Study of Fatty Acid and Fatty Alcohol Formation from Hydrolysis of Rice Bran Wax

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Rice bran wax is waste material of dewaxing process in oil refining. Dewaxing is accomplished by cooling and filtrating for separating wax from the oil to avoid turbidity in the final product. The dewaxing residue may have 20 up to 80 wt% of oil, followed by a main fraction of waxes, free fatty alcohols, free fatty acids and hydrocarbons. The wax fraction of the residue is composed by long-chain fatty alcohols esterified with long-chain fatty acids. Considering that rice bran oil has 4 – 6 wt% of wax, a large amount of this natural source of fatty compounds is undervalued. Noweck and Rider (1987) describe a process based on hydrolysis of waxes with sodium hydroxide, followed by distillation of fatty alcohols and soap. According to best of our knowledge no work has been reported on the formation of fatty acids and alcohols from the hydrolysis of the dewaxing residue using supersaturated stripping steam under high temperatures and high vacuum. Therefore, present research work was carried out for studying the decomposition of the dewaxing residue of rice bran oil in a mixture of fatty acids and fatty alcohols under low pressure, high temperatures and the injection of stripping steam. Experiments were carried out in laboratory-scale batch equipment, loaded with the raw material and placed in an oven with controlled temperature. The independent variables were final oven temperature (ºC), stripping steam flow (mL water/min) and time (h). Their effect on the production of fatty acids and alcohols were investigated following a simple factorial design (2^3 + central points). In each trial, samples were collected for the residue and distillate, and analyzed for acid value and Fourier-transform infrared (FTIR) spectra. The results showed that the formation of free fatty acids increased for higher temperatures and longer heating times. FTIR analysis evidence the occurrence of de-esterification reaction.

1. Introduction

Narrowly defined, wax is a long-chain fatty acid esterified to a fatty alcohol, which has a high melting point and crystallizes at low pressures (Perkins, 1993). Dewaxing is accomplished by cooling and filtrating for separating wax from the oil to avoid turbidity in the final product at room temperature (Tubaileh et al., 2002a). The dewaxing residue may have 20 up to 80 wt% of oil, followed by a main fraction of waxes, free fatty alcohols, free fatty acids and hydrocarbons. Considering that wax content in rice bran oil ranges up to 6.2 wt% (Orthoefer, 2005), a large amount of this natural source of fatty compounds is undervalued. In fact, wax can be decomposed by a de-esterification reaction (Figure 1) forming fatty alcohols and acids, valuable products for food and cosmetic industries.

The reaction takes place in oil (which is not an alcoholic, aqueous, or water–alcohol medium), without the use of any catalyst, at temperatures between 180 and 270 °C and under vacuum. It is reversible and it is from prime importance the removal of volatiles products to push chemical equilibrium towards products formation (Tubaileh et al., 2002b). Noweck and Ridder (1987) described a process for fatty alcohol production from natural sources based on hydrolysis of waxes with sodium hydroxide, followed by distillation of fatty alcohols and soap. Moreover, Tubaileh et al. (2002a,b) observed the degradation of fatty wax during olive oil physical refining and the volatilization of fatty alcohols and acids within these process conditions. According to best of our knowledge no work has been reported on the formation of fatty acids

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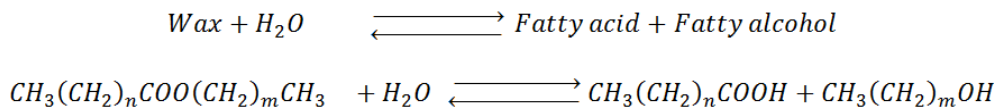
$$Wax + H_2O \rightleftharpoons Fatty\ acid + Fatty\ alcohol$$

$$CH_3(CH_2)_nCOO(CH_2)_mCH_3 + H_2O \rightleftharpoons CH_3(CH_2)_nCOOH + CH_3(CH_2)_mOH$$

Figure 1: De-esterification reaction

2. Experimental Procedures

2.1 Material
The dewaxing residue of rice bran oil was kindly supplied by Irgovel, Indústria Riograndense de Óleos Vegetais (Brazil). It contained around 44 % of rice bran oil. Its acidity was 0.43 ± 0.01, expressed as % of oleic acid.

