Received: 15 August 2017 | Revised: 25 September 2017 | Accepted: 30 September 2017

DOI: 10.1111/jfpp.13533

ORIGINAL ARTICLE

WILEY Journal of Food Processing and Preservation Institute of Food Science + Technology ifst

Variation of density and flash point in acid degummed waste cooking oil

Gina Vlahopoulou[1] | Giacomo Luigi Petretto[1] | Sebastiano Garro
Carlo Piga[1] | Alberto Mannu[1]

[1]Department of Chemistry and Pharmacy, University of Sassari, Sassari, Italy
[2]International Research Centre in Critical Raw Materials-ICCRAM, University of Burgos, Plaza Misael Banuelos s/n, 09001 Burgos, Spain
[3]Advanced Materials, Nuclear Technology and Applied Bio/Nanotechnology. Consolidated Research Unit UIC-154. Castilla y Leon. Spain. University of Burgos. Hospital del Rey s/n, 09001 Burgos, Spain

Correspondence
Alberto Mannu, Department of Chemistry and Pharmacy, University of Sassari, Sassari, Italy.
Email: albertomannu@gmail.com

Abstract

Recycling of waste cooking oil represents a source of convenient raw materials for industry. Within the large number of products derived from the treatment of waste cooking oil, eco-friendly lubricants grown in importance during the last years. Recycling process for such application consists usually of acid or basic degumming followed by a filtration step. The effect of the specific type of acid degumming on the density and on the flash point of the recycled oil was evaluated employing full factorial design. Two mathematical equations were derived which allow to estimate respectively the density and the flash point of the recycled oil, depending on the: (a) pH of the washing solution, (b) oil/water ratio, (c) temperature of the system, and (d) the stirring time.

Practical applications

Recycle of waste cooking oil presents several advantages. Mainly it is beneficial for the environment and considered as mandatory by law in several countries, and could furnish a useful low price raw material for several kind of industries. Recently, a multitude of local small scale industries have based their business on this topic and the recycling process employed often consists in a degumming step followed by filtration. This article deals with the tuning of the main parameters of the degumming step related with the density and the flash point of the final product. These parameters are important especially for lubricant synthesis.

1 | INTRODUCTION

Worldwide, consumption of vegetable oils has constantly grown in the last 20 years and its current global market can be estimated in about 160 million tonnes per year (Lin et al., 2013).

Most of the produced vegetable oil is used directly as food ingredient (80% of the total production) and as cooking oil generating a large quantity of wastes.

In the last years, the transformation of vegetable oils in chemical feedstock has attracted a lot of attentions with the aim to replace synthetic mixture derived from petroleum, much more impacting on the environment and, in general, on public health (Boyde, 2002; Rac & Vencl, 2012; Singhabhandhu & Tezuka, 2010a).

Recycling waste cooking oils allows to provide biodegradable, non-toxic, and green feedstocks to the industry of vegetable oil derivatives, which ranges from energy (direct burning, Singhabhandhu & Tezuka, 2010b) or bio-diesel (No, 2011; Talebian-Kiakalaieh, Amin, & Mazaheri, 2013) to raw material, bio-lubricant (Petran, Pedisic, Orlovic, Podolski, & Bradac, 2008; Shashidhara & Jayaram, 2010) and fermentation media to soap industry (Panadare & Rathod, 2015).

Additionally, considering the economical aspect, the exploitation of waste cooking oil instead of pure vegetal oil represents the cheaper solution for industry. The waste cooking oil has been sold for decades as animal feed until its unconditional banning emitted by the European Commission, in 2002, due to the great number of potentially harmful compounds generated during frying which could migrate in food chain by contamination of animal meat (Cvengros & Cvengrosova, 2004). Furthermore, storage and disposal of waste cooking oil may contaminate environmental water requiring specific and expensive methods.

