23474,29	45,6447,79	0,9851	31,25	104,16	12
26	C20:3	6	10-200	177,794777,23	76,3048,28	0,9867	29,52	94,41	7
27	C20:3	6	10-200	18,384764,44	41,8246,81	0,9864	29,82	99,40	7
28	C20:4	6	10-200	67,604855,60	43,4747,63	0,9843	32,14	107,12	8
29	C20:4	6	10-200	180,834311,48	42,6746,88	0,9818	34,45	114,85	17
31	C22:0	6	20-400	410,884833,57	44,4648,16	0,9828	67,18	223,92	7
32	C22:1	6	10-200	15,564844,86	43,6447,53	0,9848	31,88	105,27	1
33	C22:2	6	10-200	159,054367,94	42,9541,14	0,9805	35,70	119,00	9
35	C23:0	6	10-200	117,894975,14	45,4548,69	0,9814	35,00	116,67	15
36	C24:0	6	20-400	126,064722,16	41,7747,70	0,9827	67,46	224,83	13
34,37	C22:0, C24:0	6	20-400	267,954204,95	39,6048,79	0,9817	69,01	230,02	16

- ✓ Identification of peaks corresponding to each FAME compound in the standard mix, and establishment of the typical retention times;
- ✓ Identification of FAME's present in each biodiesel sample;
- ✓ Quantification of FAME's in each biodiesel sample, using a calibration procedure based on the known FAME contents in the standard mix.
- ✓ All batches of biodiesel are very similar, being constituted essentially by palmitic acid (C16:0), stearic acid (C18:0), oleic acid (C18:1) and linoleic acid (C18:2);
- ✓ The total content of FAME equal or exceed 98% in all samples (well above the minimum content limit - 96,5%);
- ✓ For linolenic acid methyl ester (C18:3) contents, all the samples show values well below the maximum allowed value (12,0%).



## 6. FTIR fingerprinting



- ✓ FTIR analyses of liquid samples carried out using a BOMEM spectrometer, model MB154S, in a 650-4000 cm<sup>-1</sup> range;
- ✓ Qualitative tests for establishment of typical biodiesel spectra, and identification of main bands;
- ✓ Great similarity between all spectra;
- ✓ The presence of esters clearly visible by a band at 1745 cm<sup>-1</sup>.