2.2 Methods
Experiments were carried out in a laboratory-scale batch deodorizer (Figure 2), the same described by Sampaio et al. (2011), following a 2^3 + 3 central points factorial design (Box et al., 1978). Factorial design has been used for investigations dealing with fatty reactive systems (Rios et al., 2012). The selected independent variables were temperature of heating jacket (260 - 286 °C), sparge steam injection (2.25 – 6.75 mL/min) and time (120 – 180 min). The response was generated acidity, expressed both in weight (g) and in percentage (in relation to initial weight).
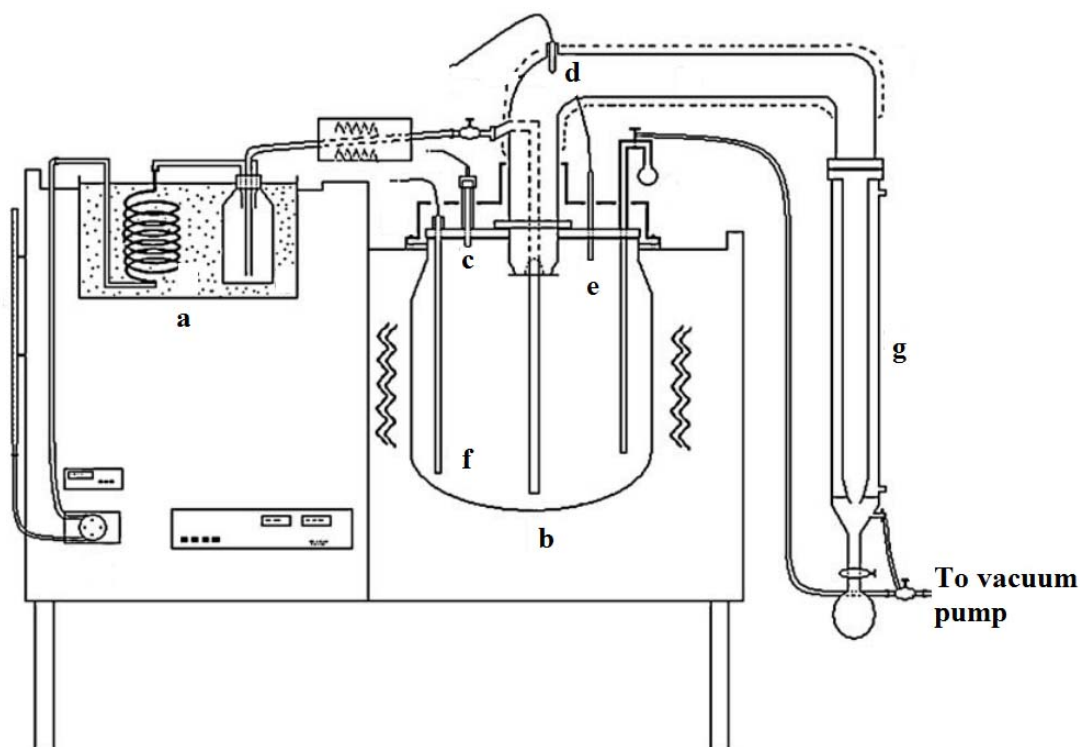

Figure 2 - Scheme of the lab-scale batch deodorizer: (a) steam formation system; (b) glass batch deodorizer; (c) digital manometer; (d,e,f) thermocouples; (g) condenser (Sampaio et al., 2011)

The batch deodorizer was loaded with 900 g of dewaxing residue and placed in an electric aluminium mantle with controlled and monitored temperature. The wax was heated under atmospheric pressure. Two thermocouples placed inside the glass deodorizer flask, allowed for a precise control of the temperature. The first one was completely covered by the wax layer (thermocouple f) and measured the wax temperature. The second one was placed 26.5 cm from the bottom (thermocouple e), and measured the temperature of the gas phase. The sparge steam injection started when the dewaxing residue temperature inside the reactor reached 70 % of the temperature of heating jackets; for instance, in case of Trial 1 (260 °C) steam injection started when dewaxing residue reached 182 °C. The reaction took place under low pressure provided by a vacuum pump (model 56, Kohl Bach, Brazil) connected to the condenser. A digital manometer measured the absolute pressure inside the deodorizer

In the end of each trial, samples of the dewaxing residue remaining in the reactor and of the distillate were collected. Free acidity of each samples were determined by titration according to IUPAC official method, adapted by Gandra (2006), using toluol and ethanol as solvents. Generated acidity was estimated using mass balance equations. Fourier-transform infrared (FTIR) spectra were obtained from an Infrared Red Spectroscopy with attenuated total reflection (Bruker, Model Vector 22). Spectra were obtained in the region $600 - 4000$ cm^{-1} and 4 cm^{-1} spectral resolution. This analysis provides information about the chemical bonds presented in a sample and it was used in this work to confirm the presence of fatty alcohols and fatty acids.

3. Results and Discussion

3.1 Tables
The conditions tested in each trial done in this work with its respective response are presented in Table 1. It was observed in all trials acidity generation, evidencing the occurrence of de-esterification reaction.

Acidity generation was low for all trials. Its lowest (0.28 %) and highest (1.47 %) values were obtained in trials 5 and 6, respectively, in which X_1 varied from -1 to +1, while X_2 and X_3 were kept constant. We believe that water volatility influenced the acidity generation, which is a hydrolysis reaction. It may be interesting to study the influence of water (de-esterification reactant) volatility in the conditions tested, varying the system pressure, and also the influence of different steam baffles to improve the contact between sparge steam and wax.