The choice of the recycling process of waste cooking oils depends on the field of application of the final product but usually consists of the following three main steps: degumming, distillation or filtration, and clarification. Sometimes, as in the case of crude vegetal oils, the degumming process can be included in the filtration step (Haas, 2005; Koris & Vatai, 2002; Tiwari, Kumar, & Raheman, 2007).

During the degumming step, the amount of phospholipids, free fatty acids, waxes, metal ions, and coloring pigments present in the waste oil in large amount as consequence of the process of frying is drastically reduced (De Moura, Goncalves, Cunha Petrus, & Viotto, 2005; Ochoa, Pagliero, Marchese, & Mattea, 2001). The standard degumming treatment is usually performed by acidic, neutral, or basic water treatment, ultrafiltration, or enzymatic treatment (Boyde, 2002; Sampaio et al., 2015; Yang, Wang, Yang, Mainda, & Guo, 2006).

Local recycling of waste cooking oil for application different from bio-diesel can be a rentable business for small industries, in particular in the field of bio-lubricants (Fox & Stachowiak, 2007; Vintila, 2009). As confirmation of this growing interest, a large number of small-scale apparatuses for vegetable oil recycling are currently available on the market.

The common recycle processes available with most of the commercial apparatuses consist in a filtration under vacuum, sometimes followed by a clarification step (Pohler, Modler, Bruhnkeh, & Hidenberg, 2004).

Supercritical CO_2 extraction represents an alternative process, already applied to olive oil purification (Sesti Ossèoa, Caputoa, Graciab, & Reverchona, 2004).

Little attention has been dedicated to the degumming step of waste cooking oil for small-scale application as recycling in small areas where the transport of the waste cooking oil to the industrial plant represents an important cost of the overall process.

In order to shed some light on the usefulness of the specific water degumming of waste cooking oils, a systematic study of the influence of the main parameters of water degumming of waste cooking oils on the density and on the flash point of the final product has been conducted.

2 | MATERIALS AND METHODS

2.1 | Waste oil samples

Waste cooking oil samples were collected from domestic supplier in the geographic area of north Sardinia. Sulfuric acid 99.999% was purchased from Sigma Aldrich. Deionized Water was used for all the experiments.

AQ1

Alberto Mannu (albertomannu@gmail.com)
2017-10-13 16:22:16

Sigma Aldrich Italy

2.2 | General degumming procedure

The selected quantity of waste cooking oil was mixed to the opportune amount of water in a round bottom flask, and the mixture was stirred for the indicated time (Tables 1 and 4). Then, the mixture was transferred in a separatory funnel and decanted for 2 hr. The organic layer was then collected and stored in the dark at room temperature until analysis.

2.3 | Determination of density

The density, defined as "the mass of liquid per unit volume at 15 8C with the standard unit of measurement being kilograms per cubic metre," was determined according standard method ASTM 1298-12b (ASTM 1298, 2012) with minor modification. Briefly, 15 g of degummed oil were transferred in a hydrometer cylinder. The sample was homogenized by stirring with a glass rod. The densimeter was then lowered into the test portion and allowed to settle until the temperature equilibrium has been reached.

2.4 | Determination of flash point

The flash point, defined as "the lowest temperature at which application of an ignition source causes the vapours of a specimen of the sample to ignite under specified conditions of test," of the degummed oil was determined with a Pensky-Martens—SDM 750/E instrument according to standard method ASTM D93-13 (ASTM D93-13e1, 2013) with minor modifications. Briefly, 10 g of degummed oil were heated at constant rate of 5 8C/min. A natural gas flame was directed toward the oil sample at constant intervals of 10 s until a flame occurred over the entire surface of the sample.

2.5 | Experimental design

A multivariate methodology was applied in order to optimize the independent variables (k) oil/H_2O ratio pH, temperature, and stirring time. Full factorial design (n^k 5 16 experiments) (Box, Stuart-Hunter, Hunter, Stuart-Hunter, & Hunter, 2005) model was employed to study the response density and flash point of the degummed oils. 21 and 11 denoted the low and high levels (n) of the independent variables, respectively. The Statgraphics Centurion v 15.1.02 software was used for the experimental design data analysis and constructs the response surface.

