

## Supplementary materials

### ZnO/Ionic Liquid Catalyzed Biodiesel Production from Renewable and Waste Lipids as Feedstocks

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#### Contents

1S. Materials and methods .....	S2
2S. General properties of feedstocks .....	S2
3S. Analytical methods: determination of biodiesel yields and FAMES products composition ....	S3
4S. Characterization of FAMES: GC-MS analyses and Mass Spectra .....	S6
5S. Studies of surface and particles size distribution of ZnO catalyst .....	S12

## 1S. Materials and methods

All manipulations were carried out in air. All vials and magnetic bars were cleaned with queen-water. Solvents, metal oxides, ionic liquids are Aldrich or Fluka and Carlo Erba products and were used as received. Commercial soybean Oil (Valsoia S.p.A. Bologna, Italy) was employed for optimization step. Jatropha oil was furnished by Agroils TECHNOLOGY S.p.A. (Sesto Fiorentino, Italy). Linseed oil and oleic acid (>99%) were Sigma Aldrich (Milan, Italy). Waste cooking oil was a domestic source and Olein residue was furnished by an Apulian oil company. Real sewage scum was sampled from municipal wastewater treatment plant of Polignano (Bari, Italy). Fish oil was a gift of Greenswitch Biorefinery (Ferrandina, Italy) and lard was a commercial animal fat (COOP; ITALY).

NMR spectra were recorded on an Agilent Technologies 500 MHz spectrometer; the  $^1\text{H}$  resonance signals were referenced to residual isotopic impurity of  $\text{CDCl}_3$  (7.26 ppm). FAMES products were identified by comparison of their mass spectral data with the literature or with the aid of authentic samples. GC-MS analyses were run on a Agilent 6850/MSD 5975C instrument using a HP-INNOWAX column (30 m  $\times$  0.25 mm id, film thickness 0.25  $\mu\text{m}$ ). Mass spectra were performed in EI mode (70 eV). For quantitative determination, GC-FID analyses were carried out on a Varian 3800 gaschromatograph, equipped with a HP-INNOWAX column (30 m  $\times$  0.25 mm id, film thickness 0.25  $\mu\text{m}$ ), using methyl heptadecanoate as an internal standard. Standard deviations of biodiesel yields were calculated based on at least 4 replicates.

ATR spectra were recorded on PerkinElmer Spectrum Version 10.4.3 instrument, while granulometric analyses were carried out on a HELOS (H3599) & RODOS/M, R1 instruments and data were elaborated by PAQXOS 2.2.2 software.

## 2S. General properties of feedstocks

General properties, FFAs fraction and fatty acids composition of the several feedstocks were determined by literature methods or obtained from the supplier and are reported in Tables 1S and 2S.

**Table 1S.** General proprieties of feedstocks.

Feedstock	FFA (wt.%) <sup>a)</sup>	Saponifiable (wt.%) <sup>b)</sup>	Water (wt.%) <sup>c)</sup>
Soybean Oil <sup>d)</sup>	1	97.2	0.6
Linseed Oil <sup>d)</sup>	0.5	99	0.5
Jatropha Oil <sup>d)</sup>	2	98	0.15
Lard (animal fat) <sup>d)</sup>	0.8	94	0.5
Waste Cooking Oil <sup>e)</sup> (WCO)	1.5	96	0.5
Fish oil <sup>d)</sup>	0.22	90	1.1
Olein residue <sup>d),f)</sup>	75.5%	95.3	0.9
Municipal sewage scum <sup>g)</sup>	32	60	2.0

<sup>a)</sup> Determined via titration using a 0.1 N KOH normalised solution and phenolphthalein as indicator in a 1:1 diethylether: ethanol medium (1 g sample dissolved into 150 mL solvent). <sup>b)</sup> Both esterifiable and transesterifiable fraction. <sup>c)</sup> Evaluated by Karl-Fisher titration. <sup>d)</sup> Properties furnished by supplier. <sup>e)</sup> Coming from domestic use. <sup>f)</sup> Waste fraction coming from apulian oil industry processing. <sup>g)</sup> Lipid fraction of municipal sewage scum of Polignano (Italy), extracted and characterized according to the procedure reported into section 2.2.

**Table 2S.** Fatty acids composition of feedstocks.

Feedstock	Fatty acids (w%) <sup>a)</sup>												
	Myristic	palmitic	palmitoleic	stearic	Oleic	linoleic	linolenic	arachidic	Eicosenoic <sup>b)</sup>	behenic	lignoceric	EPA <sup>c)</sup>	Erucic
Soybean Oil	/	10.45	/	4.45	22.55	50.95	6.79	0.36	3.1	0.36	/	/	/
Linseed Oil	/	5.1	/	4.3	15.8	16.5	58.3	/	/	traces	traces	/	/
Jatropha Oil	/	14.71	/	6.42	44.83	32.04	/	/	/	/	/	/	/
Lard (animal fat)	1.4	20.1	2.6	14.3	47.7	12.3	0.5	0.2	0.9	/	/	/	/
WCO	/	8	/	5	25	60	/	1	traces	traces	/	/	/
Fish Oil	4.5	13.0	6.9	3.6	39.3	10.1	2.9	0.3	7.2	/	/	7.1	5.1
Olein residue	0.03	13.71	1	2.9	68.79	11.4	0.9	0.5	0.3	0.2	0.1	/	/
Municipal sewage scum	5	34	3	9	48	/	/	/	/	/	/	/	/

<sup>a)</sup> Determined by a literature transesterification method with MeOH/BF<sub>3</sub> [1]. <sup>b)</sup> cis-11-Eicosenoic Acid. <sup>c)</sup> Eicosapentaenoic acid.

### 3S. Analytical methods: determination of biodiesel yields and FAMES products composition

FAMES compositions and yields were determined by GC-FID areas employing methyl heptadecanoate as an internal standard.

