

# Biodiesel obtained from supercritical carbon dioxide oil extracts of *Cynara cardunculus* L.

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## Abstract

Suitable and alternative crops are recently being explored as efficient and sustainable sources for fuel and energy production. The present work evaluates the use of cardoon (*Cynara cardunculus*, L.) seed oil as a renewable raw material for biodiesel production and aiming to find an alternative to petroleum-based fuels at a regional scale, as cardoon is an endogenous plant of the Mediterranean Flora. Cardoon seed oil was extracted using a supercritical carbon dioxide (scCO<sub>2</sub>) extraction method and varying scCO<sub>2</sub> density from 0.65 up to 0.93 g/cm<sup>3</sup>. Hexane Soxhlet extractions were also performed for comparison purposes. Depending on the employed extraction conditions and/or methods, different oil yields and compositions were obtained. In general terms, higher scCO<sub>2</sub> densities led to higher cardoon oil yields (around 22%) which were similar to soxhlet oil yields (around 25%). Two biodiesel synthesis approaches were then used: *i*) direct cardoon oil transesterification in methanol, using an alkali-based process (to convert oil esters into fatty acid methyl esters, FAME); and *ii*) cardoon oil acid pre-esterification in methanol (to reduce the cardoon oil free fatty acids contents) followed by a methanolic transesterification reaction using an alkali-based process. Employed alkaline catalyst was sodium methoxide while acid catalyst was sulphuric acid. All the obtained biodiesel samples were chemically and physically characterized according to the European Standard EN14214 methods. Results showed that the second approach (acid-catalyzed esterification followed by alkaline transesterification) led to higher biodiesel yields as well as to higher FAME contents (for all employed oils obtained by different methods and conditions). In addition, other obtained properties fulfilled, with a few exceptions, the specified EN14214 values.

## INTRODUCTION

Cardoon (*C. cardunculus*, L.) seed oil can be regarded as a renewable raw material for biodiesel production in the search for alternatives to petroleum-based fuels. It may represent a sustainable and efficient source for fuel and energy production at a regional scale as cardoon is an endogenous plant of the Mediterranean Flora. It is well known that vegetable raw materials to be used for biodiesel production must be able to lead to high oil extraction yields and to present some specific physical-chemical characteristics which are strongly dependent on the obtained oil composition. Therefore, the employed raw materials as well as the used oil extraction method are of paramount importance in biodiesel production processes. The most common oil extraction technique is solid-liquid extraction using low polarity organic solvents (such as *n*-hexane). Mechanical extraction approaches can also be considered thus avoiding the use of solvents. Another advantageous method is supercritical carbon dioxide (scCO<sub>2</sub>) extraction where the variation of operational conditions (namely pressure and temperature) will change scCO<sub>2</sub> density and its selectivity to some compounds [1,2] leading to oil extracts with different compositions (which is an important advantage of the method).

In this work, cardoon seed oil was extracted using a scCO<sub>2</sub> extraction method and varying scCO<sub>2</sub> density from 0.65 up to 0.93 g/mL. *n*-hexane Soxhlet extractions were also performed for comparison. Two biodiesel synthesis approaches were then used: *i*) direct cardoon oil transesterification in methanol, using an alkali-based process (to convert oil esters into fatty acid methyl esters, FAME); and *ii*) cardoon oil acid pre-esterification in methanol (to reduce the cardoon oil free fatty acids contents) followed by a methanolic transesterification reaction using an alkali-based process. The employed alkaline catalyst was sodium methoxide while the acid catalyst was sulphuric acid. All the obtained biodiesel samples were chemically and physically characterized (esters and FAME composition/yields, viscosity, density, acidity, and thermal degradation) according to the European Standard EN14214 methods [3].

## MATERIALS AND METHODS

*Raw material preparation and characterization* - Cardoon seeds were obtained from randomly selected plants in Santiago de Cassurrães, Portugal. The dry seeds were then milled in a knife-mill and separated/classified in mechanical stirred sieves.

