Productivity and Quality of Hybrid Canola Oil and Seeding Time

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Abstract — Biofuels are the main alternative for changing the world’s energy matrix, which is now centralized in fossil fuels. The characterization of alternative sources of biomass, mainly regionally, shapes database for decision making. For this purpose, a factorial experiment was carried out with three canola cultivars (Hyola 43, 61 and 571), seeded in four times (April 4th, April 16th, May 2nd and May 14th). As biomass characterization, grain yield, oil content and yield, specific mass, oxidative stability, acidity and lipid profile were determined. There was significant difference for the hybrids in the variables oil content, induction time and in the stearic, linoleic and linolenic contents. The highlight was the hybrid Hyola 43. There was significant difference for the periods in the grain yield, oil content, oil yield, and induction time and in the palmitic, stearic, oleic and linoleic contents. Considering values of dependent, quantitative and qualitative variables, the best seeding season of canola would be between the second fortnight of April and the first week of May.

Keywords — Biodiesel, vegetable oils, fatty acid.

I. INTRODUCTION

Directly or indirectly biomass is the basis for alternative energies. The biomass is responsible for 14% of world energy used [1].

For the production of biodiesel, biomass (raw material) is the most important and costly part of the process. In Germany, the main producer and consumer of biodiesel in the world, and in the European Union, canola accounts for 80% and 60%, respectively, of the cultivation of oilseeds for this purpose[2]. The planted area with canola in Brazil in 2015 was 53,610 ha, an expansion of 8% in relation to the previous harvest [3].

Oil crops for the production of biofuels must offer good oil yield and physicochemical characteristics consistent with use and current standards [2]. The determination of the fatty acid profile is one of the main characterizations of an oilseed. The main fatty acid found in canola oil is the oleic acid, also known as Omega-9[4].

An issue in biofuels, oxidative stability is closely related to the structure of fatty acid chains, being more susceptible those with a higher proportion of unsaturated lipids[5]. Canola oil has a high percentage of unsaturated fats, close to 93% [6].

The natural decomposition of triglycerides can be accelerated by light and heating, and rancidity is almost always followed by the formation of free fatty acids. High levels of acidity reflect in negative effects on oils, which may make them inappropriate for food or even for fuel purposes.

The mentioned characteristics may vary according to genetics and the environment agricultural management and environmental, such as water availability and frost, are control variables in the qualitative and quantitative yield of canola[7, 8].
II. MATERIAL AND METHOD

The field experiment was conducted in the municipality of Tibagi, state of Paraná, with the approximately coordinates 24° 16’ 29” South and 50° 05’ 42” West, and average elevation of 952 m. The experiment consisted of two factors, seeding times (four) and canola (Brassica napus) hybrids (three). The experiment was conducted in randomized blocks. The seeding times were: April 4th, April 16th, May 2nd and May 14th. The used hybrids were Hyola 43, Hyola 61 and Hyola 571.

At the seeding time, we used 18 seeds per meter and spacing between rows of 0.45 m. There was applied, in the furrow, 100 kg ha\(^{-1}\) of fertilizer (NPK formula 13-33-00). On the 45th day after seeding, there were applied, on total area, 100 kg ha\(^{-1}\) of urea and 100 kg ha\(^{-1}\) of KCl. During the crop cycle no fungicides, insecticides or herbicides were applied.

For the monitoring of the climatic conditions during the crop development, information on minimum, maximum, daily mean and cumulative rainfall index were used. They were recorded in a meteorological station of IAPAR - Instituto Agronômico do Paraná, located in the TelêmacoBorba city (approximate coordinates: latitude 24° 20’ S - longitude 50° 37’ W).

For oil and biodiesel characterization, 150 g of seeds were ground in a Willey knife mill, with 20 mesh sieve. For lipids extraction, a Soxhlet apparatus was used, using n-hexane as solvent, for 6 hours.

The obtained oil was submitted to an aqueous degumming process, aiming to remove phosphatides, by adding 5% of water mass in relation to the total lipid mass. The mixture was stirred for 30 minutes, at 65 °C, in a refrigerated ultracentrifuge, Hitachi Himac, model CR21GI. The mixture was subjected to 5000 rpm at a constant temperature of 4 °C for 15 minutes.

After degumming the lipid specific mass was determined, at 20 °C, using the Anton Paar digital densimeter, model DMA 4500 M.

The oxidative stability was determined in an accelerated oxidation test, under a temperature of 110 °C and 10 L h\(^{-1}\) airflow, with RancimatMetrohm apparatus, model 893. The acid index was determined according to [9].

