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Quality of residues of the biodiesel chain in the energy field

D. Duca[1], G. Toscano[1], G. Riva[1], C. Mengarelli[1], G. Rossini[1], A. Pizzi[1], A. Del Gatto[2], E. Foppa Pedretti[1]

1 - Dipartimento di Scienze Agrarie, Alimentari e Ambientali - Università Politecnica delle Marche,

Corresponding author: E. Foppa Pedretti; via Brecce Bianche - 60131 - Ancona Tel.: +39 71 2204918; fax: +39 71 2204167; e-mail: e.foppa@univpm.it

2 - Consiglio per la ricerca in agricoltura e l'analisi dell'economia agraria, Centro di ricerca per le colture industriali, Via Cagiata, 90, 60027 Osimo (AN) Italy

Abstract

The first generation biofuels still have the role of leader in global production of biofuels. In Europe biodiesel is produced mostly from rapeseed (*Brassica napus* L. *oleifera* Metzg) and sunflower (*Helianthus annuus* L.). The EU policy is giving attention to the valorization of residues deriving also from those chains. The present work had the objective of evaluating the quality of residues deriving from biodiesel chains based on rapeseed and sunflower crops as well as on other interesting crops in the Mediterranean area, such as Ethiopian mustard (*Brassica carinata* A. Braun) and cardoon (*Cynara cardunculus* L.). For this purpose an energetic characterization of straws, hulls and press cakes were performed following the official technical normative, as well as the evaluation of their energetic potential. The energy content of residues resulted to be interesting and their quality compatible in general with an energetic use. Crop residues seem to have the most energy potential in quantitative terms, and their exploitation can improve the energy balance of first generation biodiesel production chain improving their sustainability. Concerning quality, crop residues should be employed in medium-large sized plants to limit problems related to plant management and emissions.

Keywords: straw, stalks, press cake, sunflower, rapeseed, cardoon, Ethiopian mustard

1. Introduction

Fossil fuels are still the main energy source at global level, with consequent implications for energy supply, environmental issues and climate changes. Fossil consumption is progressively and constantly increasing and the projections on 2040 show an increase 45% higher than the estimated for 2020, most of which due to China and India and in particular to transport, that consumes the

75% of the petrol produced annually (EIA, 2013; Popp et al., 2014). For these reasons there is a deep interest on nonpetroleum liquids resources, in fact every year they increase 3.7% on average in substitution of petrol derivatives (it is forecasted that in 2040 the global substitution will be the 4 % the overall consumption). Among these alternative resources the biofuels play an important role and are considered, even in controversial debates having different opinion on the part of both public opinion and scientific community, as one of the useful means to oppose environmental imbalances and to improve energy independence (Nigam and Singh, 2011; Smith, 2013; Erakhrumen, 2014).

The principal biofuels are bioethanol and biodiesel, produced mainly from food crops (first generation biofuels), from non-food biomass or waste (second generation biofuels) or also from seaweed (third generation biofuels). In the case of first generation biofuels, the processing technologies are well known, while concerning second and third generation biofuels, promoted by European energy policy (European Parliament and Council, 2009), the processing technologies are still relatively immature with pilot plants supplying a shortened percentage of world biofuel production (Sims et al., 2010; Nigam and Singh, 2011; Maity et al., 2014; Popp et al., 2014). For this reason, on local scale, when there is a need for improving a farmers' agricultural budget by means of even a small income or savings from bioenergy production, first generation biofuels could still be considered (Spinelli et al., 2013).

The world production of ethanol is concentrated in Brazil and in USA (80% of ethanol production in 2012). Europe, instead, is the main producer of biodiesel, with 43% of world production in 2012 (Popp et al., 2014).

In Europe, rapeseed (*Brassica napus* L. *oleifera* Metzg) and sunflower (*Helianthus annuus* L.) are seen as the most interesting among the herbaceous crops dedicated to first generation biodiesel, which is the 95% of global biodiesel (Atabani et al., 2012). In Mediterranean environments (characterized by a warm and dry summer) also less widespread crops as Ethiopian mustard (*Brassica carinata* A. Braun) and cardoon (*Cynara cardunculus* L.) assume a certain interest (Cardone et al., 2003; Gominho et al., 2011; Atabani et al., 2012; Bouriazos et al., 2014).

