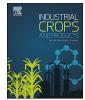
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## Chemical characterization of oil and biodiesel from four safflower genotypes

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#### ABSTRACT

The global energy matrix is concentrated on non-renewable sources. Thus, in short time, the demand for energy could exceed its production. The use of renewable energy sources is paramount for the actions of current and future generations. Thus, the use of biodieselenergy has been pointed out a viable source for energy production with low concentrations of toxic pollutants. The use of renewable energy sources such as the safflower has been an interesting option. Safflower is a short cycle oil crop, with high production and optimum adaptation to Brazilian climate. This study aims to analyze the behavior from oil and biodiesel from four genotypes of safflower, making use of their physical and chemical aspects. The parameters adopted for oil analysis were viscosity, acid index, free fatty acid (FFA) and peroxide index. For biodiesel it verified its calorific value. Analyzing the results, it can be concluded that the genotypes connected with the oil showed adequate viscosity, low acidity, FFA and peroxides in the pattern within acceptable levels. In addition, biodiesel presented calorific value close to that found in mineral diesel, which indicates a good burning. The safflower oil is a promising source for the biodiesel production.

#### 1. Introduction

At the current state of human development, the demand for energy is already showing signs that will exceed its production capacity very soon. Heads of state have assumed this condition and seek, through agreements and global partnerships, to voice their concerns and investigate possible solutions. They will come, but in the long term given the intensity and complexity of the problem (Lucon, 2007).

In this context, renewable energy has become important in discussions and agendas of nations in general. The future points to the necessity of a shift towards a new energy matrix that has its roots in renewable energy sources (Knothe et al., 2006; Sajjadi et al., 2016).

From the evolution of researches and the possibilities to expand energy sources to adopt a renewable one, it comes the process of transformation of biomass. This process acts to generate energy by burning or by fuel production. Examples of biomass are wood, forest residues, stalks, vegetable oils, grains and biological treatment sludge from varied wastewaters. Considering the rise of laws and the addition of biodiesel to the mineral one, researchers began to bring their attention to grain production for this specific purpose (Grimoni et al., 2004).

At the beginning of the century, a research showed that biodiesel production in Brazil is mainly concentrated in the Northeast region with 42% of total production in 2007, followed by the Midwest with 31%, South with 11%, Southeast with 9%, and North with 7% (Osaki and Batalha, 2011). It is considered that this biodiesel from oilseeds has better characteristics than the mineral one, for it has smaller amount of toxic gases and because it roots carbon particles during the development of crops (Demirbas, 2007).

In this context, when inserting the point of fuel oils is considered that their use in engines is not a novelty. Rudolf Diesel was the precursor of this procedure (Shay,1993). According to Shahid and Jamal (2008), the production of biodiesel from vegetable oils is made from species such as: castor bean, soybean, cotton, sunflower, safflower,

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Abbreviations: ANP, National Agency of Petroleum, Natural gas and Biofuels; UNIOESTE, State University of Western Parana; FFA, free fatty acid \* Corresponding author.

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moringa (Juhaimi et al., 2016a,b, 2017), among others that have properties and energy efficiency like the mineral diesel (Beyyavas et al., 2011; Sampaio et al., 2016).

According to Beyyavas et al. (2011), safflower (Carthamus tinctorius L.), Asteraceae family, is a plant from Asia which supports high temperatures and semiarid climates. Historically the flowers of safflower have been used like ornament, colorant in food and dyeing of clothes (Oelke et al., 1992). The main purpose today is as an oilseed crop. Its maximum production cycle is equal to 130-140 days, so it can be intercropped in temperate climates or have two crops in semi-arid climate. Its average size is up to 30–150 cm, and it has a developed root system with up to 1 m depth. The harvest of this species is similar to the common cultures in Brazil as sovbean and corn; its grain production can reach 1000-3000 kg or 300-1440 kg of oil per hectare (Herdrich, 2001). Safflower oil varies from 35 to 50% and 90% of unsaturated fatty acids (Galavi et al., 2012). Faced with these properties, safflower seeds have been used intensely in the production of herbal capsules, but it remains its potential to be used to produce biodiesel (Bretanha et al., 2007).

In biodiesel production process one must be aware that their method of production is conditioned to its sources of origin. In the specific case of mineral diesel, this is obtained by cracking of petroleum, and methyl biodiesel is produced by transesterification; and its physical characteristics, the esters of fatty acids, are very close to the ones from mineral diesel. This process is a change in some oil properties and this reduces its molecular weight by 70% compared to triglycerides levels. These changes, as Geris et al. (2007) points out, transform oil into a fuel which lubricates and it has good firing favoring the engine life. However, biodiesel provides an amount of energy about 10% less than petroleum diesel; but, when analyzing the power and torque performances, these are virtually the same (Gerpen, 2005).

The oil transesterification consists of adding methanol and catalysts classified as acid and base. The basic route provides a higher performance when compared to the biodiesel obtained by acid route. The most common catalysts used in the basic route are: potassium and sodium hydroxide, KOH and NaOH respectively (Ferrari et al., 2005).