2.6 | Statistical analysis

All experiments were conducted in triplicate. All statistical analyses were performed comparing data with unpaired Student's t-test. When the data followed a normal distribution, the sample was evaluated by the Kolmogorov–Smirnov and Shapiro tests. A $p < .05$ was considered statistically significant.

3 | RESULTS AND DISCUSSION

Sixteen waste cooking oils from domestic origin collected in the area of north of Sardinia (Italy) were submitted to water degumming taking in consideration the following parameters: pH of the aqueous solution, oil/water ratio, temperature of the process, and stirring time.

Since the studied variables are not independent from each other, the optimization approach would be multivariate instead one variable at time. Then, to optimize the number of experiments and to screen the interaction of all the variables considered, experimental design (DOE) was employed.

Sixteen experiments were obtained by the full factorial design (n^k) combining two levels (n) and four independent factors (k): pH, oil/H_2O ratio, temperature, and stirring time. The combination of the four independent variables considered allows evaluating their effect on the density and the flash point of the recycled oil.

For every output (density and flash point), a mathematical equation describing the correlation of the four factors considered has been derived as reported in the next section.

TABLE 1 Density measured (g/L) for every experiment conducted

Experiment	pH	Oil/H_2O ratio (%)	Temperature (8C)	Time (hr)	Density (g/L)
1	4.0	30.0	20.0	5.0	0.910
2	4.0	30.0	20.0	24.0	0.948
3	6.0	60.0	20.0	5.0	0.924
4	4.0	60.0	20.0	5.0	0.926
5	4.0	60.0	20.0	24.0	0.922
6	4.0	30.0	60.0	24.0	0.920
7	6.0	60.0	60.0	24.0	0.928
8	6.0	30.0	20.0	5.0	0.932
9	4.0	60.0	60.0	5.0	0.922
10	6.0	60.0	20.0	24.0	0.920
11	4.0	60.0	60.0	24.0	0.926
12	6.0	30.0	20.0	24.0	0.974
13	6.0	60.0	60.0	5.0	0.926
14	4.0	30.0	60.0	5.0	0.924
15	6.0	30.0	60.0	5.0	0.922
16	6.0	30.0	60.0	24.0	0.930

3.1 | Effect of pH, oil/H_2O ratio, temperature, and stirring time on density

For every experiment, the density value was determined in agreement with the standard method ASTM 1298-12b (ASTM 1298, 2012) at 22 8C; the results are reported in Table 1.

The effect of the factors considered on the density and their interaction was determined according to Box et al. (2005) (Table 2).

All the parameters are comparable, indicating an absence of a predominant effect on density of the final product. The relationship between the values confirms this conclusion. The analysis of the

TABLE 2 Effect of the factors on density

Effect	Value	Standard error	*p* Value
Average	0.92837	0.00293949	–
pH	0.00725	0.00587899	.2723
% of H_2O	20.00825	0.00587899	.2195
Temperature	20.00725	0.00587899	.2723
Time	0.01025	0.00587899	.1417
pH 3%: H_2O	20.00675	0.00587899	.3029
pH 3 temperature	20.00375	0.00587899	.5516
pH 3 time	0.00175	0.00587899	.7779
%: H_2O 3 temperature	0.00975	0.00587899	.1581
%: H_2O 3 time	20.01075	0.00587899	.1270
Time 3 temperature	20.00775	0.00587899	.2446

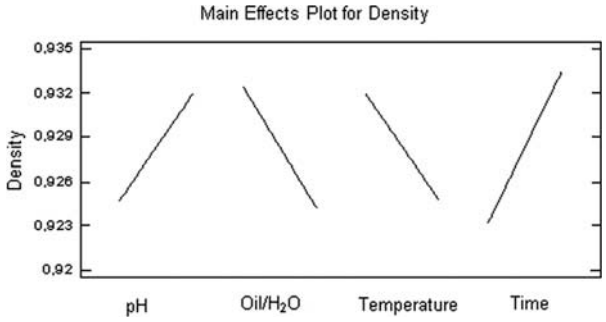

FIGURE 1 Medium effect of the passage of the levels from 21 to 11 for every single parameter

