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Carinata FAME Production Process and Biofuel Oxidation

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Title: *Carinata FAME Production Process and Biofuel Oxidation*

An Honors Thesis submitted in partial fulfillment of the requirements for Honors in Chemistry and Biochemistry.

By

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Under the mentorship of *Dr. Brian Koehler and Dr. Valentin Soloiu*

ABSTRACT

In this experiment, the contribution of a standard production method for biofuels on their oxidative stability was investigated. Peroxide values were measured at different steps of the production process of Brassica carinata and peanut-based biofuels. The washing and drying steps in this production method showed significant increases in peroxide values for both biofuels and was identified as a major contributor of biofuel oxidation. Further analyses of the physical and thermal properties showed a more pronounced affect in the biofuel from Bassica carinata, and indicated an unusual composition much higher in saturated fatty acids much longer than those found in peanut. This unusual difference in the naturally produced fatty acids may indicate the need for extra care in the handling and refining of Carinata-based biofuels.

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Introduction

Fatty acid methyl esters (FAMEs) make up the chemical composition of biodiesels, also termed "biofuels". Fatty acids (and the fatty acid methyl esters derived from them) are made of long chains of hydrogenated carbon atoms, which contain a high-energy content released during combustion reactions 1 . This property of fatty acids makes biodiesel a reliable replacement for exhausting fossil fuels². Furthermore, biofuels present more environmental benefits compared to fossil fuels due to their cleaner emission characteristics³⁴. However, biofuels cannot be viewed as the definitive solution when applied to a triple bottom line framework that considers the social, environmental and financial aspects of their use^{4e, 5}. A major issue facing the mass adaptation of biofuels is their low chemical stability, as their FAMEs tend to undergo oxidation that results in a mixture of chemicals that can form gums and sediments - potential clogging factors that deteriorate engine injection systems⁶. These oxidative processes typically involve the formation of peroxides, aldehydes and various unidentified small chemical species (Figure 1). The factors that affect oxidation in biofuels are complex and broad and include variations in the fatty acid compositions of the source oils, their age, the presence of natural antioxidants, impurities and degradation products, etc.⁷. Because biofuels are composed of a variety of FAMEs, multiple oxidation reaction paths are possible $⁸$ (Figure 1). In this study, we investigate</sup> the contribution of a standard biofuel production method, in particular the washing and drying steps, on biofuel oxidation. The experiment was conducted on biodiesel made from *Brassica Carinata* (Ca*)*, an emerging biodiesel crop, and on biodiesels made from both freshly obtained as well as old, stored peanut (Pa) oil. Thermal and physical analysis of all samples was then conducted using a variety of techniques including gas chromatography, thermo-gravimetric

differentiation, viscometry, calorimetry, and rancimat oxidation to assess the necessity and the importance of each step regarding the quality of the biofuel produced.

Figure 1. Approximate oxidation mechanism. X represents chemical triggering agents for an oxidation mechanism. Biofuel being a mixture of fatty acids esters, it is difficult to draw a single oxidation mechanism⁹ . Depending on the nature of the radical initiator, the storage temperature, the variety of fatty acids in the oil, the degree of impurities etc. many pathways of oxidation mechanism are possible.

Why Carinata?

The growing demand for energy has brought energy companies and researchers together to seek alternative sustainable forms of energy. Thus, diverse forms of oils and fats have been explored as potential sources of biofuels. However, many concerns have been raised regarding the use of agricultural resources, including land and food crops, as biofuel sources. These concerns have environmental, ethical and moral aspects. They are also of qualitative nature as the produced biofuels need to meet engines requirements to be of practical use. Damage to the soil and the amount of water used to grow seeds that could otherwise be directed to more urgent needs such as the fight against poverty, hunger, desertification, etc. are a few of the ethical and environmental concerns. *Brassica carinata*, a non-food oil crop known locally as Ethiopian mustard, has many advantages as a biofuel source and could be a suitable solution to the problems facing the biofuel industry¹⁰. Carinata seeds are easy to grow and do not require high volumes of water or care. In addition, the seed was found to be easy to modify genetically to produce an oil abundant in long-chain fatty acids such as erudic acid (C22:1) and nervonic acid (C24:1) 4d . Regarding oxidative concerns, biodiesel produced from *Brassica carinata* has been reported to have a relatively high stability allowing for longer storage times^{7c}

