Industrial Crops and Products 46 (2013) 111–116

Contents lists available at SciVerse ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Rheological properties of rice bran (*Oryza sativa* L.) oils processing and soapstock distillation residue

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ARTICLE INFO

Article history:
Received 19 July 2012
Received in revised form 9 January 2013
Accepted 10 January 2013

Keywords:
Rice bran oil processing
Viscosity
Rheological models
Fatty acids

ABSTRACT

The oil extraction process involves different temperatures and the knowledge of viscosity is necessary for the design and development of appropriate equipment and processes calculations. The aim of this study was to evaluate the effect of temperatures (30, 45, 60, 75, 90 °C) in the initial stage of rice bran (*Oryza sativa* L.) oil processing (crude oil, degummed oil) and evaluate the effects of temperature on viscosity in the rice bran oil soapstock distillation residue (RDS), with great potential for use in food and pharmaceutical industry. The rheological behavior of the oils was determined by using a concentric cylinder rotational viscometer, with a thermostatic bath attached to the equipment. The viscosity values found at constant shear rate (40 s^{-1}) and 30 °C was 0.1240, 0.0699, 0.1720 Pa s for crude oil, degummed oil, and RDS, respectively. The viscosity curves vs. shear rate were applied to Bingham and Casson models, except for the crude oil where only the Bingham model has obtained a good adjustment. The shear stress curves vs. shear rate were applied to Newton and Ostwald-de-Waele models. Excepting the crude oil, all the other adjustments had a coefficient of determination (R^2) greater than 0.97, indicating a good adjustment of the experimental curves. Based on the degree of viscosity reduction (DVR) and it was found that the viscosity of all the three oils reduced approximately 90% from 30 to 90 °C and the Andrade model was obtained a good adjustment to the data of viscosity curves vs. temperature. Finally, it was found that the viscosity of the three oils studied decreases sharply with increasing temperature, and the RDS has the highest viscosity among the tested oil, followed by crude oil and crude degummed oil. A correlation between the unsaturation degree of fatty acids and oils viscosity has not been found.

1. Introduction

Rice (*Oryza sativa* L.) oil, also called rice bran oil, has been used extensively in Asian countries such as Japan, Korea, China, Taiwan, Thailand, and Pakistan. It is the preferred oil in Japan for its subtle flavor and odor (Kahlon et al., 1992; Fereidoon, 2005).

Vegetable oils have become increasingly important; not only for nutritional purposes, but also as raw materials for a wide range of industrial products which include biofuels, skin care products, and high pressure lubricants (Ibemesi, 1993; Foidl et al., 1996; Eromosele and Paschal, 2003).

The viscosity of vegetable oils is affected by a number of factors. These factors include the physical and chemical properties of oils such as density, molecular weight, melting point, and degree of unsaturation (Igwe, 2004). A factor that greatly affects the viscosity of oils is its temperature. The viscosity of oils and fats decreases linearly with increasing temperature (Igwe, 2004; Kim et al., 2010).

Some studies of the influence of temperature on refined oils viscosity have been reported in the literature (Eromosele and Paschal, 2003; Hasan et al., 2010; Kim et al., 2010; Quinchia et al., 2010); however, there is a gap regarding the influence of temperature on viscosity in the initial stages of several oils processing.

The oil extraction process involves different temperatures and the knowledge of viscosity is necessary for equipment design and processes development (Brock et al., 2008). For example, degumming, a stage of oil purification, is performed from 60 to 70 °C while stirring from 20 to 30 min (Zin, 2006).

One application of the rice bran oil neutralization byproduct is the production of rice fatty acids. In this case, the neutralization residue is reacidified and fatty acids obtained through acid cleavage are separated through vacuum distillation (Das et al., 1998; Jesus, 2010). This process forms distillation slurry as residue, or RDS. This residue has been studied by a few authors and has great potential for use in food and pharmaceutical industry. Studying its viscosity can help to advance work and development projects for their industrial application. Such residue has great potential for use in food and pharmaceutical industry, because it is rich in fatty acids and γ-oryzanol, a powerful antioxidant in rice and can serve as raw material for the manufacturing of environmentally friendly greases (Jesus, 2010).

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http://dx.doi.org/10.1016/j.indcrop.2013.01.015

Therefore, the aim of this study was to evaluate the effects of temperature on oils viscosity in the initial stage of rice bran (*O. sativa* L.) oil processing (crude oil, degummed oil) and to observe the effects of temperature on the viscosity of rice bran oil soapstock distillation residue (RDS).

2. Materials and methods

2.1. Raw material characterization

2.1.1. Physical–chemical analysis

The oils (crude oil, degummed oil and RDS) of rice bran (*O. sativa* L.) processing was kindly supplied by IRGOVEL Ltda. (Pelotas/RS, Brazil) and stored in a domestic refrigerator ($2 \pm 1\,^{\circ}C$ and $50 \pm 5\%$ relative humidity – Freezer 220, Consul, Joinville/SC, Brazil) until the moment of analysis.

The analyses were performed according to methods described by Instituto Adolfo Lutz (IAL, 2005) and the American Oil Chemists' Society (AOCS, 1990): free fatty acids as oleic acid (IAL 325/IV), density at 25 °C (AOCS Cc 10a - 25), insolubles in ether (AOCS Ca 3a-46), lipids (IAL 032/IV), refractive index at 40 °C (AOCS Cc 7 - 25), and pH (IAL 017/IV).