The biofuel production chain is divided in three main phases: cultivation, first transformation, biofuel production (Sidibé et al., 2010; Buratti et al., 2012; Spugnoli et al., 2012). From the three phases many principal outputs and by-products are obtained and generally a small fraction of plant biomass is used and a large fraction as residue is left (Nigam and Singh, 2011), above all during the first two phases (Fernández et al., 2006; Nassi o Di Nasso et al., 2011). Although this clear evidence, by-products produced along the first generation transformation chain often are not fully valued.

From the cultivation phase the residues obtained are straw (for rapeseed and Ethiopian mustard), stalks and heads (for sunflower), or only stalks (for cardoon). Generally these residues have an agronomic use, with the technique of burial of residues. In literature, also reuse of residues in many other productive contexts are taken into consideration. In energy sector the residual biomass deriving from cultivation is used for combustion (Fernández et al., 2006; Alaru et al., 2011), for biogas production (Garcia-Peña et al., 2011; Oliveira et al., 2012; Bacenetti et al., 2013; Mönch-Tegeder et al., 2014; Pagés-Díaz et al., 2014) and in more complex processes such as pyrolysis, gasification (Encinar et al., 2000, 2002) and hydrolysis (Luo et al., 2011) with the consequent production of new biofuels. Moreover, following different process techniques the crop residues can be used for the production of bio-based (Cherubini and Ulgiati, 2010; Pronyk and Mazza, 2012).

Also their use as insulating material for buildings is interesting (Binici et al., 2014; Mati-Baouche et al., 2014).
The transformation phases consider a first processing with vegetable oil extraction and refinery, then a chemical transformation in biodiesel. Concerning residues deriving from the first transformation, namely meal (chemical extraction) and press cake (mechanical extraction), they are used above all for animal feed, where their use is completely useful and has a full economical value (Taheripour et al., 2010; Fore et al., 2011; Lomascolo et al., 2012). Other uses are as fertilizers, as culture medium for mycotic growth in replacement of commercial medium (Wang et al., 2010; Chatzifragkou et al., 2014), as starting material to obtain bio-active compounds through classical chemical modifications (Daubos et al., 1998), and also their energetic valorization through combustion and pyrolysis (Smets et al., 2011; David, 2013) and the production of press cakes having an interesting mechanical resistance (Evon et al., 2014).
Actually, the predominant process of biodiesel production includes a transesterification phase, which consists of a chemical reaction between animal fat or vegetable oil with an alcohol (methanol or ethanol) in the presence of a catalyst; this reaction also yields glycerol as by-product, considered an unrefined raw product (Leoneti et al., 2012). Generally, 10 to 20% of the total volume of biodiesel produced is made up of glycerol. At present, it is estimated that there are more than two thousand uses for glycerol. However, in the majority of products it is only used in small quantities. There are few end uses that need large amounts of glycerol. Due to the large surplus of glycerol formed as a by-product during the production of biodiesel, new opportunities for converting glycerol into value-added chemicals have emerged in recent years. Refined glycerol can be used in the chemical, textile, pharmaceutical and food industries. Unrefined glycerol can be used converted into promising commodity chemicals and fuels additives, production of hydrogen, development of fuel cells, ethanol or methane production, animal feed, co-digestion and co-gasification, waste treatment and feedstock for microbial oil production (Ayoub and Abdullah, 2012; Leoneti et al., 2012; Quispe et al., 2013; Leiva-Candia et al., 2014).
In literature there are important papers and reviews introducing energetic characteristics of residual materials of a great number of products deriving from agriculture, forestry and agro-industry (Vassilev et al., 2010, 2012, 2013; Rossini et al., 2013; Toscano et al., 2013) but those data frequently derive from the analysis of few samples so that they cannot be considered as representative. In this paper it is proposed a contribution in relation to the first generation biodiesel production chain, performing an analysis of a possible scenario of energy production (heat and electricity) based on a great amount of analytical data about residues and by-products deriving from cultivation phase and first transformation, which are less known but constituting the major part of biodiesel chain residues.