Methods

1**.** Biofuel Preparation

Four methods, direct and blending, microemulsions, pyrolysis (thermal cracking), and transesterification are commonly used to make biodiesels¹¹. Transesterification, the most commonly used method, consists of reacting the crude oil with an alcohol to yield esters and glycerol, and was the method used in this study. A catalyst was also used to increase the reaction rate and yield. Using this method, it has been found that a minimal molar ratio of 6:1 alcohol to triglycerides is required to drive an efficient transesterification reaction $11a, 11c$. In this experiment, anhydrous methanol (CH₃OH) and sodium hydroxide (NaOH) were used as the

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catalyst and were added to the crude oils while heating on a hot plate set at a constant 55 °C for 60 minutes. After transesterification, the reaction yielded a mixture of fatty acid methyl-esters (biofuel), glycerol, alcohol, catalyst and other unidentified residues. The biofuel was then centrifuged to precipitate out the glycerol, after which a washing procedure was conducted on the biodiesel layer to eliminate any excess alcohol content remaining in the fuel. The final step of the process involved drying the biofuel by air to eliminate water moisture resulting from the washing process, along with filtering the refined fuel to remove any remaining small residues.

Figure 2. The reaction above represents the transesterification reaction that transforms triglycerides into fatty acid methyl esters (FAME's). The catalyst used is a mixture of dry methanol (CH3OH) and sodium hydroxide (NaOH). The reaction was further conducted at 55 °C for 60mn.

2. Peroxide Value Determination

Peroxide value (PV) is an analytical parameter important in defining the oxidative state of lipidcontaining substances. It is defined as the milliequivalents (mEq) of peroxide per kilogram of sample and is based on the assumption that the compounds reacting under the conditions of the

test are peroxides or lipids oxidation products¹². This property is mostly used in the food industry¹³ but it is also used by biofuel industries to assess the amount of oxidative agents present (mostly peroxide elements) to monitor and to predict the stable storage life of the prepared fuel^{6d, 14}. In this experiment, a series of peroxide value titrations were conducted at specific stages of the peanut (Pa) and Carinata (Ca) biofuel production process. The procedure used followed AOCS method Cd 8-53. The PV was measured after each step of the biofuel preparation.

3. Oxidative Stability Test

The stability test was conducted using a 873 Metrohm Biodiesel Rancimat instrument. The term "oxidation stability" in this case refers to the sample resistance to oxidation, which is conducted by the measurement of the sample conductivity. The samples were tested in quadruplet at 100°C, 110°C, 120 °C and 130 °C while exposed to an air flow of 10L/h. Each sample tube contained 3g of biodiesel. This test further allowed for the preparation of artificially oxidized fuel used for additional studies.

4. Fatty Acid Composition

Gas chromatography is a technique widely used for qualitative and quantitative analysis of biofuels compositions. While many different types of detectors exist, a flame ionization detector (FID) was decided to be suitable for use in determining the fatty acid composition of these biodiesel mixtures. A Shimadzu GC-17A ga This foreshadowed that refining Carinata biofuel was going to require subsequent steps than peanut or lesser weight biofuel. In fact, during the washing process, a neutral peanut biofuel was obtained just after the second wash, while Carinata biofuel required five washing to reach a neutral pH. The more temperature resistant of the unwashed carinata biofuel can so be related to the presence of residual components and unknown impurities.

s chromatograph, installed with a RESTEK 2330 column (30 m, 0.25mmX0.20micrometer) was used in this experiment, and commercially available fatty acid methyl-estyers (FAME-5 and FAME-7, Matreya LLC) were used to identify the fatty acids methyl esters in the biofuel samples.

Table 1. Gas chromatography instrumental parameters used in this study.