*Extractions* - Cardoon oil was obtained from two different extraction methods namely scCO<sub>2</sub> extraction (SFE) and Soxhlet extraction (Sox). For SFE extractions, experimental conditions were set to several specific pre-determined operational temperatures (35, 45 and 55 °C), and pressures (15, 22.5 and 30 MPa) in order to reach pre-determined and fixed scCO<sub>2</sub> densities (from 0.65 up to 0.93 g/cm<sup>3</sup>). For all the performed extraction experiments, a static period of 30 min preceded a continuous extraction period (300 min) that was carried out at a fixed solvent flow rate (4.7 L/min). Soxhlet extractions were performed using *n*-hexane as a solvent (1:10 solid-solvent ratio) for a 2.5 hours extraction period. In the end, obtained extracts were vacuum evaporated. All performed extraction experiments were duplicated.

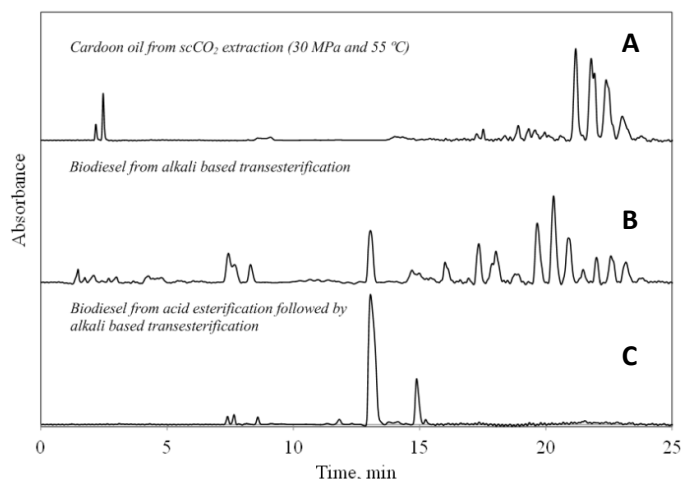
*Biodiesel production* – Extracted oils were converted into biodiesel following two different methods: a single alkali based transesterification process and a two-step process composed by acid esterification followed by alkali transesterification. The alkali-based transesterification reactions were carried out at ~65 °C using sodium methoxide as catalyst and methanol as solvent (in a 6:1 methanol:oil molar ratio). Oil reacted for 90 min under magnetic stirring (at 700 rpm) [4]. The acid esterification followed by alkali-based transesterification reactions were carried out using pre-heated methanol in a volume ratio of 1:3 followed by the addition of 0.5% (v/v) of H<sub>2</sub>SO<sub>4</sub> to the oil. The mixture was then heated and stirred for 30 min (at 60 °C and at 700 rpm). Methanol was later removed by vacuum evaporation. Then and after acid esterification reactions, base-catalyzed transesterifications were performed according to a procedure previously described in the literature [5]. All performed reactions were duplicated.

*Oil and biodiesel characterization* – Extracted oils and obtained biodiesel samples were characterized by HPLC following the literature and in order to identify and quantify FAME's composition [6]. Samples densities were measured by helium pycnometry. Biodiesel samples were further characterized following other methods presented on the EN14214 standard [3]. Additionally, samples were analyzed by thermogravimetric analysis (TGA) using a simultaneous differential scanning calorimeter and thermo gravimetric analyser (SDT).

## RESULTS

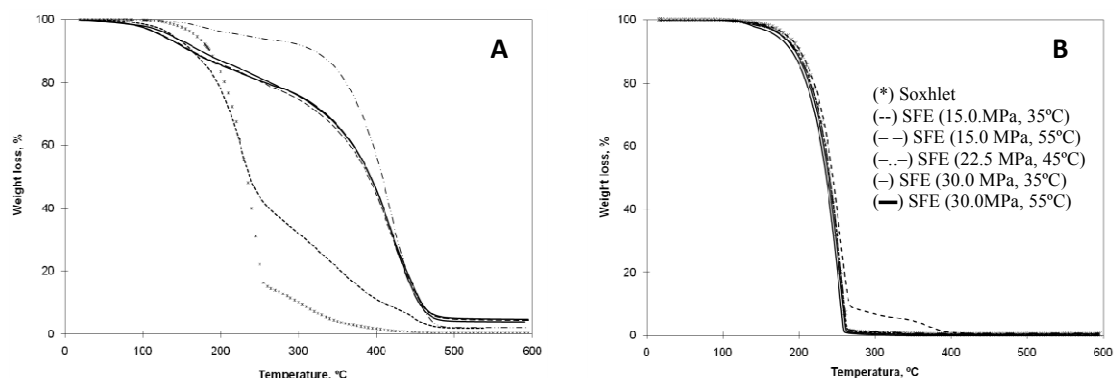
When comparing the two biodiesel production approaches studied in this work, these preliminary results showed that the second approach (acid-catalyzed esterification followed by alkaline transesterification) led to higher biodiesel yields as well as to