2. Material and methods

2.1 Sampling, processing and physical-chemical characterization of materials

During a three-year period many types of residual products were collected from different phases of the biodiesel chain from dedicated crops. Samples refer to different species, years (2011-2013), Italian regions (Sicily, Marche and Friuli Venezia Giulia), varieties and cultivation systems.

With respect to the cultivation phase the following materials were studied:
- sunflower stalks and heads (20 varieties);
- rapeseed straw (43 varieties);
- Ethiopian mustard straw (4 varieties);
- cardoon straw (1 variety).

All these raw materials derive from experimental tests performed by the sub-project “Raw Materials” within the Extravalore Project funded by MiPAAF (Italian Ministry of Agricultural, Food and Forestry Policies). Most of them are described in this issue (Del Gatto et al., 2015a this issue; Del Gatto et al., 2015b this issue). In more details some varieties were cultivated a single year in the three locations mentioned above while others were cultivated all the three years. In some cases the material was not available for the analysis. Samples of about 6 kg each of crop residues were taken from the experimental field.

From the first processing phase the following materials were studied:
- sunflower seeds;
- dehulled sunflower seeds;
- rape seeds;
- Ethiopian mustard seeds;
- cardoon seeds;
- sunflower cake;
- dehulled sunflower cake
- rapeseed cake;
- Ethiopian mustard cake
- cardoon cake;
- sunflower hulls;

The materials listed above were produced at the Biomass Lab of D3A Department of Polytechnic University of Marche within Extravalore project and starting from a part of the seeds produced by the sub-project “Raw Materials” so that they refer to the same years, varieties and regions mentioned above.
Seeds were analyzed as reference.
The sunflower hulls were produced using a small impact dehuller (NamadImpianti - Tecnologie Alimentari) with 1,5 kW power and equipped with adjustments of power flow and hull extraction speed, set to obtain a partially dehulled seed suitable to be extracted mechanically. In fact for the mechanical extraction it is necessary that a part of hull is present with the seed to enable a proper drainage of the oil. Specific tests has been performed to find the correct setting allowing to maximize oil production, the main product. Sunflower hulls hence derive from the partial dehulling of seeds.
Press cakes and oils were obtained using a small continuous press of 2.27 kW power (Bracco Company Ltd, S205), with a capacity of 15 kg h^{-1} seeds. Tests were carried out on 5 kg seed samples. Before this, the potential oil content of seeds was measured through chemical extraction with hexane (Sigma Aldrich) performed in a Soxhlet extractor followed by the recovery of the

extracted oil performed with a rotary evaporator (Heidolph, Laborota 4000). Comparing the extracting performances of mechanical press with the potential of different seeds it was possible to optimize the mechanical extraction. The analyzed press cake thus refers to optimal extraction conditions.
All materials have been reduced in size using an analytical mill (IKA A11 Basic) with 28,000 rpm nominal speed and then stabilized in the Biomass Lab by means of drying ovens (MPM, M-120 and VF 400eVF models). Representative samples were then prepared according to the method UNI EN 14780:2011.
A total of about 1300 samples were then analyzed to find their physical-chemical characteristics.
In detail, moisture content, net heating value (NHV), lower heating value (LHV), higher heating value (HHV) and ash content were determined. Carbon (C), hydrogen (H), nitrogen (N), chlorine (Cl) and sulphur (S) contents were also determined.
In addition a series of other chemical elements and ash fusibility were also determined on 48 samples to better evaluate the suitability for energy application.
The analyses have been carried out according to the CEN standards regarding solid biomass for energy use (Table 1).