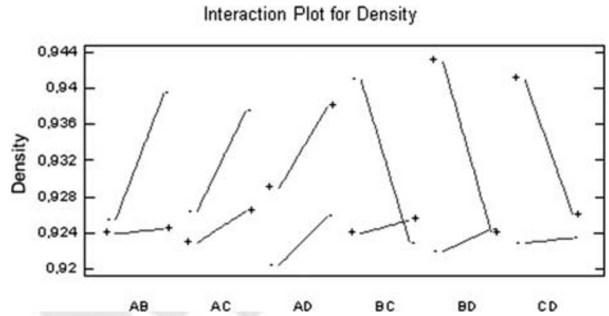

FIGURE 2 Graphic representation of the interaction of the parameters on density. A 5 pH, B 5 oil/H_2O ratio, C 5 temperature, D 5 stirring time

TABLE 3 Density values calculated with the theoretical model developed

Experiment	Observed Value	Calculated Value	Lower LC 95.0%	Upper LC 95.0%
1	0.910	0.918625	0.893564	0.943686
2	0.948	0.945625	0.920564	0.970686
3	0.924	0.920625	0.895564	0.945686
4	0.926	0.918125	0.893064	0.943186
5	0.922	0.923625	0.898564	0.948686
6	0.920	0.924625	0.899564	0.949686
7	0.928	0.920625	0.895564	0.945686
8	0.932	0.934625	0.909564	0.959686
9	0.922	0.932125	0.907064	0.957186
10	0.920	0.929625	0.904564	0.954686
11	0.926	0.922125	0.897064	0.947186
12	0.974	0.965125	0.940064	0.990186
13	0.926	0.927125	0.902064	0.952186
14	0.924	0.913125	0.888064	0.938186
15	0.922	0.921625	0.896564	0.946686
16	0.930	0.936625	0.911564	0.961686

variance (ANOVA) shows that no significant effect can be attributed to any of the parameters considered ($p < .05$) (Figure 1).

The lack of a significant effect of the interaction between the parameters is reported in Figure 2.

A mathematical representation of the model obtained has been implemented:

Density50:85216410:01616453pH

10:000746933oil3H2 O20:0001480263temperature

10:002592113time20:0002253pH3oil3H2 O

20:000093753pH3temperature10:00009210533pH

3time10:000016253oil3H2 O3temperature

20:00003771933oil3H2 O3time

20:00002039473temperature3time:

All the values calculated with the mathematical model developed lay inside the confidence limit (LC) of 95% with respect to the observed values indicating the goodness of the model (Table 3).

TABLE 4 Prevision of the best experimental conditions for minimum and maximum density

Parameter	Minimum (0.913)	Maximum (0.965)
pH	4.0	6.0
Oil/H_2O ratio	30.0	30.0
Temperature	60.0	20.0
Time	5.0	24.0

TABLE 5 Flash point values (8C)

Entry	pH	Oil/H_2O (%) ratio	Temperature (8C)	Time (hr)	Flash point (8C)
1	4.0	30.0	20.0	5.0	270
2	4.0	30.0	20.0	24.0	n.d.
3	6.0	60.0	20.0	5.0	274
4	4.0	60.0	20.0	5.0	276
5	4.0	60.0	20.0	24.0	272
6	4.0	30.0	60.0	24.0	278
7	6.0	60.0	60.0	24.0	284
8	6.0	30.0	20.0	5.0	284
9	4.0	60.0	60.0	5.0	276
10	6.0	60.0	20.0	24.0	284
11	4.0	60.0	60.0	24.0	286
12	6.0	30.0	20.0	24.0	280
13	6.0	60.0	60.0	5.0	278
14	4.0	30.0	60.0	5.0	286
15	6.0	30.0	60.0	5.0	290
16	6.0	30.0	60.0	24.0	284

n.d., not determined.