The biodiesel production process was carried out by mixing 0.0675 g of sodium methoxide dissolved in 5 ml of methanol and added in 10 ml of oil. The reaction mixture was kept under constant stirring and heating at 55 °C for one hour. After resting for 30 minutes the glycerol was removed, were performed two steps of aqueous washing and drying with anhydrous calcium chloride and washing with organic solvent (petroleum ether)[10].

The biodiesel was evaluated by Nuclear Magnetic Resonance Spectroscopy\(^{1}\)H – RMN, with deuterated chloroform as solvent, with a BRUKER ASCEND spectrometer, of 400 MHz.

Chromatographic analyzes were performed on a Perkin-Elmer Gaseous Chromatograph, Clarus 580, with FID detector, capillary column type Elite-Wax, 60 m long, 0.25 mm in diameter and with a stationary phase of 0.5 mm thickness. Heating ramp with initial temperature of 190 °C, heating rate of 10 °C min\(^{-1}\) to 250 °C was used. An injection volume of 1.0 mL of sample in hexane and internal standard methyl nonadecanoate was used.

All dependent variables were submitted to the F test for analysis of variances and, when pertinent, Tukey’s regression analysis and mean test were performed. The Sisvar software was used for the analysis, version 5.3[11].

III. RESULTS AND DISCUSSION

The temperatures observed during the experiment conduction are shown in Fig. 1. In the initial stage, from emergence to flowering, temperatures of 13 to 22 °C are recommended [6]. At this stage, for the first and second seeding season, temperatures were higher, which may have led to lower productivity.

According to the stadium basal temperatures are different, for example, there were determined for canola - 0.8 °C for vegetative stage stadium and 10.0 °C for flowering [8]. Therefore all seeding times were harmed. Low temperatures, with frost occurrence, at the start of flowering can reduce up to 50% of flowering, whereas frostings at the end of flowering can reduce from 80 to 100% of flowering [7]. The only negative temperatures cataloged were recorded on July 25th, the only day
where the mean temperature was also below 5 °C (Fig. 1). This may have adversely affected the first and second seeding seasons.

When the temperature of the air rises above 27 °C, thermal stress occurs in the crop, reducing or even inhibiting the canola processes of growth and development, mainly in the final period of flowering and initial filling of the grains [12]. This is what happened to the fourth seeding season. Water stress at the end of flowering and beginning of grain filling has negative effects on the concentration of oil in the grain [13]. As the beginning of flowering and the duration of this period may vary a few days, it was considered that there was no water stress (Fig. 2).

The productive potential of an agricultural crop is defined through genotype-environment interaction. According to analysis of variance, the grain yield variable did not present a significant difference for the hybrid factor, but there was a significant difference (p<0.01) for the seeding time factor, and no significant difference was observed for the interaction of the factors and for the blocks (Table 1).
TABLE 1
Grain Yield, Oil Content, Oil Yield, Oil Specific Mass, Induction Time (Oxidative Stability) and Acidity of the Oil and Test of Means, When Pertinentes, of the Three Canola Hybrids

| Hybrid   | Productivity kg ha⁻¹ | Oil content* g kg⁻¹ | Oil yield kg ha⁻¹ | Specific mass kg m⁻³ | Induction time* h | Acidity mg KOH g⁻¹ |
|----------|-----------------------|---------------------|-------------------|---------------------|-------------------|-------------------|
| Hyola 43 | 1,556.90              | 382.7 a             | 641.8             | 901.0               | 9.95b             | 1.70              |
| Hyola 61 | 1,703.17              | 350.4b              | 616.9             | 898.0               | 8.66 a            | 1.72              |
| Hyola 571| 1,663.76              | 370.6 ab            | 716.2             | 899.0               | 9.50b             | 1.61              |

*means followed by equal letters in the columns do not differ from each other to 0.05 of probability by the Tukey test.

Linear regression analysis showed a positive relationship between time and yield (Fig. 3a). The canola seeded on April 4th reached the lowest productivity, with an mean of 382 kg ha⁻¹. The effect of the high temperatures recorded for this month and the occurrence of frost at the end of flowering/beginning of filling caused a negative impact (Fig. 1).

![Graph A](image-a)

**FIGURE 3** – Values found and adjusted regression for grain yield (a) and oil content (b) for Hyola hybrids 43, 61 and 571, according to seeding dates. Tibagi, PR.

The mean yield of canola grains in the State of Paraná in the 2011 harvest was 1,368 kg ha⁻¹, while the 2012 harvest was 813 kg ha⁻¹, due to strong frost. The harvest of 2013 had an average of 1,436 kg ha⁻¹[14].