Table 1 - Physical-chemical characterization and related standard methods

Parameter	*Instruments*	*Analytical Method*
Sample preparation	Laboratory mill IKA mod. A11 Basic	UNI EN 14780:2011
Moisture	Oven MPM Instruments s.r.l. series PID System, type M-VF	UNI EN 14774:2009
Ash	Muffle furnace mod. ZA 3.9 kW, T_{max}=1100°C	UNI EN 14775:2010
HHV, LHV, NHV	Calorimeter IKA mod. C2000 Basic; CHNS/O Analyzer Perkin Elmer 2400 series II	UNI EN 14918:2010
C, H, N, S, O	CHNS/O Analyzer Perkin Elmer 2400 series II	UNI EN 15104:2011
Cl, S	Calorimeter IKA mod. C2000 Basic; Ion Chromatographer Metrohm mod. 761 Compact IC	UNI EN 15289:2011
Cr, Cu, Mn, Ni, As, Cd, Hg, Pb, Zn	Microwave Reaction System Anton Paar mod. Multiwave 3000; Optical Emission Spectrometer Perkin Elemer mod. Optima 2100 DV	UNI EN 15297:2011
Na, K, P, Ca, Mg	Microwave Reaction System Anton Paar mod. Multiwave 3000; Optical Emission Spectrometer Perkin Elemer mod. Optima 2100 DV	UNI EN 15290:2011
Determination of ash melting behavior	Muffle furnace mod. ZA 3.9 kW, T_{max}=1100°C; Ash melting behavior Analyzer Sylab IF 2000F	UNI CEN/TS 15370-1:2006

According to the results of energy characterization and mass balances of dehulling and mechanical extraction, a mass balance of residues of biodiesel chain has been evaluated. The related energy potentials in terms of thermal, electrical and CHP potentials have been evaluated as well.

2.3 Statistical analysis

Results were statistically evaluated with the Tukey-Kramer test at the 0.05 level of significance using the JUMP 7.0.1 (SAS) software.

3. Results

The results of physical-chemical characterization carried out on all the samples are reported in Table 2.

Table 2 - Chemical-physical characterization of materials

	Sample size	NHV	HHV	LHV	Moisture content	Ash content	Cl	S	C	H	N
MATERIALS	(n)	(MJ/kg a.r.)	(MJ/kg d.m.)	(MJ/kg d.m.)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Sunflower seeds	144	25.117ab	28.598ab	26.752ab	5.6cd	3.2e	0.06cd	0.09c	59.2a	8.7a	2.3cd
Dehulled sunflower seeds	144	27.605a	30.959a	28.922a	4.2d	3.2e	0.05cd	0.13bc	63.1a	9.6a	2.1cd
Rape seeds	180	25.216ab	28.806ab	26.981ab	6.0c	4.3d	0.01d	0.26b	58.9a	8.6a	3.1c
Ethiopian mustard seeds	24	23.765b	27.395b	25.528b	6.3c	5.3cd	0.01d	0.60a	59.4a	8.8a	4.3b
Cardoon seeds	6	22.315b	25.720b	23.980b	6.3c	4.5d	0.04d	0.15bc	56.4ab	8.2ab	3.6bc
Sunflower cake	96	19.184c	22.386c	20.837c	7.1bc	5.2cd	0.10c	0.16bc	52.3b	7.3b	4.9ab
Dehulled sunflower cake	96	19.360c	22.639c	21.026c	7.1bc	6.6c	0.12bc	0.27b	51.2b	7.6ab	5.4a
Rapeseed cake	180	18.971c	22.146c	20.682c	7.4bc	7.0bc	0.01d	0.33b	49.8bc	6.9bc	5.3a
Ethiopian mustard cake	24	18.833c	22.090c	20.583c	7.6bc	7.2bc	0.01d	0.52a	50.3b	7.1b	6.2a
Cardoon cake	6	18.459c	21.485c	19.936c	6.6c	5.5cd	0.05cd	0.19bc	51.1b	7.3b	4.4b
Sunflower hulls	64	19.153c	22.253c	20.704c	6.7c	3.6de	0.05cd	0.14bc	54.4b	7.3b	1.6d
Sunflower stalks	64	14.252d	17.718d	16.190d	10.4a	8.3b	0.13bc	0.06c	44.6c	7.2b	0.8e
Sunflower heads	144	13.824d	17.529d	15.980d	11.7a	12.5a	0.30b	0.16bc	44.3c	7.3b	1.4de
Rapeseed straw	120	14.616d	17.788d	16.324d	9.1ab	7.5b	0.19bc	0.31b	44.9c	6.9bc	0.9e
Ethiopian mustard straw	16	15.725d	18.535d	17.283d	7.9b	5.5cd	0.21bc	0.33b	45.1c	5.9c	0.6e
Cardoon straw	6	14.841d	17.848d	16.405d	8.3b	8.1b	0.94a	0.11c	45.4c	6.8bc	1.3de