The density in the degummed oil ranges from a minimum value of 0.913 g/L to a maximum value of 0.965 g/L, and it can be reached working at the following conditions (Table 4).

3.2 | Effect of pH, oil/H_2O ratio, temperature, and stirring time on flash point

The flash point has been determined in agreement with standard method ASTM D93-13 (ASTM D93-13e1, 2013), the result for every experiment is reported in Table 5.

The effect of the factors on the flash point and their interaction has been determined in agreement to Box et al. (2005); the results are reported in Table 6.

The values referred to the effects of pH and temperature, which are significantly bigger than all the others. As regard of the interaction of the factors, the percentage of H_2O 3 time shows a p-value of <.05 indicating that the passage from levels 21 to 11 has an influence on the flash point with a probability higher than 95%. The positive value referred to this interaction means an incremental contribute of all the three factors on flash point (Figure 3).

The lines obtained in Figure 3 represent the medium effect of the passage from levels 21 to 11, and as expected for the factors pH and

TABLE 6 Effect of the factors on the flash point and statistic inference

Effect	Value	Standard error	p Value
Average	279.0	1.06066	–
pH	6.5	2.12132	.0375
% H_2O	20.5	2.12132	.8252
Temperature	7.5	2.12132	.0241
Time	20.5	2.12132	.8252
pH 3 %: H_2O	24.0	2.12132	.1324
pH 3 temperature	24.0	2.12132	.1324
pH 3 time	2.0	2.12132	.3992
%: H_2O 3 temperature	23.0	2.12132	.2302
%: H_2O 3 time	6.0	2.12132	.0474
Time 3 temperature	1.0	2.12132	.6619

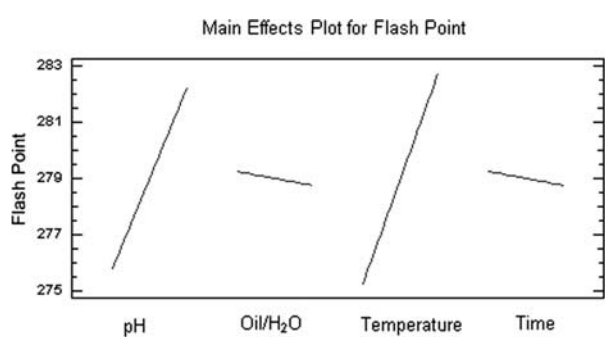

FIGURE 3 Graphic representation of the effect of the factors on flash point

Journal of Food Processing and Preservation Institute of Food Science + Technology ifst WILEY

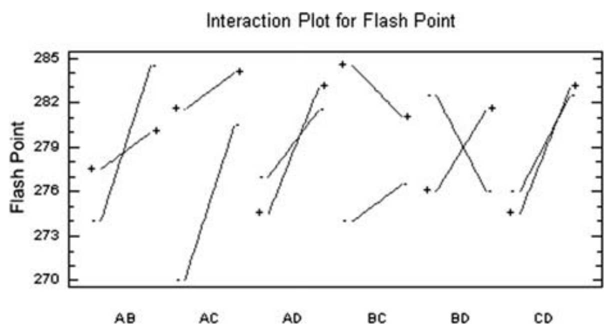

FIGURE 4 Graphic representation of the interactions between the factors on flash point. A 5 pH, B 5 oil/H_2O ratio, C 5 temperature, D 5 stirring time

TABLE 7 Estimated values of flash point

Entry	Observed value	Calculated value	Lower LC 95.0%	Upper LC 95.0%
1	270.0	271.5	261.882	281.118
2	n.d.	262.0	246.05	277.95
3	274.0	276.5	267.503	285.497
4	276.0	272.0	263.003	280.997
5	272.0	274.5	264.882	284.118
6	278.0	277.5	267.882	287.118
7	284.0	284.5	275.503	293.497
8	284.0	284.0	275.003	292.997
9	276.0	279.5	270.503	288.497
10	284.0	283.0	274.003	291.997
11	286.0	284.0	275.003	292.997
12	280.0	278.5	268.882	288.118
13	278.0	276.0	266.382	285.618
14	286.0	285.0	276.003	293.997
15	290.0	289.5	280.503	298.497
16	284.0	286.0	277.003	294.997

n.d., not determined.