In the reacted solution 50 mg of methyl heptadecanoate were added and after workup (sect. 2.3) the final ethyl acetate solution was analysed via GC-FID. The obtained methyl esters ( $M_{ME}$ ) were quantified and calculated by the following equation:

$$M_{ME} = (A_{ME} \cdot M_s) / (A_s \cdot R)$$

where  $A_{ME}$  is the total GC-FID areas of the various fatty methyl esters products (unless methyl heptadecanoate),  $A_s$  is GC-FID area of the internal standard and  $M_s$  the added standard mass. Then, the molar amount of FAMES ( $n_{ME}$ ) was calculated using the average molecular weight ( $AMW_{ME}$ )

$$n_{ME} = M_{ME} / AMW_{ME}$$

which was calculated as follows:

$$AMW_{ME} = \sum(A_i MW_i) / \sum A_i$$

where  $A_i$  and  $MW_i$  are the area (gas-chromatographically detected) and the molecular weight of an identified FFA, respectively.

Finally, yields reported in Fig. 1,2,5 and Table 2 were calculated with equation:

$$\text{Yield} = n_{\text{ME}} \cdot 100 / T_{\text{nME}}$$

where  $T_{\text{nME}}$  is the teoretical molar amount obtainable from 0.5 mL of oil.

The FAMES composition coming from the various feedstocks is reported in table 3S.

**Table 3S.** FAMES composition obtained from the various feedstocks.

Feedstock	Fatty acid portion of FAMES (wt.%)												
	Myristic	palmitic	palmitoleic	stearic	Oleic	linoleic	linolenic	arachidic	eicosenoic	behenic	lignoceric	EPA	Erucic
Soybean Oil	/	10	/	4	25	50	6	/	3	2	/	/	/
Linseed Oil	/	5	/	2	15	19	58	/	/	traces	traces	/	/
Jatropha Oil	/	13	1	5	43	36	/	2	/	/	/	/	/
Lard (animal Fat)	1.5	18.6	2.9	14.1	47.9	13.6	0.7	/	0.7	/	/	/	/
Waste Cooking Oil	/	6	/	4	28	60	/	2	/	/	/	/	/
Fish Oil	5.3	14.5	7.7	3.4	38.6	9.4	2.6	0.2	6.3	/	/	7.0	5.0
Olein residue	traces	13	1	2	67	12	1	0.5	traces	traces	traces	/	/
Municipal sewage scum	4	35	4	10	47	/	/	/	/	/	/	/	/

Conversion of oils into FAMES was ascertained either by weighing the unreacted oil phase or by  $^1\text{H-NMR}$  of the whole reaction mixture. As regards the latter case, the biphasic (MeOH + unreacted oil) post-reaction mixture, after eliminating ZnO (by centrifugation), was evaporated to remove MeOH. The resulting mixture was dissolved in ethyl acetate to permit the precipitation of tetraalkylammonium salt (TBAI), filtered and evaporated to small volume to separate glycerol. Then, on a portion of the EtOAc solution the solvent was evaporated and the residue re-dissolved in  $\text{CDCl}_3$  for recording the  $^1\text{H-NMR}$  spectrum. Conversion of the starting oil into FAMES was evaluated based on signals at 4.2 ppm and 3.75 ppm due to the glycerol portion of triglyceride and methoxy groups of FAMES, respectively [2] (Fig. 1S).

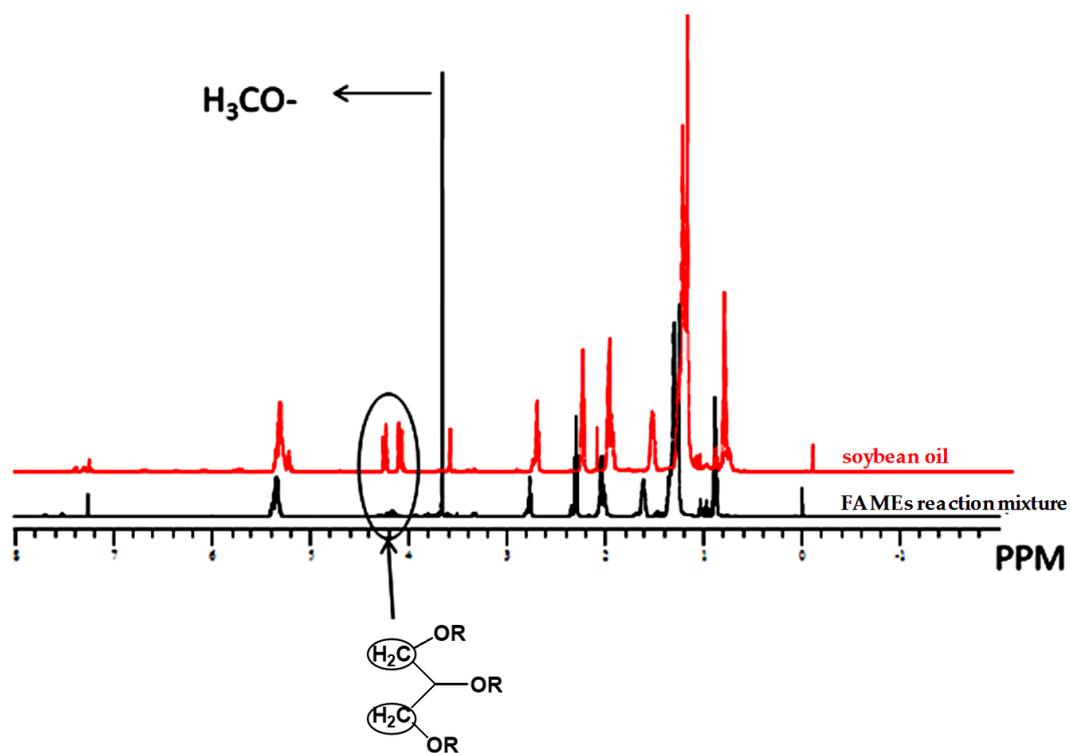


Figure 1S.  $^1\text{H}$ -NMR spectra of soybean oil and reaction mixture of biodiesel products

Likewise, the purity of TBAI recovered after reactions was assured by  $^1\text{H}$ NMR as reported in Figure 2S.