Carrier	Helium
Gas Pressure	85 kPa
Total Flow	9.0 mL/min
Purge Flow	2.0 mL/min
Colum Flow	0.61 mL/min
Linear velocity	20.4 cm/sec
Injector Temperature	250 °C
Injection	Split $(10:1)$
Oven Temperature	170 °C, hold 20min
	170 °C - 210 °C, 4 °C/min, hold 10 min
	210 °C, hold 10 min.
Flame Ionization Detector Temperature	250 °C

5. Thermal Analysis

Thermal analyses can provide a wide variety of physical and chemical information on a given biodiesel. The instrument used in this experiment, a Shimadzu DTG-60, combined two simultaneous apparatus: a thermo gravimetric (TG) and a differential thermal analysis (DTA), data from which can be complementary in analysis. Thermogravimetric analysis allows for the measurement of sample weight loss occurring during increasing temperature changes. This technique helps to determine the thermal stability of the samples and to predict their thermal behavior (phase changes) in a mechanical engine combustion chamber. Fuels with lower vaporization temperatures are more efficient in starting and warming up mechanical engines and contribute less to deposits¹⁵. However, they are consumed faster and provide less energy. Fuels with higher vaporization temperatures have the opposite characteristics but at the cost of increased exhaust emissions.

6. Viscosity

Viscosity was tested using a Brookfield LVDV-II+P Viscometer. The samples were exposed to temperatures increasing from 27 ºC to 60 ºC with a 200-rpm rotational speed SC4-18 spindle, 7.92-14.81 D/cm² shear stress, 20-37.40% torque. Viscosity was recorded through a Rheocalc V3.2 Build 47-1 program**.**

Results and Discussion

Peroxide value (PV) measures a transient product of oxidation, providing a qualitative indication of the amount of complex and unstable compounds resulting from an oxidation reaction (Figure 1). A low peroxide value could then represent a beginning or an advanced oxidation state, which can be determined by measuring over time^{12b}. Generally, low peroxide values (between 1-5 mEq/Kg) connotes with a high and stable lipid and fatty acid composition, while peroxide values over 20 mEq/Kg correspond to very poor, highly oxidized oils 12b . Analysis of the peroxide

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value in this experiment allowed monitoring the oxidation state of the biodiesels during their production.

The analysis of samples from approximately 3-year-old crude Carinata and peanut oils showed peroxide values of 25.7 mEq and 31.8 mEq, respectively, while a more recently obtained fresh peanut oil showed a PV of 9.9 mEq (Table 2). The high PV values of both of the old stored oils indicate the presence of large amounts of peroxide molecules, which are products of oxidation reactions. These high PV are then an indication of the oxidative degradation the old oils had undergone during their storage. Measuring the PV for a year-old Ca and biodiesel showed a high PV of (42 mEq). A similar result (45 mEq) was found for a year-old Pa biodiesel, corroborating the damaging consequences of storage and time on both unrefined oils and their respective biofuels^{6d, 13d}.

Table 2. Peroxide Values (mEq) measured after major stages of the biofuel preparation from fresh Peanut (Pa) and old Carinata (Ca) oil.

	Pa(fresh)	Pa(old)	Ca(old)
Crude Oil (initial)	9.9	31.8	25.7
After transesterification	2.8	3.1	9.9
After centrifugation	3.8	3.5	12.0
After roto- evaporation	3.9	3.5	11.9
After washing step	6.8	7.2	13.9
After drying step	11.8	15.4	19.9

Based on the PV determination, the transesterification reaction seems to be an important reducer of oils oxidative agents. The peroxide values dropped significantly for both Peanut and Carinata oils, particularly in the "old" oils samples where the transesterification step reduced the PV values to that of freshly obtained (peanut) oil. The transesterification reaction breaks apart fatty acids from their glycerol backbone and yields two separate layers, one of glycerol mixed with unreacted catalysis and other residues, and the other a clear layer of fatty acid methyl-esters (the biofuel) that also contains floating glycerin molecules and some excess methanol (that is washed out in later steps). The notable decrease in the peroxide values after this reaction could have multiple explanations, but it is possible that components of oxidative damage present in the old oil primarily separate into the aqueous glycerol layer and hence the transesterification process naturally acts as a "cleansing" step resulting in fresh biofuel with low peroxide values.