TABLE 8 Experimental conditions corresponding to the maximum and the minimum flash point value

Factor	Minimum (262.9 8C)	Maximum (289.5 8C)
pH	4.0	6.0
Oil/H_2O	30.0	30.0
Temperature	22.4	60.0
Time	23.9	5.0

temperature, they have a positive slope, higher in value with respect to the lines referred to the other factors

In the case of the interactions (Figure 4), the combination of BD corresponding to the variables % H_2O–time shows an antiparallel trend. The regression coefficients are reported in the following equation:

```
Flash point5220:276111:72373pH10:5447373oil3H2 O
1 0:8743423temperature21:605263time
20:1333333pH3Oil=H2 O20:13pH3temperature
10:1052633pH3Time20:0053oil3H2 O3temperature
10:02105263Oil3H2 O3time
10:002631583temperature3time
```

All the values obtained using the model lay in the interval determined from the confidence limits of 95% with respect to the observed data as confirmation of the goodness of the model (Table 7).

The flash point after degumming ranges within the minimum value of 262.98C and the maximum value of 289.58C and the corresponding operating conditions are reported in Table 8.

4 | CONCLUSIONS

Through experimental full factorial design 2^4, the effects of pH, percentage of H_2O, temperature and time during water degumming of waste cooking oil on the density, and the flash point of the final product have been studied.

None of the factors considered affect significantly the density in the passage from level 21 to level 11.

In contrast, the flash point is significantly influenced from pH, temperature, and the interaction between factors such as percentage of H_2O and time.

Two mathematical models based on experimental data have been implemented for estimate the best operative conditions in water degumming of waste cooking oils in order to tune the density and the flash point of the recycled oil.

Determination of analogues models for other characteristic parameters of waste cooking oil are currently subject of research.

ACKNOWLEDGMENT

The authors thank Sardegna Ricerche and the regional programme INSIGHT for the support in the developing of the business idea.

ORCID

Alberto Mannu http://orcid.org/0000-0001-7623-7475

REFERENCES

ASTM D1298-12b. (2012). *Standard test method for density, relative density, or API gravity of crude petroleum and liquid petroleum products by hydrometer method*. West Conshohocken, PA: ASTM International, www.astm.org.

ASTM D93-13e1. (2013). *Standard test methods for flash point by Pensky-Martens closed cup tester*. West … tional, www.astm.org.

Box, G. E. P., Stuart-Hunter, J., & … *experimenters: Design, innovation* … Hoboken, NJ, USA: Wiley.

Boyde, S. (2002). Green lubricants. Environmental benefits and impacts of lubrication. *Green Chemistry*, [illegible], 293–307.

Alberto Mannu (albertomannu@gmail.com)
2017-10-13 16:24:17
Location is correct

Cvengros, J., & Cvengrosova, Z. (2004). Used Frying oil and fat and their utilization in the production of methyl esters of higher fatty acid. *Biomass Bioenergy*, *27*, 173–181.

De Moura, J. M. L. N., Goncalves, L. A. G., Cunha Petrus, J. C., & Viotto, L. A. (2005). Degumming of vegetable oil by microporous membrane. *Journal of Food Engineering*, *70*, 473–478.

Fox, N. J., & Stachowiak, G. W. (2007). Vegetable oil-based lubricants—A review of oxidation. *Tribology International*, *40*, 1035–1046.

Haas, M. J. (2005). Improving the economics of biodiesel production through the use of low value lipids as feedstocks: Vegetable oil soapstock. *Fuel Processing Technology*, *86*, 1087–1096.