higher FAME contents (for all the employed oils which were obtained from different extraction methods and conditions). HPLC analyses of obtained biodiesel samples revealed the presence of converted methyl esters but also of triglycerides when the reaction was less complete (for the direct cardoon oil transesterification and for biodiesel obtained from Soxhlet extracted oil). Figure 1 shows an example of this behavior: the two-steps procedure promoted FAME production (retention time between 10 and 15 min) and simultaneously reduced the amount of triglycerides down to a few traces (retention time > 15 min), thus leading to a higher biodiesel conversion. On the contrary, it is possible to observe that the one-step procedure revealed a biodiesel which is characterized by an incomplete FAME conversion, with significant amounts of unreacted triglycerides (Figure 1 B).



**Figure 1.** HPLC chromatograms for cardoon oil obtained by SFE at 30.0 MPa and 35 °C (A) and corresponding biodiesel samples produced by alkali-based transesterification (B) and acid esterification plus alkali-based transesterification (C).

These results are in good agreement with those obtained by thermogravimetry (TGA) which showed the potential presence of high molecular weight compounds (triglycerides that achieve complete degradation just around 400 °C) in those biodiesel samples obtained from the single step transesterification (namely in the case of the employed oils that were obtained by scCO<sub>2</sub> extraction, Figure 2A).



**Figure 2.** TGA thermograms of biodiesel samples obtained by different reaction conditions: (A) direct cardoon oil transesterification and (B) cardoon oil acid pre-esterification followed by a transesterification reaction using oils extracted by Soxhlet and SFE.

The second approach led to biodiesel samples that present quite similar thermal stabilities and degradation profiles (which confirms samples homogeneity in terms of composition) regardless of the employed extraction methods and conditions that were

used to obtain cardoon oils. All samples presented a single step weight-loss thermogram with a maximum degradation temperature located at around 250°C (Figure 2B). These results agree with others already reported in the literature for biodiesel samples obtained from different vegetable raw materials and from oils extracted by different methods [7,8]. Moreover, the transesterification efficiency of the second approach was also qualitatively confirmed by FTIR analysis which showed an evident displacement of the characteristic ester C=O band: from 1743.33 cm<sup>-1</sup> (in oils) down to 1740.44 cm<sup>-1</sup> (in the corresponding biodiesel samples). This is an indication that the esters conversion into methyl esters was effective [9,10].

## CONCLUSIONS

The use of *Cynara cardunculus*, L. to produce biodiesel had already been reported in literature. However and as a novelty, this work reports the use of supercritical carbon dioxide to perform the oil extractions which, and due to its well-known tunable character, led to distinguishable oil composition profiles (depending on the employed pressure and temperature conditions). Furthermore and as a consequence, cardoon oils that are extracted with supercritical carbon dioxide at some specific extraction conditions may also be used in other fine chemistry processes beside those oriented for biodiesel production. Oil extraction yields obtained by SFE were quite similar to those obtained by Soxhlet extractions. However, SFE avoids the use of organic solvents and leads to solvent-free oil extracts (without the use of thermal-based solvent-removal processes). Higher extraction yields were obtained at 30.0 MPa (at 35 °C and 55 °C). Biodiesel production employing the one-step alkali-based transesterification process led to the occurrence of unexpected saponification reactions that decreased the biodiesel conversion yields. Nevertheless, when acid esterification was applied to the oil prior to the alkali-based transesterification, biodiesel production yields had an increment that varied from 21 up to 50 % with a consequent FAME production that also increased up to values already acceptable by the EN14214 standard for biodiesel. Finally, the preliminary results obtained in this work showed that it is possible to produce biodiesel from cardoon oils (obtained using scCO<sub>2</sub> extraction) through a sequential two-step transesterification method which comprises an acid pre-esterification followed by a transesterification reaction. This process originates biodiesel samples that meet most of the EN14214 standard specified values.

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