In contrast, in experiments performed in Aw climate, with mild temperatures, with nine canola varieties, using flowering irrigation, yields ranged from 1,494 kg ha⁻¹ to 2,268 kg ha⁻¹[15]. In this case, the authors related terminal flower abortion and lower filling of the silicas with elevation of temperature.

The variable oil content showed a significant difference for the hybrid factors and time (p<0.01), showing no difference for the interaction of the factors. The mean lipid value expected in Brazil is 380 g kg⁻¹[6]. In Cfa climate, varying sowing dates, [16] obtained, for two hybrids, values between 346 and 399 g kg⁻¹. This variation, according to the authors, was correlated with water stress.

The mean for the Hyola 43 hybrid was statistically equal to the Hyola 571 hybrid and higher than the Hyola 61 hybrid. The Hyola 571 hybrid was statistically equal to the Hyola 61 hybrid (Table 1). In this case, there was a positive linear relationship between grain oil content and seeding time (Fig. 3b). The mean temperature increase in the filling stage of the grains can provide deformities and decrease in oil content [17]. As was the case with seeding season 1 and 2.

The canola seeded in the first season may have its oil content reduced due to the low temperatures, below 5 °C, observed in the second half of July, which also presented negative temperatures (Fig. 1). At that time, the crop was at the end of the flowering phase and beginning of the grains filling, critical phases to the crop [13].

According to analysis of variance, the variable oil yield per area did not present a significant difference for the hybrid factor (Table 1), but there was a significant difference (p<0.01) for the seedingtime factor (Fig. 4a), with no difference for the interaction between the factors. There was a positive linear correlation between the oil yield per area and the seeding times. These values are consequences of the productivities and oil content present already presented and discussed.

The variance analysis showed a significant difference for the induction time (oxidative stability) for the factors hybrid (Table 1) and time (p<0.01) (Fig. 4b). There was no significant difference for the factors interaction. The hybrids Hyola 43 and...
Hyola 571 were statistically equal and superior to the hybrid Hyola 61. The values can be considered coherent compared to [18] that obtained a mean of 7.2 hours. There was a tendency to increase the induction time with seeding times. Oxidative stability was affected by climatic conditions, especially in the case of the first seeding season.

The specific mass did not present significant difference for the hybrid factors and times, with mean value of 899.3 kg m⁻³ (Table 1). According to [19] the value of the specific mass of canola lipids is 878 kg m⁻³ (25 ºC). For different temperatures, [20] found a variation of 908 kg m⁻³ (10 ºC) to 921 kg m⁻³ (30 ºC).

The variable acidity did not present significant differences for the hybrid factor (Table 1), while there were significant differences for the time factor (p<0.05), and no significant difference was observed for the interaction (Fig. 4c).

The fatty acids determined were palmitic, stearic, oleic, linoleic and linolenic. The palmitic acid variable (C 16:0) did not present a significant difference for the hybrid factor (Table 2), whereas there was a significant difference for the time factor (p<0.01).

### Table 2

| Hybrid | Palmitic (C 16:0) g kg⁻¹ | Stearic (C 18:0)* g kg⁻¹ | Oleic (C 18:1) g kg⁻¹ | Linoleic (C 18:2)* g kg⁻¹ | Linolenic (C 18:3)* g kg⁻¹ |
|--------|--------------------------|--------------------------|-----------------------|---------------------------|---------------------------|
| Hyola 43 | 46.7                     | 28.7 a                    | 644.8                 | 195.4 a                    | 77.3a                     |
| Hyola 61 | 46.2                     | 25.5 b                    | 652.1                 | 172.4 b                    | 92.8b                     |
| Hyola 571 | 43.5                     | 28.3 a                    | 654.2                 | 176.1 b                    | 86.3ab                    |

*means followed by equal letters in the columns do not differ from each other to 0.05 of probability by the Tukey test.
Regarding the temporal evaluation, there was a tendency to decrease the palmitic content (C16:0) with advance in the seeding dates (Fig. 5a). Evaluating two varieties of canola, and two varieties of rapeseed, [22] found values of 80.8 g kg\(^{-1}\) and 59.0 g kg\(^{-1}\) in canola and 47.8 g kg\(^{-1}\) e 39.8 g kg\(^{-1}\) in rapeseed. [23] found the presence of 39.0 g kg\(^{-1}\) palmitic acid in canola oil. The stearic acid variable (C18:0) presented a significant difference for the hybrid factors and times (p<0.01), and no significant difference was observed for the interaction. The highest concentrations of stearic acid were found in the Hyola 43 and 571 hybrids, 28.71 and 28.29 g kg\(^{-1}\), respectively. The hybrid Hyola 61 obtained the lowest concentration; 25.5 g kg\(^{-1}\) (Table 2). Fig. 5b shows the concentrations of stearic acid according to sowing time. Comparing stearic acid in canola and rapeseed, [22] obtained 16.9 and 16.5 g kg\(^{-1}\) for canola, and 20.2 and 25.0 g kg\(^{-1}\) for rapeseed. [23] found 16.0 g kg\(^{-1}\) canola.