Fatty acid as an input to produce biodiesel has a higher cetane number (Junior, 2008). The biodiesel of vegetable oils is not always the same, because its qualities and characteristics are linked to its plant of origin. Therefore, oilseeds produce biodiesel with different physical and chemical characteristics, and the source choice may not be linked only to the amount produced or to the amount of oil present in the seed, but also to the final qualities of the seed.

The essence of the constituent material of biodiesel can influence the quality of its performance. This occurs because, in the process of obtaining the oil, it can acquire contaminants, or contamination can occur in the storage procedures, and there are still variations in the carbon chain (Lôbo et al. (2009)).

It is necessary to produce biodiesel within the parameters established by ANP (National Agency of Petroleum, Natural gas and Biofuels) to ensure quality and to make sure its attributes are like the mineral one. Given this concern, this study aims to evaluate the potential use of biodiesel produced from four safflower (*Carthamus tinctorius* L.) genotypes.

#### 2. Material and methods

#### 2.1. Location of the experiment and genotypes

The research was conducted in the biofuels laboratory of State University of Western Parana (UNIOESTE), in Cascavel, state of Parana, Brazil. The safflower used was conducted in the field of Farm School of University Adventist Center of São Paulo, in Engenheiro Coelho, state of Sao Paulo, Brazil (22° 29′ 18″ S, 47° 12′ 54″ W), in the fall and winter of 2014 on an Arenic Hapludult (Soil Survey Staff, 2014), whose chemical characteristics (Van Raij and Quaggio, 1983) and physical (Embrapa, 

 Table 1

 Chemical characterization at 0–0.20 m depth of experimental area.

Soil pH	4.8
Clay (g kg <sup>-1</sup> )	172
Silt $(g kg^{-1})$	123
Sand (g kg <sup>-1</sup> )	705
Organic matter (g kg <sup>-1</sup> )	10
Available P (mg kg <sup>-1</sup> )	7
$H + Al (cmolc kg^{-1})$	28
Al saturation (%)	7.55
Exchangeable Al (cmolc kg <sup>-1</sup> )	2
Exchangeable K (cmolc kg <sup>-1</sup> )	23
Calcium (cmolc kg <sup>-1</sup> )	1.7
Magnesium (cmolc kg <sup>-1</sup> )	0.5
CEC (cmolc kg <sup>-1</sup> )	5.2
Soil base saturation (%)	47

CEC = Cation Exchange Capacity.

1997) prior to the implementation of experiments are shown in Table 1. The climatic classification, according to Köppen, is humid subtropical (Cwa), with temperatures of the hottest month exceeding 22 °C and the coldest month below 18 °C. The region's annual rainfall is 1328 mm. Daily and historical climatic data of precipitation were obtained in a meteorological station located near the experimental area and are in Table 2.

The genotypes used were IAPAR, IMA-2109, IMA-2232 and IMA-4409. Safflower was sown on April 14, 2014. Each experimental plot was 1.35 m wide  $\times 4.0 \text{ m}$  long (3 rows per plot). Line spacing was 0.45 m and plant spacing was 0.10 m.

Fertilization, sowing, cultural practices and harvest were done manually. The seeding depth was three centimeters. For fertilization  $500 \text{ kg ha}^{-1}$  of the formula 4-14-8 (N-P<sub>2</sub>O<sub>5</sub>-K<sub>2</sub>O) was applied.

#### 2.2. Extraction of oil and determination of analyzes

Extraction of oil and determination of analyzes were performed based on the methodology proposed by the Instituto Adolfo Lutz (2008).

The grains were pressed in cold extruder to obtain the oil, and biodiesel was processed through transesterification. In the biodiesel production was used 300 g of oil heated to 50 °C (122 °F), six grams of NaOH (at a rate of 2% m/m in relation to the oil mass) dissolved in methyl alcohol, forming sodium methoxide, Na (CH<sub>3</sub>O).

It was placed a beaker with the preheated oil and added sodium methylate while stirring with temperature around 60  $^{\circ}$ C (140  $^{\circ}$ F) on a plate with a magnetic stirrer. The oil was decanted for 20–30 min until a clear color was obtained.

The obtained methyl ester was transferred to a separating funnel where it was stored for enough time, about 1 h, so that one could observe a separation between the phases, allowing glycerin to precipitate in the beaker because it is denser.

After separated the glycerin, it was necessary a cleaning that was

#### Table 2

Average Temperature, precipitation and long-term precipitation (27-year) measured in Engenheiro Coelho, SP.

Month	Average temperature (oC)	Long-term temperature (oC)	Precipitation (mm)	Long-term precipitation (mm)
April	22.07	22.9	51.2	66.9
May	19.3	19.4	9.9	52.7
June	19.3	18.4	10.9	37.0
July	20.8	18.1	20.8	34.7
August	21.01	19.8	7.2	23.0
September	23.02	21.1	97.3	70.7

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