Note: Values in the same column followed by different letters are significantly different at p-value 0.05.
a.r. means as received by the analyst, value expressed on wet basis
d.m. means dry matter, value expressed on dry basis

There are significant differences in terms of quality for energy application among residues deriving from the biodiesel chain: seeds, press cakes and crop residues.

In particular, the energy content of sunflower hulls is similar to that of the press cake.

Ashes of seeds then concentrate in their respective cakes. Result about ash content in sunflower hulls is interesting because it is in line with that of seeds. In general crop residues show higher ash

contents than other materials. In particular, a difference between sunflower stalks and heads is noticed. Cl is particularly present in cultivation residues of cardoon. The other cultivation residues show moderate contents while seeds and press cakes show the smallest contents. Concerning S content, the highest values are registered with the *Brassicaceae* crops. C and H contents follow the same trend of energy contents, while N concentrates in press cakes.
The results of other chemical elements analyses and ash melting behavior determined on 48 samples are reported in Table 3 and 4 respectively.
The results of the analysis of other chemical elements and ash fusibility determined on 48 samples are reported in Table 3 and 4 respectively.

Table 3 - Results of ultimate analysis

MATERIALS	As	Cd	Cr	Cu	Hg	K	Mn	Na	Ni	Pb	Zn	P	Ca	Mg
Sunflower seeds	< 1	< 0,5	< 1	29	< 0,1	13484	15	12	7	< 1	74	6452	2130	2698
Dehulled sunflower seeds	< 1	< 0,5	< 1	8	< 0,1	11728	18	28	5	< 1	85	8765	3123	3421
Rape seeds	< 1	< 0,5	< 1	5	< 0,1	13182	62	10	2	< 1	49	7650	5132	2786
Ethiopian mustard seeds	< 1	< 0,5	< 1	5	< 0,1	17420	48	14	2	< 1	62	7565	4988	2896
Cardoon seeds	< 1	< 0,5	< 1	7	< 0,1	23377	52	15	3	< 1	42	6587	3243	3321
Sunflower cake	< 1	< 0,5	< 1	35	< 0,1	21276	21	20	5	< 1	96	11710	3149	5448
Dehulled sunflower cake	< 1	< 0,5	< 1	44	< 0,1	23645	31	12	6	< 1	139	14232	4523	7354
Rapeseed cake	< 1	< 0,5	< 1	6	< 0,1	19813	92	9	2	< 1	67	7989	6454	3769
Ethiopian mustard cake	< 1	< 0,5	< 1	8	< 0,1	22964	69	15	2	< 1	78	11098	2570	3120
Cardoon cake	< 1	< 0,5	< 1	9	< 0,1	24872	45	13	2	< 1	89	8350	5433	2768
Sunflower hulls	< 1	< 0,5	< 1	12	< 0,1	7442	8	186	1	< 1	53	446	2115	1845
Sunflower stalks	< 1	< 0,5	< 1	19	< 0,1	19878	19	112	1	< 1	62	413	3914	2123
Sunflower heads	< 1	< 0,5	< 1	24	< 0,1	30438	25	210	2	< 1	71	434	4230	2322
Rapeseed straw	< 1	< 0,5	< 1	4	< 0,1	19111	32	557	3	< 1	107	486	12672	633
Ethiopian mustard straw	< 1	< 0,5	< 1	5	< 0,1	18152	20	395	< 1	< 1	113	686	14354	1045
Cardoon straw	< 1	< 0,5	< 1	45	< 0,1	20170	26	1288	2	< 1	232	745	18876	2450