Because the methanol and sodium hydroxide catalyst are used in excess to drive the reaction for maximum yield, the traces of methanol and other residues must be removed. The steps following the transesterification reaction were designed for this purpose, a centrifugation procedure was conducted primarily to remove suspended glycerin, solid NaOH, and other residues after the mixture had cooled down. A PV increase of only 1 mEq and 2 mEq was observed in fresh Pa and old Ca biofuel, respectively, during this step. The following step of the purification process was the removal of excess methanol through rotatory evaporation. The boiling point of methanol being 64.7 \degree C, the containing vessel was warmed to 65 \degree C in water bath to facilitate methanol evaporation. Peroxide value measurements did not considerably change from values observed in the previous step. However, a cloudy precipitate, most likely still-remaining trace glycerin resulting from either incomplete transesterification or from the clustering of suspended glycerin and residues, was noticed and removed in both Ca and Pa

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biofuels by application of a second centrifugation process (no additional change in PV values was observed from this second filtration of excess glycerin).

Many biofuel production methods include a step washing with warm water following the removal of solid glycerin and excess methanol¹⁶. Even though most methods suggest washing until a clear rinse is observed, in this experiment the washing was stopped only after a neutral pH was obtained. Following the washing step is a drying process meant to remove water and moisture content resulting from the previous washing. While the drying process can be performed by warming the sample under a vacuum to increase evaporation, in order to avoid any unexpected reactions that heating the biofuels under rotary evaporation might cause (free fatty acid reacting with water in presence of heat, or between fatty acids themselves), in this experiment the drying process was performed by blowing dry air through the biofuels overnight. A filtering process concluded the biofuels preparation. The washing, and even more so the drying processes were revealed to be significant triggers of oxidation in the biofuel production. The PV for the peanut biofuels almost doubled in each of these two steps, and the Carinata biofuel almost reached what is considered high oxidation levels. The produced refined biofuels are therefore highly susceptible to oxidative reactions and their long term (or even short term) storage quite guarantees their degradation.

Based on results of the peroxide value analysis, the washing and drying steps were identified as major oxidative agent triggering steps. To further, study the biofuels at this step in their preparation, a biodiesel rancimat instrument was use to measure their resistance to oxidation. This test measures the conductivity of the biofuels exposed to air over time (figure 3) and is a good way to estimate how long a given fuel will remain stable before undergoing oxidation. At all temperatures studied the Carinata biofuel before washing had an increased

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resistance to oxidation (longer stability times) compared to that of the biofuel after washing and drying (see Table 3).

Figure 3. Sample graph showing typical result of an rancimat test for a washed and dried Ca biodiesel at 110 °C. The vertical red line indicates the point where the biodiesel conductivity reaches an unstable region.

Table 3. Average Stability Time for Carinata Biofuel before and after washing and drying at 100, 110, 120, 130° C

Carinata	100° C	110° C	120° C	130°C
Before Washing and Drying (h)	4.78	2.34		0.62
After Washing and Drying (h)	\overline{H}			$0.08\,$

It was clear from the increased peroxide values and decreased rancimat times observed in the biofuels after the washing and drying step that these steps increase the FAME's likelihood of engaging in oxidation. In other words, the washing and drying steps appear to cause qualitative damage to the biofuels. The next step of the study was to investigate differences in the physical and thermal properties of the biofuels before and after washing, and look for any links to the

composition (of the FAME's) of the biofuels during this final step in their preparation. A minor change in these properties between the biofuel samples could be an indication that the final washing and drying steps should perhaps be skipped in the production process, or at the very least that the method of washing and drying may need to be carefully considered in order to produce more stable and long storage-capable biofuels.

Viscosity was the first property measured in the biofuel samples before and after the washing and drying step. Viscosity is an important parameter regarding suitability of an oil (biofuel) for use in an internal combustion engine¹⁷. It is a key qualitative property because it affects atomization quality, droplet size and penetration,¹⁸ all important parameters in the design of an engine to use that fuel. Lower viscosities can damage engines following a system leakage, while higher viscosities can lead to poor biofuel atomization and incomplete combustion, both of which contribute to an increase in the formation of sediments and engine deposits as well as carbon deposition on the injectors¹⁹. All the biofuel samples tested in this study showed no considerable change in their viscosities comparing the unrefined (before washing and drying) biofuel to the refined (washed and dry) fuels (Figures 4 and 5). The results obtained were all within acceptable range for use in internal combustion although the Carinata biodiesel was found to be more viscous than the peanut biodiesel both before and after the washing/drying step.

Figure 4. Viscocity measurements on unrefined (before washing) and refined (after washing) biofuel made from ages Carinata seed oil.