The fatty acid composition was performed through gas chromatography (GC) according to methods described by American Oil Chemists' Society no. 996.06 (AOCS, 1998 – Method Ce 1F 96).

2.2. Procedures for viscosity measurement

The rheological behavior of the oils was determined by using a VT 550 Thermo Haake DC 10 (Thermo Fisher Scientific, California, USA) concentric cylinder rotational viscometer (NV geometry). The measurements were made at temperatures: 30, 45, 60, 75 and 90 °C (±0.5 °C), adjusted by a thermostatic bath (DC 30, Thermo Fisher Scientific, California, USA) attached to the equipment. The instrument provides direct data on shear stress, viscosity, and shear rate. Rheological analyses were obtained with shear rate from 0 to 700 s^{-1} (upward curve) and 700 to 0 s^{-1} (downward curve), measured for 3 min in each curve. The values used to fitting the data to the model are related to the downward curve of the shear rate.

The viscosity curves vs. shear rate were applied to both Bingham and Casson models, except for the crude oil where only the Bingham model has obtained a good adjustment. The shear stress curves vs. shear rate were applied to both Newton and Ostwald-de-Waele models. The model adjustment was performed by using the Haake Rheowin 3 (Thermo Fisher Scientific, California, USA) software.

2.3. Statistical analysis

The results were submitted to variance analysis (ANOVA) and Tukey's test (5% probability) using the software Assistat 7.6 (2011).

3. Results and discussion

3.1. Raw material characterization

The fatty acid composition of all three oils is very similar (Table 1). The crude, degummed, and RDS oil are composed mainly by palmitic acid (C 16:0), oleic acid (C 18:1*n*-9 *cis*) and linoleic acid (C 18:2*n*-6 *cis*), comprising more than 90% of total fatty acids for each oil.

It can be noted that some fatty acids were conformed in *trans* structure in the RDS oil; this has occurred because of the chemical reactions necessary and due to the high temperature used in the distillation to obtain the fatty acids (Jesus, 2010). The similarity of the RDS oil, a residue, with the oils involved in the processing of rice bran oil makes it an alternative source of important compounds such as ω-6 (C 18:2*n*-6 *cis*), present in 33% of RDS oil. The results found were similar to those found by Paucar-Menacho et al. (2007) for rice bran oil.

Table 1
Fatty acids composition of crude, degummed, and RDS oils.

Fatty acids (g/100 g)	Oils		
	Crude oil	Degummed oil	RDS
C 14:0	0.22	0.20	0.20
C 16:0	19.71	19.60	17.70
C 16:1	0.15	0.10	0.10
C 18:0	1.56	1.50	1.80
C 18:1*n*-9 *cis*	39.43	39.30	40.30
C 18:1*n*-9 *trans*	–	–	0.20
C 18:2*n*-6 *cis*	35.00	34.60	33.00
C 18:2*n*-6 *trans*	–	–	0.50
C 18:3*n*-3 *cis*	1.76	1.80	1.20
C 18:3*n*-3 *trans*	–	–	0.20
C 18:3*n*-6	0.67	0.70	1.30
C 20:1	0.47	0.50	0.70
C 20:3*n*-6	0.36	0.30	0.70
C 21:0	–	–	0.20
C 22:6*n*-3	–	0.10	0.40
C 24:0	0.67	–	–
$\sum$SAFA[a]	22.16	21.20	19.90
$\sum$MUFA[b]	40.05	39.60	41.10
$\sum$PUFA[c]	37.79	37.30	36.60

[a] Saturated fatty acids.
[b] Monounsaturated fatty acids.
[c] Polyunsaturated fatty acids.

Table 2 presents the characterization of crude oil, degummed oil and RDS. Free fatty acid (FFA) content is one of the most important parameter features in the quality of oils. According to Fereidoon (2005), oil in intact bran contains 2–4% free fatty acids; once bran is milled from the kernel, a rapid increase in the FFA occurs. In high humidity storage, the rate of hydrolysis is 5–10% per day and about 70% in a month as previously shown (Fereidoon, 2005). The higher acidity has been found in degummed oil (13.45 g/100 g), followed by crude oil (11.20 g/100 g) and RDS (7.00 g/100 g). The RDS comes from the neutralization sludge of rice bran oil and therefore it contains the lowest FFA between the three oils studied. Both crude and degummed oil have been obtained from the previous steps of neutralization, in order to neutralize FFA levels.

Density is an important physical characteristic of any substance, being a measurement of mass per volume unit of such substance. It is an accepted fact that vegetable oil density decreases linearly with increasing temperature (Esteban et al., 2012). The measure density at 25 °C for crude oil, degummed oil, and RDS, were of 0.923, 0.919, and 0.933 g/m^3, respectively.

The analysis of impurities insoluble in ether determines the amount of organic substances insoluble in petroleum ether. The value found for crude oil was 0.305 g/100 g and degummed oil and RDS the values found were <0.1 g/100 g, indicating that the degumming process removes most of the impurities (insoluble in ether) contained in the crude oil. The low value found for RDS could be due to the production of some salts during de soapstock acidification.

Lipids present in the samples were 99.65% for the crude oil and 100% and degummed oil and RDS, this fact confirms the removal of impurities such as phospholipids, proteins, and colloids in the degumming stage.

The same refractive index at 40 °C (1.466) was found for crude and degummed oils. It was not possible to obtain a refractive index for RDS due to a staining of the sample. The pH values were 4.5 for crude and degummed oil and 5.4 for RDS.