Note: all values are expressed as mg/kg

No irregular contents of As, Cd, Cr, Hg, Ni and Pb are noticed in the analyzed samples. In general, values seem to be in line with those present in literature (Gilbert et al., 2009). In particular, it is noticed that P in seeds tends to concentrate in press cakes.

Table 4 - Results of ash melting behavior analysis

MATERIALS	Shrink Temperature (°C)	Deformation Temperature (°C)	Hemisphere Temperature (°C)	Fusion Temperature (°C)
Sunflower seeds	1.051	1.158	1.184	1.235
Dehulled sunflower seeds	921	1.161	1.230	1.306
Rape seeds	936	1.169	1.177	1.184
Ethiopian mustard seeds	878	983	1.086	1.111
Cardoon seeds	917	1.102	1.148	1.165
Sunflower cake	930	1.145	1.240	1.320
Dehulled sunflower cake	925	1.155	1.243	1.314
Rapeseed cake	930	1.190	1.205	1.220
Ethiopian mustard cake	920	1.160	1.190	1.212
Cardoon cake	911	1.191	1.195	1.200
Sunflower hulls	897	1.002	1.020	1.070
Sunflower stalks	920	1.100	1.300	1.340
Sunflower heads	960	1.130	1.350	1.370
Rapeseed straw	890	1.103	1.285	1.323
Ethiopian mustard straw	905	1.098	1.267	1.320
Cardoon straw	881	1.311	1.454	1.462

Results about ash melting behavior show in general that all materials are more low-melting than classical woody biomass, except for cardoon straw showing similar values.

An important aspect other than residues quality is their potentially available quantity. Using data acquired with the study of the biodiesel chain from the cultivation phase till the first processing phase and with data taken from literature for the esterification phase, it is possible to give an hypothesis of some scenarios to evaluate the energy derivable from residues.

Table 5 shows mass balances of the biodiesel production chain starting from dedicated crops. In Figure 1 the relative energy balances obtainable from the energetic use of residues and by-products are reported. The seed yields and crop residues of sunflower, rapeseed and Ethiopian mustard considered in table 5 are the mean of the three locations tested by the subproject "Raw Materials" as reported in this issue (Del Gatto et al., 2015a this issue; Del Gatto et al., 2015b this issue).

Table 5 – Mass balances of the biodiesel chain from dedicated crops referred to a 1 ha cultivation

	Cultivation				First processing						Esterification			
	seed		straw		vegetable oil		press cake		hulls		biodiesel		glycerin	
Crop	t a.r.	t d.m.	t a.r.	t d.m.	t a.r.	t d.m.	t a.r.	t d.m.	t a.r.	t d.m.	t a.r.	t d.m.	t a.r.	t d.m.
Sunflower[1]	2,86	2,60	6,33	5,66	0,96	0,96	0,98	0,91	0,68	0,64	0,96	0,96	0,11	0,11
	2,86	2,60	6,33	5,66	0,96	0,96	1,74	1,61	-	-	0,96	0,96	0,11	0,11
Rapeseed	2,77	2,52	6,59	5,99	0,99	0,99	1,66	1,54	-	-	0,99	0,99	0,11	0,11
Ethiopian mustard	1,98	1,80	13,03	12,00	0,53	0,53	1,35	1,26	-	-	0,53	0,53	0,06	0,06
Cardoon	1,80	1,64	14,18	13,00	0,29	0,29	1,44	1,35	-	-	0,29	0,29	0,03	0,03

Note 1: The upper row is referred to the dehulled sunflower chain; the lower one is referred to the conventional sunflower chain.