The variable oleic acid (C18:1) showed a significant difference for the time factor (p<0.01), whereas no significant differences were observed for the hybrid factor, and no significant difference was observed for the interaction. The mean concentration of this lipid found in the hybrids was 650.4 g kg\(^{-1}\) (Table 2).

Although the equations represented (Fig. 5) were significant, the mathematical adjustments presented a low R2 value, so the seeding time can influence in approximately 20 g kg\(^{-1}\) for oleic (18:1) and 30 g kg\(^{-1}\) linoleic (18:2).

The concentration of oleic tended to increase as the seeding dates progressed (Fig. 5c). Studying canola and rapeseed, [22] observed oleic acid concentrations of 570.9 g kg\(^{-1}\) and 599.2 g kg\(^{-1}\) for canola and 604.3 g kg\(^{-1}\) and 612.4 g kg\(^{-1}\) for rapeseed. [23] Studying commercially available oils (Illinois, USA), found for canola 600 g kg\(^{-1}\). [24] evaluated twenty edible oils observed the presence of 620 g kg\(^{-1}\) oleic in canola.

Oleic acid, also known as omega-9, has only one unsaturation, being one of the healthiest sources of dietary fat [25]. The oleic acid values found in this experiment are higher than most cited in the correlative literature.
According to analysis of variance, the variable linoleic acid (C 18:2) presented significant differences for the hybrid and period factors, whereas no significant difference was observed for the interaction. The hybrid Hyola 43 had the highest concentration of this fatty acid, mean of 195.4 g kg⁻¹. The concentrations in Hyola 61 and 571 hybrids were 172.4 and 176.0 g kg⁻¹, respectively (Table 2). Linoleic acid also known as omega-6 plays a key role in maintaining human health.

Qualifying canola and rapeseed varieties, [22] found 231.2 and 230.7 g kg⁻¹ of linoleic acid to canola and 232.7 and 236.3 g kg⁻¹ to rapeseed, and [23] found 220 g kg⁻¹ of linoleic acid in canola. The linoleic acid values found in this experiment are lower than those reported.

The linolenic acid variable (C 18:3) presented a significant difference for the hybrid factor, and no significant differences were observed for the time factor and for interaction.

For the linolenic acid, the hybrid Hyola 43 presented the lowest concentration of this variable, reaching the percentage of 77.3 g kg⁻¹, while Hyola 61 showed the highest percentage of this fatty acid, obtaining 92.7 g kg⁻¹. Hyola 571 had a mean of 86.3 g kg⁻¹ and was statistically significant to Hyola 43 and 61 (Table 2).

Linolenic acid or omega-3 has three unsaturations in its molecule and this lipid is also part of the group of essential fatty acids in the human diet because it is not synthesized by the human body.

Searching for various oils, [23] verified the presence of 101.0 g kg⁻¹ of linolenic acid in canola oil. [22] obtained values of 100.2 g kg⁻¹ and 94.6 g kg⁻¹ of linolenic acid in two varieties of canola, and 95.0% and 116.5% in two varieties of rapeseed. The values of linolenic acid found in this experiment are lower than those mentioned.

According to the time evolution, there was a tendency to exchange values between oleic (one saturation) that increased and linoleic (two saturations) that decreased, expected physiological process. This process is interesting for the use of the oil as fuel and would harm the oil if the final destination was the human food. Considering the results of dependent, quantitative and qualitative variables, the best sowing time of canola would be between the second fortnight of April and the first week of May.

IV. CONCLUSION

There was a significant difference for the hybrids in the variables oil content, induction time and in the stearic, linoleic and linolenic contents. Highlighting Hyola 43.

There was a significant difference for the periods in the grain yield, oil content, oil yield, and induction time and in the palmitic, stearic, oleic and linoleic contents. The most interesting seeding season would be between April 16th and May 2nd.

ACKNOWLEDGEMENTS

To the Instituto Agronômico do Paraná (Iapar) for the availability of climatic data and Capes for the Masters scholarship?

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