Koris, A., & Vatai, G. (2002). Dry degumming of vegetable oils by membrane filtration. *Desalination*, *148*, 149–153.

Lin, C. S. K., Pfaltzgraff, L. A., Herrero-Davila, L., Mubofu, E. B., Abderrahim, S., Clark, J. H., … Luque, R. (2013). Food waste as a valuable resource for the production of chemicals, materials and fuels. Current situation and global perspective. *Energy & Environmental Science*, *6*, 426–464.

No, S. Y. (2011). Inedible vegetable oils and their derivatives for alternative diesel fuels in CI engines: A review. *Renewable and Sustainable Energy Reviews*, *15*, 131–149.

Ochoa, N., Pagliero, C., Marchese, J., & Mattea, M. (2001). Ultrafiltration of vegetable oils: Degumming by polymeric membranes. *Separation and Purification Technology*, *22–23*, 417–422.

AQ3 Panadare, D. C., & Rathod, V. K. (2015). Applications of waste cooking oil other than biodiesel: A review. *Iranian Journal of Chemical Engineering*, *12*(3), 55–76.

Petran, J., Pedisic, L., Orlovic, M., Podolski, S., & Bradac, V. (2008). Biolubricants from natural waste oils and fats. *Goriva i Maziva*, *47*, 463–478.

Pohler, J., Modler, M., Bruhnkeh, D., & Hidenberg, H. (2004). Method for reprocessing waste oils, base oils obtained according to said method and use thereof. *US Patent No. 6,712, 954 B1*.

Rac, A., & Vencl, A. (2012). Ecological and technical aspects of the waste oils influence on environment. *Tribology* (1), ISSN 1221-4590.

Sampaio, K. A., Zyaykina, N., Wozniak, B., Tsukamoto, J., DE Greyt, W., & Stevens, C. V. (2015). Enzymatic degumming: Degumming efficiency versus yield increase. *European Journal of Lipid Science and Technology*, *117*, 81–86.

Sesti Ossèoa, L., Caputoa, G., Graciab, I., & Reverchona, E. (2004). Continuous fractionation of used frying oil by supercritical CO_2. *Journal of the American Oil Chemists' Society*, *81*, 879–885.

Shashidhara, Y. M., & Jayaram, S. R. (2010). Vegetable oils as a potential cutting fluid—An evolution. *Tribology International*, *43*, 1073–1081.

Singhabhandhu, A., & Tezuka, T. (2010a). The waste-to-energy framework for integrated multi-waste utilization: Waste cooking oil, waste lubricating oil, and waste plastics. *Energy*, *35*, 2544–2551.

Singhabhandhu, A., & Tezuka, T. (2010b). Prospective framework for collection and exploitation of waste cooking oil as feedstock for energy conversion. *Energy*, *35*, 1839–1847.

Talebian-Kiakalaieh, A., Amin, N. A. S., & Mazaheri, H. (2013). A review on novel processes of biodiesel production from waste cooking oil. *Applied Energy*, *104*, 683–710.

Tiwari, A. L., Kumar, A., & Raheman, H. (2007). Biodiesel production from jatropha oil (*Jatropha curcas*) with high free fatty acids: An optimized process. *Biomass Bioenergy*, *31*, 569–575.

Vintilà, I. (2009). The physical-chemical mechanism of the edible oils deep refining. *Scientific Study and Research*, *X*(2), 179–183.

Yang, J. G., Wang, Y. H., Yang, B., Mainda, G., & Guo, Y. (2006). Degumming of vegetable oil by a new microbial lipase. *Food Technology and Biotechnology*, *44*(1), 101–104.

Alberto Mannu (albertomannu@gmail.com)
2017-10-13 16:23:20

Page numbers are correct

How to cite this article: Vlaho… Piga C, Mannu A. Variation of density and flash point in acid degummed waste cooking oil. *J Food Process Preserv*. 2017; e13533. https://doi.org/10.1111/jfpp.13533