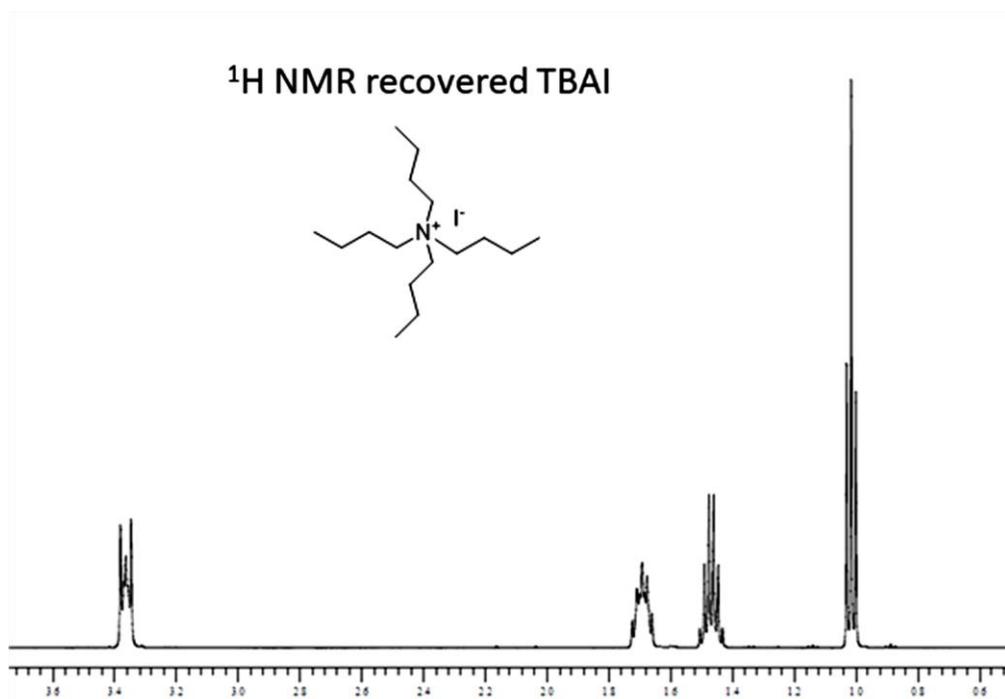
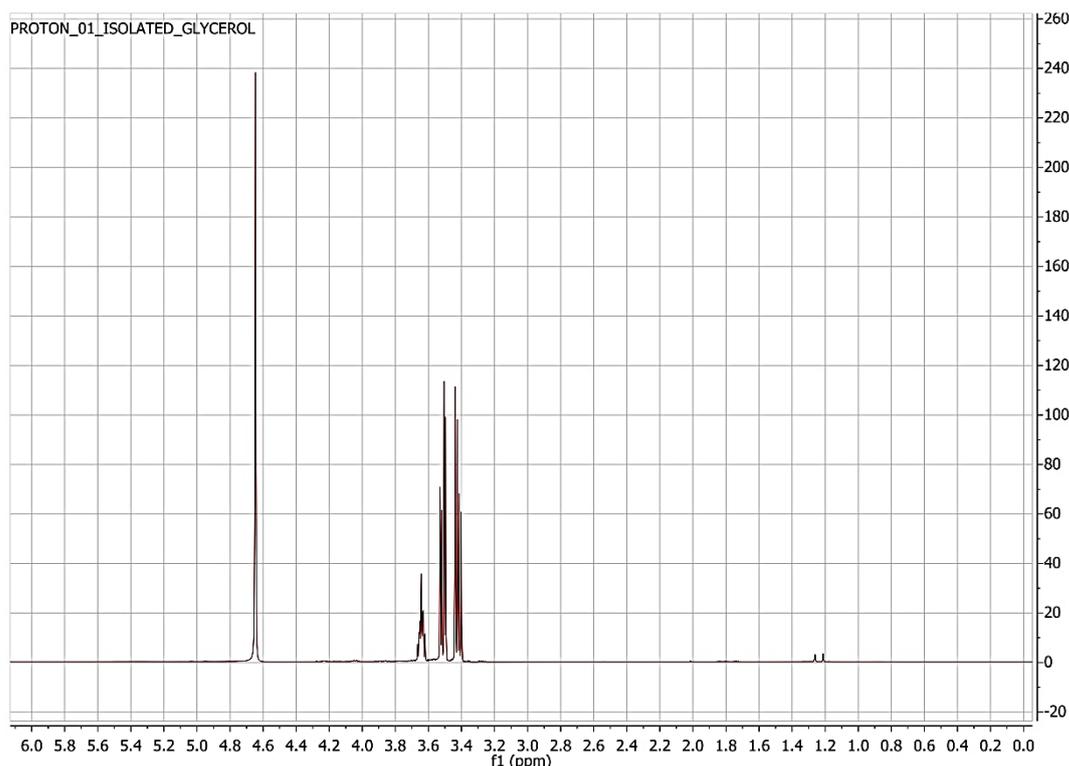


Figure 2S.  $^1\text{H}$ -NMR spectrum of recovered TBAI after reactions



**Figure 3S.** <sup>1</sup>H-NMR spectrum of recovered glycerol.

#### 4S. Characterization of FAMES: GC-MS analyses and Mass Spectra [3]

Identification and characterization of FAMES was accomplished by GC-MS analyses with the aid of literature data, NIST database and authentic samples. GC-MS chromatograms and digitalized mass spectra of main FAMES products listed in Table 3S are furnished below:

Methyl Myristate  $C_{15}H_{30}O_2$

MS m/z (%): 242 (12, M<sup>+</sup>); 199 (13); 149 (12); 87 (60); 74 (100).

Methyl Palmitate  $C_{17}H_{34}O_2$

MS m/z (%): 270 (10, M<sup>+</sup>); 227 (9); 143 (12); 87 (62); 74 (100).

Methyl Palmitoleate  $C_{17}H_{32}O_2$

MS m/z (%): 268 (15, M<sup>+</sup>); 225 (10); 147 (12); 87 (65); 74 (100).