Table 1: Factorial design

Trial	Coded Variables			Real Variables			Generated Acidity	
	X_1	X_2	X_3	T(°C)	Sparge steam (mL/min)[a]	Time (min)	Weight (g)	(wt%)
1	-1	-1	-1	260	2.25	120	4.53	0.50
2	1	-1	-1	286	2.25	120	11.20	1.24
3	-1	1	-1	260	6.75	120	5.97	0.66
4	1	1	-1	286	6.75	120	4.83	0.53
5	-1	-1	1	260	2.25	180	2.57	0.28
6	1	-1	1	286	2.25	180	13.09	1.47
7	-1	1	1	260	6.75	180	8.65	0.96
8	1	1	1	286	6.75	180	10.74	1.18
9	0	0	0	273	4.5	150	8.07	0.89
10	0	0	0	273	4.5	150	7.66	0.85
11	0	0	0	273	4.5	150	7.33	0.81

[a] Water flow measured by the peristaltic pump, which fed the glass batch reactor.

Experimental results were analysed using the software Statistica™ (Statsoft, v.5.5) to establish the effects of coded variables on the responses. Regression coefficients were obtained at 95 % confidence. The effects of independent variables on responses are shown at Table 2. It can be noted that only sparge steam amount was not significant, although its interaction with temperature and time was significant. Both R^2 obtained were higher than 0.996. Both temperature and time presented a positive effect, i.e. an increase in these variables leads to an increase in acidity generation. The same behaviour was observed for the interactions temperature X time, and sparge steam X time. On the other hand, the interaction temperature X sparge steam presented a negative effect, i.e. when using high temperature, it should be

used less sparge steam, and vice-versa. The effect of temperature is about 2 times higher than that of time. Time and its interactions with the other two variables have comparable effects.

Table 2: Effect of variables on generated acidity at 95 % confidence

	Generated Acidity (g)[a]			Generated Acidity (%)[b]		
	Effect	Pure error	p-value	Effect	Pure error	p-value
Mean	**7.695**	**0.086**	**0.000**	**0.852**	**0.010**	**0.000**
Temperature (°C)	**4.535**	**0.202**	**0.000**	**0.504**	**0.023**	**0.000**
Sparge steam	-0.302	0.202	0.209	-0.038	0.023	0.180
Time (min)	**2.133**	**0.202**	**0.000**	**0.237**	**0.023**	**0.001**
Temperature X sparge steam	**-4.060**	**0.202**	**0.000**	**-0.460**	**0.023**	**0.000**
Temperature X time	**1.768**	**0.202**	**0.001**	**0.199**	**0.023**	**0.001**
Sparge steam X time	**2.168**	**0.202**	**0.000**	**0.237**	**0.023**	**0.001**

[a]$R^2 = 0.997$; [b]$R^2 = 0.996$.

All samples of fatty distillate and some of the wax remaining on the batch reactor were submitted to FTIR analysis. Figure 3 shows the room temperature infrared absorption spectra in the range of 600 – 3600 cm^{-1} of the initial wax (IW), fatty distillates (FD) numbered according to trials and some of the final waxes (FW). It is possible to identify vibrations of carbonyl, carboxylic and hydroxyl groups, besides saturated aliphatic (alkyl) and unsaturated aliphatic (alkene) groups.

The assignments of vibrations followed Coates (2000). The broad band at around 3400 cm^{-1} (band #1) that appears only in the spectra of FD5 and FD8 is assigned to the OH stretching vibration, and indicates the presence of primary alcohols in these two samples. This fact confirms the occurrence of the hydrolysis reaction in the initial wax, with the formation and volatilization of fatty alcohols, besides free fatty acids already quantified by titration. Two intense bands appear in all spectra at 2920 cm^{-1} (band #2) and 2850 cm^{-1} (band #3), and are due to CH_2 asymmetric and symmetric stretching vibrations, respectively. At 2350 cm^{-1} (band #4), there is a double peak in all samples, assigned to the asymmetrical stretch of dissolved CO_2. The band at 1744 cm^{-1} (band #5) that appears in the spectra of final waxes (FW1, FW8 and FW9) and IW is assigned to the C=O stretching vibration of the carboxylic groups in esters. The same band appears at around 1708 cm^{-1} (band #6) for fatty acids in the spectra of fatty distillates (FD1-FD8, and CPFD). This is an important result that confirms the presence of fatty acids in the fatty distillates and of waxes (long chain fatty esters) in the waxy samples. At 1462 cm^{-1} (band #7), there is a band in all samples, which is assigned to CH_2 scissors deformation vibration. Several bands are observed in the range of 800 – 1400 cm^{-1} for all samples, and are assigned to CH_2 vibrations (wagging and twisting). The band at 719 cm^{-1} (band #8), which is also observed in all spectra, is assigned to the CH_2 rocking mode and, when appearing together with the other CH_2 vibrations, is an indicative of the presence of long-chain linear aliphatic structure.