Figure 5. Viscocity measurements on unrefined (before washing) and refined (after washing) biofuel made from freshly-obtained peanut oil.

This increased viscosity is believed to result from differences in the FAME's that comprise the Carinata biodiesel and not a result of the Carinata oil being old (compared to the fresh peanut oil. Indeed, subsequent measurements on the viscosity of biodiesel made from similarly aged peanut

oil (Figure 6) resulted in similar viscosities to that of the fresh peanut oil, indicating that the aging of the oil did not account for the higher viscosity observed in Carinata biodiesel.

Figure 6. Viscocity measurements on unrefined (before washing) and refined (after washing) peanut oil biofuel.

Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were employed to study each biofuel before and after the washing/drying step. TGA measures the sample weight loss occurring during increasing temperature changes and can further assist in characterizing the fuel before and after the final drying step. It is a common analysis used to predict their thermal behavior (phase changes) of fuels in a mechanical engine combustion chamber. Differential thermal analysis (DTA) identifies the degradation phases of a system during a uniform heating and cooling process through time and temperature change. An increase and decrease of temperature producing a peak shows the samples phase changes involving absorption (endothermic) or release (exothermic) of heat. A downward peak indicates absorption of heat (endothermic) and is synonymous of a vaporization reaction while an upward peak

describes a release of heat (exothermic process) produced during a condensation reaction. The data collection for this was conducted along with the TGA experimentation.

The TGA results for both the fresh and old peanut biofuel samples (before washing and after drying) showed nearly identical thermal behaviors, as both lose 90% of their mass within the 150-300 °C temperature range (Figure 6 and Figure 7). Only minor differences were observable in either old or fresh Peanut oil biofuels comparing their TGA results before and after the washing/drying step in each. Carinata biofuel, on the other hand, showed a TGA pattern very different from the peanut biofuels (Figure 8). The Carinata biofuel after washing and drying lost about 95% of its mass at temperatures slightly higher than the peanut biofuels, between 170-350 °C, while the unwashed Carinata biofuel seemed more stable and resistant to temperature increases, only completely evaporating at a temperature close to 600 °C.

The DTA results of the unrefined (before washing) and unrefined (after washing) peanut biofuels showed similar characteristics, a vaporization phase at a temperature approximating 345

7b.

7a.

Figure 7. a and b represent the thermo-gravimetric result for the FAME's obtained from a fresh Peanut oil source. A minor difference was noticed between the washed, dried, and unwashed biodiesel

8a.

8b.

Figure 8. a and b show the thermal behavior of the FAME's obtained from an old peanut source.

9b

Figure 9. a and b show the thermo-gravimetric data for old Carinata biodiesels. The unwashed Ca FAME's showed a different thermal behavior mass percent lost compared to the washed, dried Ca FAME's

°C. The refined Carinata biofuel vaporized at about the same temperature as peanut biofuels (345 °C) while the unrefined fuel required a higher temperature (395 °C) before beginning its vaporization phase. It also showed multiple endothermic peaks. These appearance of these peaks might possibly be explained by the presence of impurities and other residues which, would also react along with the Carinata biodiesel FAME's.

To investigate the composition of the refined and unrefined biofuels, each sample was further analyzed using gas chromatography. Thermal properties of biofuels have been related to their fatty acid methyl-ester composition³ as longer and more saturated fatty acid methyl-esters having higher boiling point temperatures and hence require higher combustion temperatures. A commercially available FAME standard of known composition was recorded (Figure 10) and its peaks used to identify peaks in the chromatograms of the sample biofuels before and after the washing/drying step for both Carinata (Figure 11) and peanut (Figure 12) biofuels. The areas under the peaks correspond to the amount of each fatty-acid methyl ester in the biofuel and used to generate a fatty acid profile of both Carinata and peanut biodiesel before and after the washing step (Table 4).

The fatty acid profile of Pa and Ca explains the differences both fuel show in the TGA/DTA at increasing temperatures. Carinata biodiesel, both washed and unwashed, showed large amounts of longer chain fatty acids (~70-80% C20 and up) compared to peanut biodiesel, which was dominated by shorter fatty acids (~75% C18 fatty acids). This unusual prevalence of heavier fatty acid methyl esters in Carinata would explain its increased temperature resistance and increased density (Crude oil molecular weight of Carinata estimated at 973g/mol, peanut

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Figure10. GC typical chromatogram of FAME-7 standard used for peak identification of the fatty acid methyl esters in Cariniata and peanut biodiesel samples.