Methyl Stearate  $C_{19}H_{38}O_2$

MS m/z (%): 298 (9, M<sup>+</sup>); 255 (9); 199 (12); 87 (66); 74 (100).

Methyl Oleate  $C_{19}H_{36}O_2$

MS m/z (%): 296 (9, M<sup>+</sup>); 264 (18); 222 (15); 97 (61); 69 (80); 55 (100).

Methyl Linoleate  $C_{19}H_{34}O_2$

MS m/z (%): 294 (12, M<sup>+</sup>); 263 (10); 109 (30); 95 (60); 81 (90); 67 (100).

Methyl Linolenate  $C_{19}H_{32}O_2$

MS m/z (%): 292 (5,  $M^+$ ); 236 (5); 121 (20); 95 (50); 79 (100).

Methyl Arachidate  $C_{21}H_{42}O_2$

MS m/z (%): 326 (25,  $M^+$ ); 283 (12); 87 (55); 74 (100).

Methyl (Z)-11-Eicosenoate  $C_{21}H_{40}O_2$

MS m/z (%): 324 (5,  $M^+$ ); 292 (18); 208 (15); 97 (50); 69 (80); 55 (100).

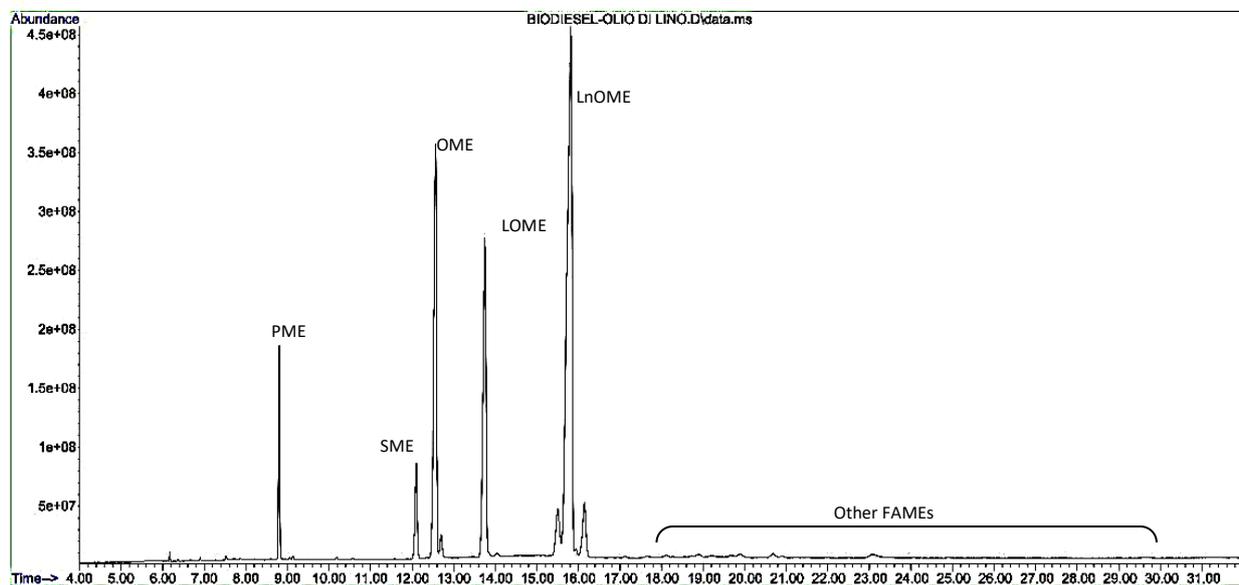
Methyl Behenate  $C_{23}H_{46}O_2$

MS m/z (%): 326 (25,  $M^+$ ); 244 (10); 87 (70); 74 (100).

Methyl lignocerate  $C_{25}H_{50}O_2$

MS m/z (%): 382 (15,  $M^+$ ); 143 (16); 87 (65); 74 (100).

File :D:\CASIELLO\Snapshot\BIODIESEL-OLIO DI LINO.D  
Operator : Casiello  
Acquired : 19 Oct 2018 10:30 using AcqMethod 30METRI 190.M  
Instrument : GCMS  
Sample Name :  
Misc Info :  
Vial Number: 1



**Figure 4S.** Chromatogram of FAMES obtained from soybean oil: PME (Palmitic Methyl Ester), SME (Stearic Methyl Ester), OME (Oleic Methyl Ester), LOME (LinOleic Methyl Ester) and LnOME (LinOlenic Methyl Ester).

File :D:\CASIELLO\Snapshot\BIODIESEL-OLIO DI LINO.D  
Operator : Casiello  
Acquired : 19 Oct 2018 10:30 using AcqMethod 30METRI 190.M  
Instrument : GCMS  
Sample Name :  
Misc Info :  
Vial Number: 1