It is interesting to understand why only in the spectra of FD5 and FD8 it was evidenced the presence of fatty alcohols. In trial 5, the lowest value of acidity generation was observed. Considering that this trial lasted 180 min, a possible explanation is that the acidity generated was totally vaporized and, in this way, the generated fatty alcohols could also be volatilized without competition. Trial 8 also latest 180 min, and in this case, temperature was at its highest value. More acidity and fatty alcohols were generated, but were also more volatile. In this case, a comparable explanation could be referred.
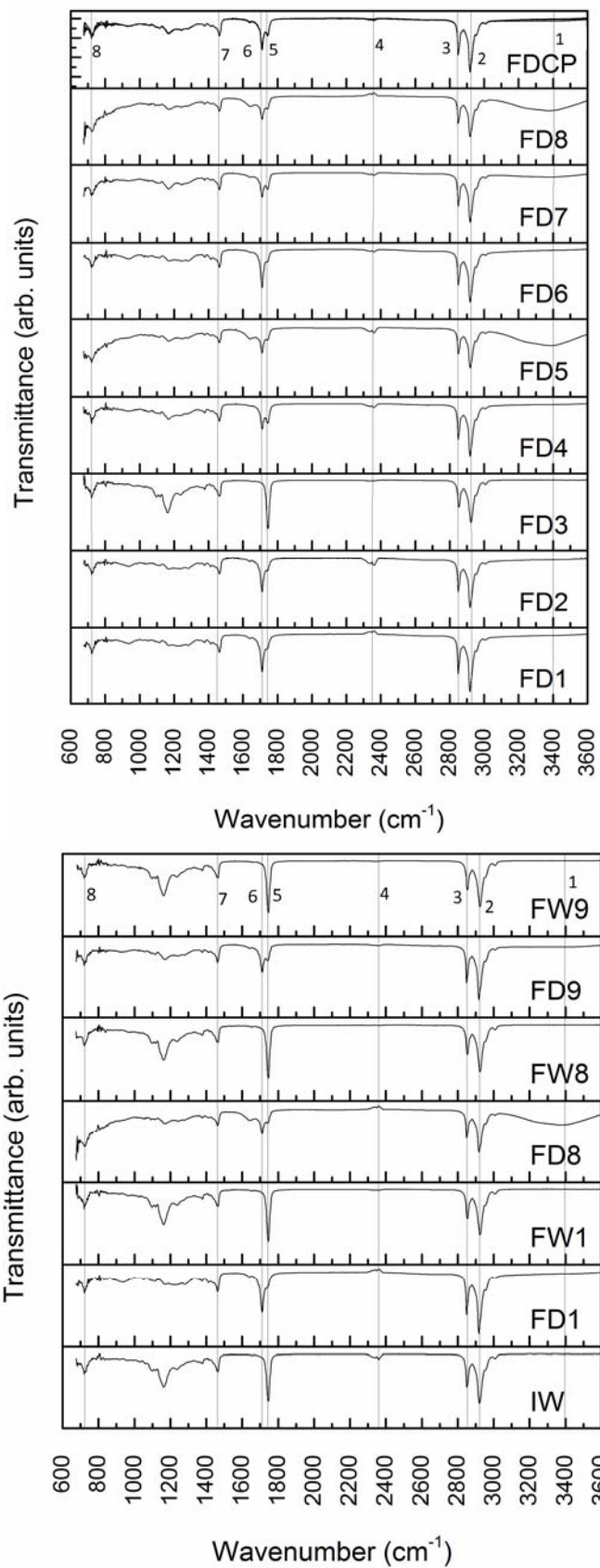
Figure 3 – Infra Red Absorption Spectra for Initial Wax (IW), Final Wax (FW), Fatty Distillates (FD) numbered according to trials and Fatty Distillate Central Point (FDCP). Numbered lines indicate bands

4. Conclusions

The experimental results show that the de-esterification reaction occurs in a low extension under tested conditions, i.e. high temperatures, low pressure and sparge steam injection, reaching up to 1.5 wt% of generated acidity. The independent variable amount of sparge steam was not significant according to statistical analysis. However, its interaction with temperature and time were significant. FTIR analysis demonstrates the presence of alcohols and acids in fatty distillates, evidencing the occurrence of de-esterification reaction. For further works, it should be studied the influence of water (reagent) volatility under tested conditions and the use of devices which can improve the contact area between both aqueous and fatty phases.

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