Figure 1 - Energy potentially obtainable from residues deriving from analyzed biodiesel production chains from dedicated crops (CE: Chemical energy; TE: Thermal energy η_{th}=85%; EE: Electrical energy η_e=35%; CHP: Combined Heat and Power η_e=35% η_{th}=50%)

Giving the mass balances and their relative energy production scenarios of residues, relevant differences are seen among different materials and also among different species. In all cases the major part of available energy derives from crop residues, above all from Ethiopian mustard and cardoon.

4. Discussion

The results allow to make some reflections on the opportunity of a direct use of studied residues in combustion processes for thermal and/or electrical energy production. First of all it is important to highlight the big quantity of potential energy contained in crop residues, varying from 80 GJ/ha for sunflower and more than 200 GJ/ha for cardoon. This energy content could be translated in around 76-178 GJ_{th} or 32-74 GJ_{el}. To better frame this possibility, factors linked to the biomass characteristics and that can limit their realization are to be considered. Among them, one of the main aspects to consider is the high ash content that entails logistic and management problems, that become important depending on the plant size. These ashes have also a low melting point entailing problems with the grids getting dirty, so that grids should be preferably mobile. Concerning cardoon straw, the high Cl content shouldn't be underestimated because could lead to corrosion problems and production of dangerous polluting compounds.

From these observations it is assumed that a correct use of crop residues can be reached in medium-sized and large-sized plants.

Concerning first transformation residues, energy quantity is lower, ranging from 25 to 33 GJ/ha, that means from 3 to 10 times lower than straw. As a consequence, also the obtainable thermal or electric energy is reduced following the same proportions. From a qualitative point of view also ash content and their melting behavior of press cakes are problematic for an energetic use. In addition, also the N content is relatively high, entailing an increase of emissions in terms of NO_x. In the case of sunflower hulls, instead, the ash content is low but however low-melting and also the N content is low as well as its relative problems.

Finally the energy potentially obtainable from glycerin is very low (about 1:100) if compared to all the other residues along the chain.

Generally speaking, from the results in this paper a series of evaluations supporting other energetic uses, such as the biogas production, can be done. If considering for example the C/N ratio it seems that extraction cakes and also hulls could be employed in anaerobic digestion. On the contrary, crop residues don't seem to be easily usable for the same purpose.

In conclusion, all these reflections must be calibrated (reduction of the available mass) on the basis of the territorial distribution characteristics of residues that affect a lot the real possibility of exploitation.

First of all, it is expected that problems related to planning and material quality will have a bearing more in the case of cultivation residues (dispersion on territory, accessibility, heterogeneity of management, pollution from soil) than in the case of transformation residues, which tend to concentrate in few processing points. Moreover, it must be taken into account that the complete removal of residues from the soil could lead to a decrease of organic matter (which is already reduced in Italian soils) and an increase of erosion events.

5. Conclusions

The results of the work show how crop residues are the materials that could be conveniently exploited by the energy point of view to significantly improve the energy balance of the production chain of the first generation biodiesel. It is interesting to consider the energy characteristics of these residues together with their potential amount in Italy. Currently this evaluation is significant for sunflower and rapeseed, consistently widespread in Italy with a mean cultivated area or 100.000 and 15.000 ha respectively (ISTAT, 2012). The potential energy content of these residues is thus important and there is interest in their energy exploitation. However the biomass distribution and its chemical-physical characteristics, like the relatively high ash content, low ash fusibility and low bulk density, must be taken into account. A use in medium-large power plants should be suggested.

It is also possible to facilitate the use of these residues by mixing with other biomass in order to balance the ash characteristics. However, the low bulk density with the related low energy density, still remains the most important limitation for the energetic use. It could be useful to study the possibility to perform some pretreatment (e.g. wet torrefaction, leaching) to enhance the characteristics in chemical-physical and logistic terms.

The press cakes and glycerin meet the requirements for a direct energy use but, given

the quantity, quality and territorial concentration, they could be better exploited in other fields.

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