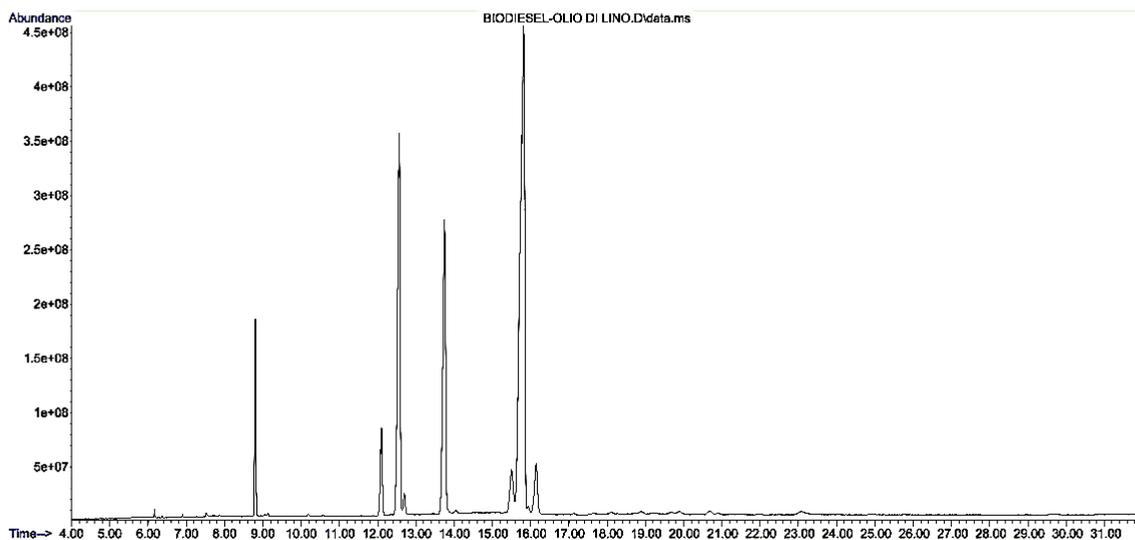


Figure 5S. Chromatogram of FAMES obtained from linseed oil.

File :D:\CASIELLO\Snapshot\BIODIESEL-OLIO DI JATROPHA.D  
Operator : Casiello  
Acquired : 19 Sep 2018 11:36 using AcqMethod 30METRI 190.M  
Instrument : GCMS  
Sample Name :  
Misc Info :  
Vial Number: 1

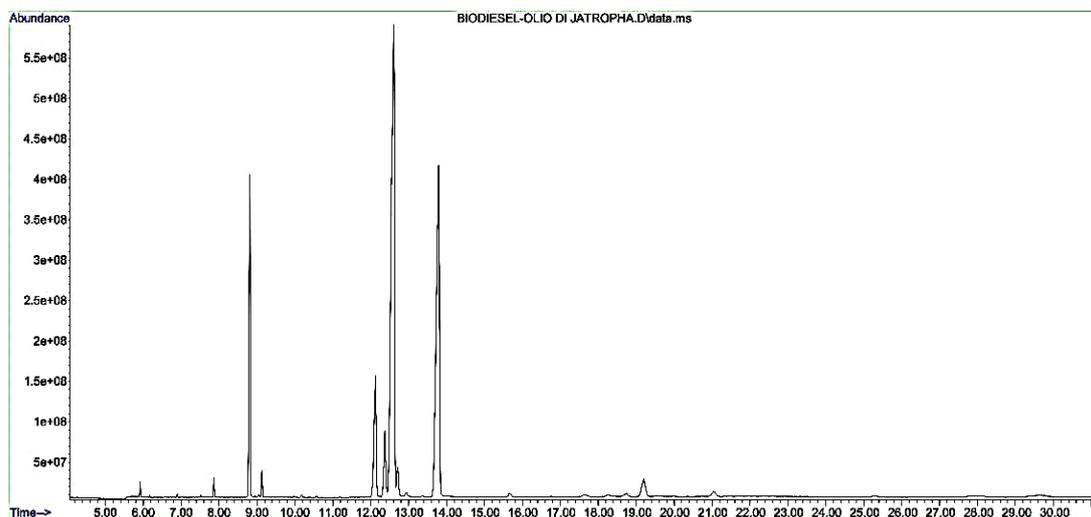


Figure 6S. Chromatogram of FAMES obtained from Jatropha oil.

File :D:\CASIELLO\Snapshot\BIODIESEL-WASTE COOKING OIL.D  
Operator : Casiello  
Acquired : 17 Sep 2018 15:00 using AcqMethod 30METRI 190.M  
Instrument : GCMS  
Sample Name :  
Misc Info :  
Vial Number: 1

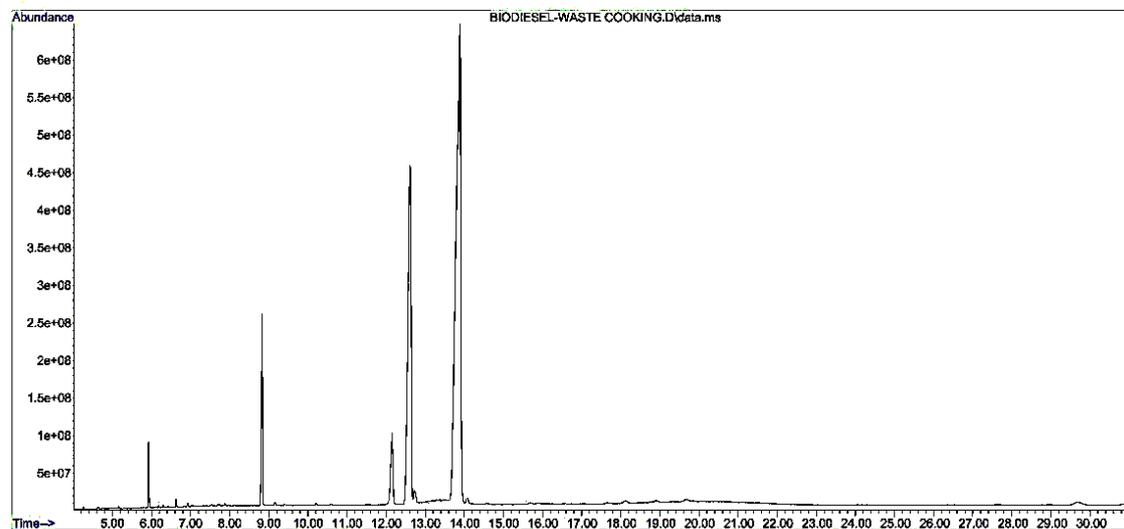


Figure 7S. Chromatogram of FAMES obtained from waste cooking oil.