Figure 11. GC chromatogram of Carinata biodiesel after (11a) and before (11b) washing and drying.

Figure 12. GC chromatogram of Peanut biodiesel after (12a) and before (12b) washing and drying.

		Ca-before	Ca-after	Pa-before	Pa-before
	FAME	%FAME	(%FAME)	$(\%FAME)$	$\%FAME$
Methyl palmitate	C16:0	0.69	1.59	5.29	4.13
Methyl stearate	C18:0	0.51	0.71	1.82	2.07
	C18:1(Z)			3.81	
Methyl elaidate	C18:1(E)	4.43	6.92	53.90	58.18
Methyl linoleate	C18:2(cis 9,12)	7.14	12.24	14.49	15.89
Methyl arachidate	C20:0	0.80	0.78		1.74
Methyl linolenate	C18:3(cis 9,12,15)	4.85	9.56		
Methyl gondoate	C20:1	6.85	7.76	1.40	2.86
Methyl eicosadienoate	C20: 2(cis 11,14)	0.75	0.85		
Methyl Behenate	C22:0	1.15	0.77	1.84	
Methyl erucate	C22:1	65.61	52.33		0.55
	$C20:5(cis-5,8,11,14,17)$	1.33	1.26		
Methyl lignocerate	C24:0	1.07	0.88	1.71	5.77
	C24:1	4.82	3.18		
	Saturated	4.2	4.7	10.5	20.6
	Unsaturated	95.8	93.4	73.6	77.5
	C18's	16.9	28.9	74.0	76.1
	$C20$'s and up	82.4	67.6	4.9	17.8

Table 4. Fatty Acid Methyl-Esters Profiles for Carinata Biodiesel before and after the washing and drying process (Percent composition of each FAME).

crude oil molecular weight was estimated to 754.5 g/mol – *See Equation below-). Also of note were the amounts of saturated and unsaturated fatty acids found in the biodiesel samples. Carinata contained ~95% unsaturated and ~5% saturated fat, while the refined peanut biodiesel contained ~75% unsaturated and 10-20% saturated fatty acids (~5% of the GC peaks were unidentified). Saturated fats are generally considered more resistant to rancidity (oxidation)²⁰ and to have higher melting points. Carinata's lower amount of saturated and increased amount of unsaturated fatty acids may indicate the need for extra care in the handling and refining of Carinata-based biofuels.

*Equation

Derived Estimated Molecular Weight Formulas

*MWT= MWFA*3*

MWT= Total Molecular Weight

MWFA= Average Molecular Weight of Fatty Acids present (table 2)

Conclusion

The results gathered in this study support our hypothesis that the production methodS used to make biofuels play a role in the oxidation of those fuels. Analysis of the major steps of the production showd that the washing and drying steps considerably increase the biofuels' peroxide values. Even though multiple variables contribute to the biofuel oxidation, a cleaner and more stable freshly produced biofuel has a longer oxidative storage time than a less clean and less stable biofuel. The presence of impurities have been identified as a major component determining biofuels 'stability and they most likely define the fuels quality in engines injection systems and combustion chambers. Therefore, it appears necessary to have the least possible residues in the final, ready to use produced biofuel. Carinata and peanut sources have different densities and molecular weight due to heavier fatty acids in Carinata. Peanut biofuels less dense and shows few variations in conducted and thermal characterizations (Viscosity and TGA/DTA) between the unwashed and washed/dried biofuels. Based on these results, it can be suggested that unwashed peanut biofuel could potentially be used as is, but further engine testing should be conducted to support this hypothesis. The washing and drying processes identified as majors

occurrences at increasing oxidation susceptibility in the biofuel can so be eliminated- from peanut biofuel production methodology to yield stable biofuel. However, while viscosity analyses showed similar behaviors for unwashed and washed/dried Carinata, a noticeable difference was observed during the thermal analysis. These differences were attributed to the presence of important residues and their removal might be a necessity for stable biofuel and a better engine efficiency. While more advanced tests should be further conducted, we do not suggest skipping the washing and drying processes as they appear important to obtain a higher quality biofuel.

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