Industrial Crops and Products 75 (2015) 91–97

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Quality of residues of the biodiesel chain in the energy field

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ARTICLE INFO

Article history:
Received 26 June 2014
Received in revised form 4 February 2015
Accepted 20 February 2015
Available online 5 March 2015

Keywords:
Straw
Stalks
Press cake
Sunflower
Rapeseed
Cardoon
Ethiopian mustard

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.

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

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http://dx.doi.org/10.1016/j.indcrop.2015.02.042
0926-6690/

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; Del Gatto et al., 2015b). 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