File :D:\CASIELLO\Snapshot\BIODIESEL-FISH-100C.D  
Operator : Michele  
Acquired : 22 Nov 2018 11:03 using AcqMethod 30METRI 190.M  
Instrument : GCMS  
Sample Name :  
Misc Info :  
Vial Number: 1

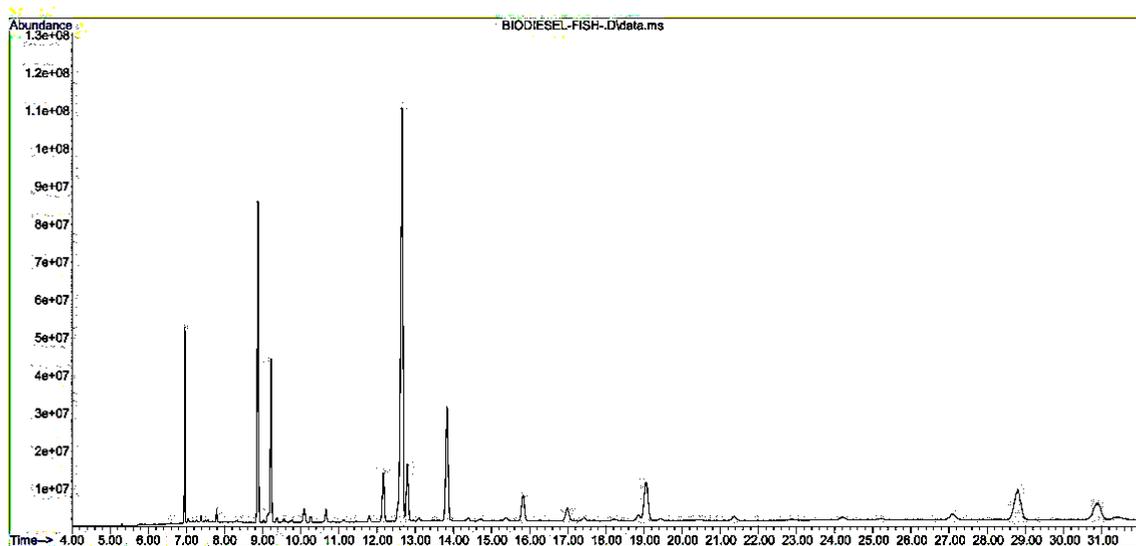


Figure 8S. Chromatogram of FAMES obtained from fish oil.

File :D:\CASIELLO\Snapshot\BIODIESEL-Strutto.D  
Operator : Michele  
Acquired : 19 Nov 2018 18:03 using AcqMethod:30METRI 190.M  
Instrument : GCMS  
Sample Name:  
Misc Info :  
Vial Number: 1

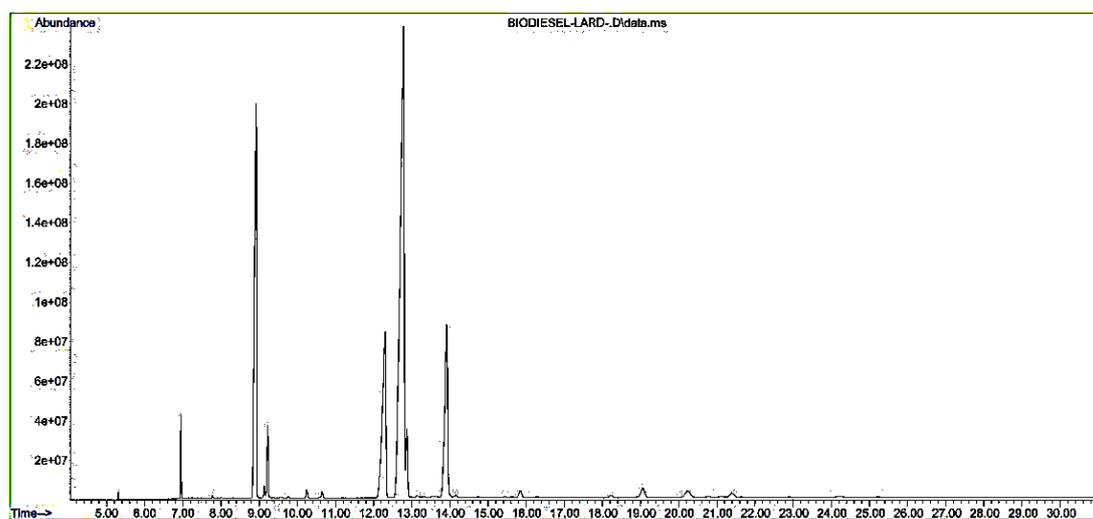


Figure 9S. Chromatogram of FAMES obtained from lard.

File :D:\CASIELLO\Snapshot\BIODIESEL-OLEINA3.D  
Operator : Casiello  
Acquired : 20 Sept 2018 9:11 using AcqMethod 30METRI 190.M  
Instrument : GCMS  
Sample Name:  
Misc Info :  
Vial Number: 1

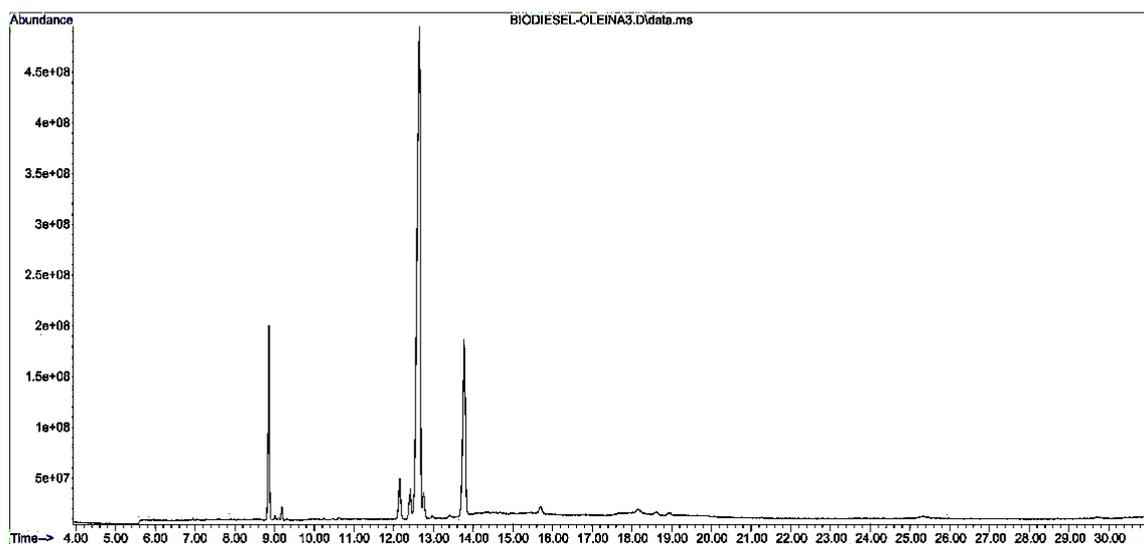


Figure 10S. Chromatogram of FAMES obtained from oleine residue.

File :D:\CASIELLO\SnapShot\BIODIESEL- Waste water.D  
Operator : Casiello  
Acquired : 12 Nov 2018 11:11 using AcqMethod 30METRI 190.M  
Instrument : GCMS  
Sample Name:  
Misc Info :  
Vial Number: 1

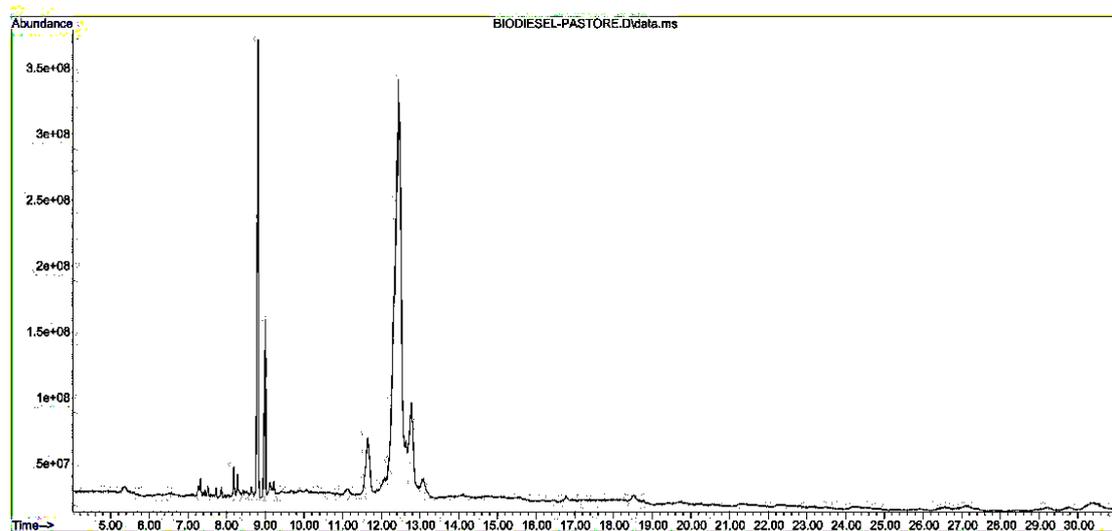


Figure 11S. Chromatogram of FAMES obtained from Municipal sewage scum.

File :D:\CASIELLO\SnapShot\BIODIESEL Oleic Acid.D  
Operator : pasquale  
Acquired : 10 Jul 2018 11:00 using AcqMethod 30METRI 190.M  
Instrument : GCMS  
Sample Name:  
Misc Info :  
Vial Number: 1

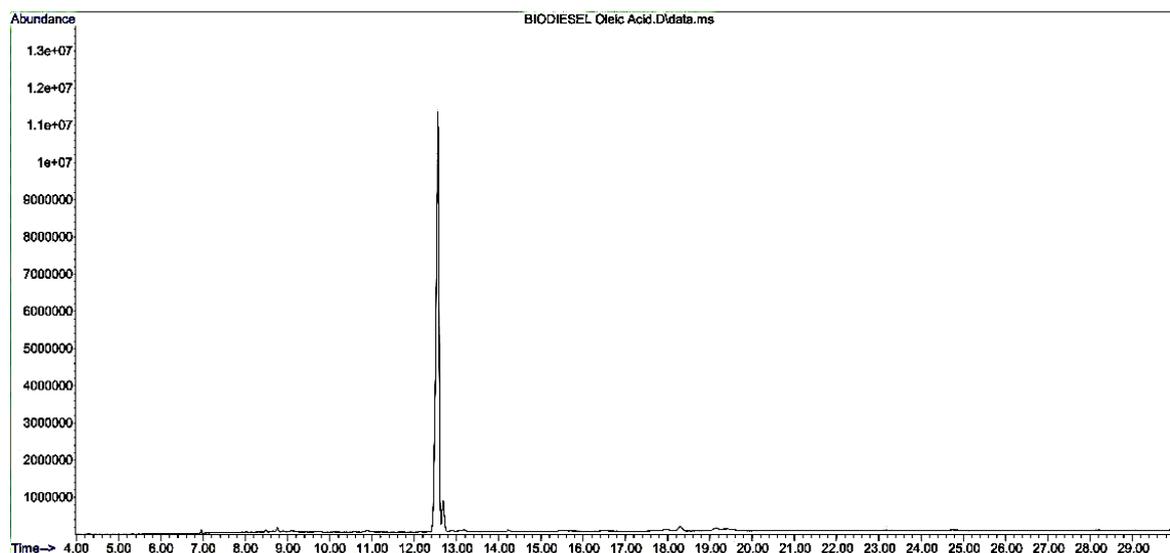
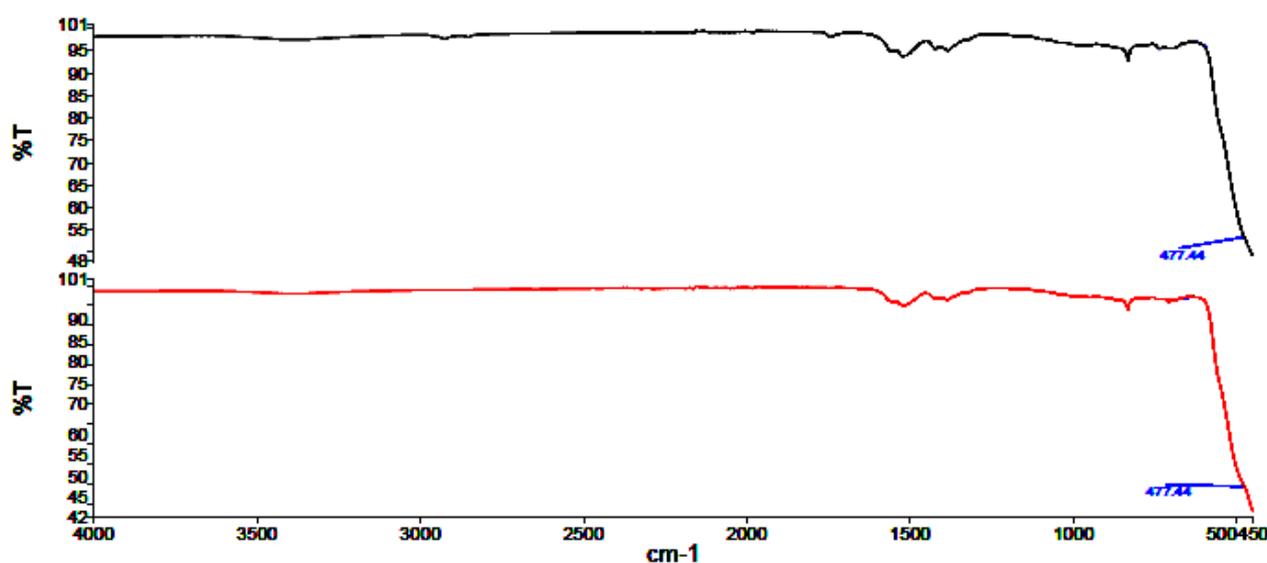


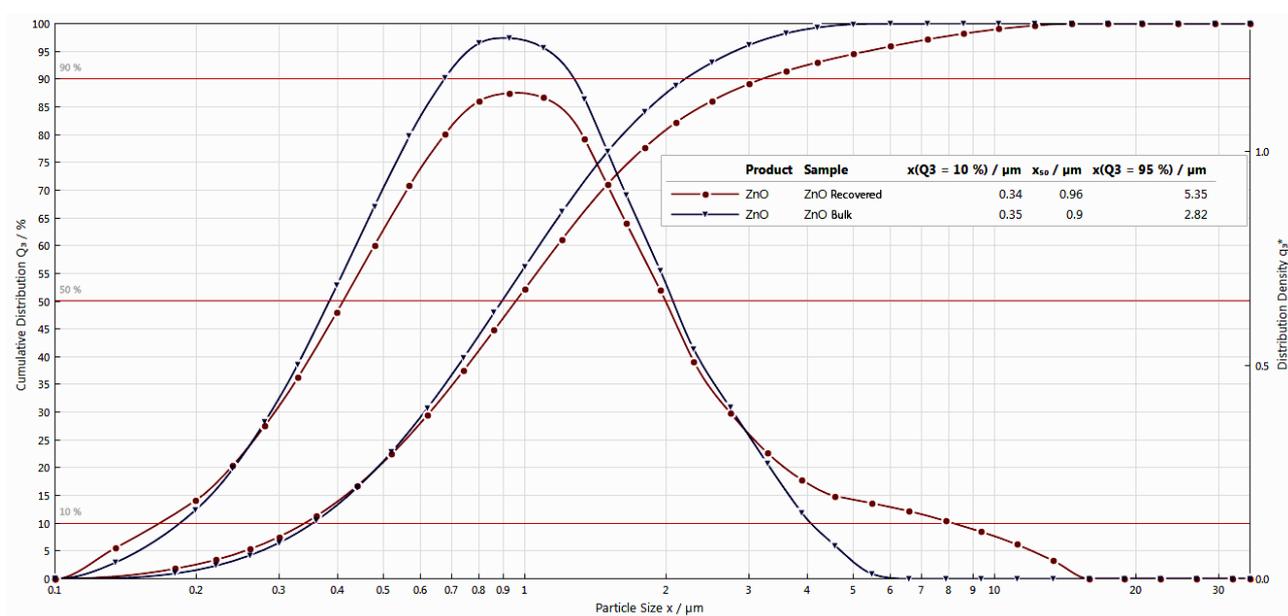
Figure 12S. Chromatogram of oleic acid methyl ester.

### 5S. Studies of surface and particles size distribution of ZnO catalyst

To ascertain that no deactivation process occurs, ZnO powder surface and particles size distribution were studied by ATR and granulometric analyses, carried out before and after catalytic experiments. As shown in Figure 13S, ATR spectrum of pristine catalyst and that obtained after transesterification experiment are virtually identical, displaying mainly the large band below  $500\text{ cm}^{-1}$  attributed to the stretching of Zn-O bond [4]. Neither bands above  $3000\text{ cm}^{-1}$  due to ZnO-H stretching, nor other absorption attributable to other species were detected. Similarly, the particles size distribution of zinc oxide powder after catalytic test is virtually the same as that of ZnO recovered after reaction (Fig. 14S).



**Figure 13S.** Attenuated total reflectance (ATR) spectra of ZnO catalyst powder: pristine (dark line) and after catalytic experiment (red line).



**Figure 14S.** Particles size distribution of ZnO bulk (blue line) and after reaction (red line).

## References

- [1] Van Wijngaarden, D. Modified rapid preparation of fatty acid esters from lipids for gas chromatographic analysis. *Anal. Chem.*, **1967**, 39 (7), 848–849.
- [2] Kataria, J.; Mohapatra, S.K.; Kundu, K. **2017**, *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 39:9, 861-866.
- [3] NIST Database and comparison with authentic sample.
- [4] Fernandes, D.M.; Silva, R.; Winkler Hechenleitner, A.A.; Radovanovic, E.; Custódio Melo, M.A.; Gómez Pineda E.A. Synthesis and characterization of ZnO, CuO and a mixed Zn and Cu oxide. *Materials Chemistry and Physics* **2009**, 115, 110–115.