Deacidification of High Free Fatty Acid-Containing Rice Bran Oil by Non-conventional Reesterification Process

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Abstract: Rice bran (*Oryza sativa*) oil is known for containing higher amount of free fatty acid (FFA) generated by hydrolytic enzyme. This FFA causes heavy neutral oil losses due to saponification and emulsification since it produces large amount of soap in the conventional alkali refining process. In the present study the FFA of degummed rice bran oil (RBO) was significantly reduced by reesterifying it with glycerol. The reesterification process was carried out by varying the temperature and amount of excess glycerol using 0.2% catalyst (SnCl_2). The maximum efficiency of the process could be attained at 200°C using 70% excess glycerol and the maximum reduction in acid value (from 24.3 to 3.0) of RBO was observed within 4 h. The reesterified RBO was used to prepare stand oil and varnish and their performance characteristics were compared with those of the products obtained from dehydrated castor oil (DCO).

Key words: FFA, RBO, reesterification, stannous chloride, DCO, stand oil, varnish

1 INTRODUCTION

Rice bran oil (RBO)¹⁾ can play a very important role towards health benefits particularly for lowering of LDL cholesterol. But utilization of this oil has remained a problem that higher amounts of free fatty acid (FFA) generated by naturally occurring hydrolytic enzymes may give off-flavor. The FFA is removed as soap-stock in the conventional alkali refining process. But in this process the neutral oil losses²⁾ are considerably high due to alkali refining as part of vegetable is also saponified in the process besides neutralization of free fatty acid. Chemical refining of oil with alkali produces large quantity of effluent. In order to avoid these problems, various non-conventional methods to remove the FFA from rice bran oil have been tried in the past : solvent extraction³⁾, steam distillation⁴⁾, alkali neutralization of miscella⁵⁾ and reesterifying back to glycerides with the help of glycerol⁶⁾. However, these processes were not completely free from the problems and limitations when applied on commercial scale. Therefore, in the present study on reesterification, we have tried to get more techno-economically feasible process conditions.

2 MATERIALS AND METHODS

2.1 Materials

The experimental sample of degummed rice bran oil (DRBD) was procured from M/s Ashwin Vanaspati pvt. Ltd., Samlaya, Gujarat (India). Rosin modified phenolic resin (Bluebell Polymers Pvt. Ltd., Ahmedabad) and dehydrated castor oil (DCO) were obtained from M/s Kanak Oil Mills Pvt. Ltd. (Anand). Glycerol (Chiti-Chem. Corporation, Baroda), catalyst?stannous chloride (S.D. Fine Chemical, Ltd, Bombay), and other chemicals used were of analytical grade. Nitrogen gas was supplied by Sophisticated Instrumentation Centre for Applied Research and Testing (SICART), Vallabh Vidyanagar.

2.2 Methods

2.2.1 Analysis

The DRBO and DCO were first analyzed for specific gravity, acid value, saponification value, iodine value, peroxide value, refractive index, colour, viscosity and unsaponifiable matter using standard methods^{7,8)}.

2.2.2 Reesterification of high FFA rice bran oil

The reesterification of DRBO was carried out with dif-

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ferent amounts of the DRBO, glycerol and catalyst SnCl_2 in three neck flask having 500 mL capacity equipped with thermometer pocket, stirrer and provision for passing N_2 gas. The mixture was continuously agitated for about 6 to 7 h at set temperature under the atmosphere of N_2 gas bubbling through the reaction mass at 50 mL/min. In order to monitor the reduction in FFA, the samples were drawn out at 1 h-interval and then analyzed for acid value by titrating with an alcoholic potassium hydroxide solution. Further, the amount of excess glycerol was increased and its effect on reaction rate was examined by carrying out the same experiment as described above.

2.2.3 Preparation of stand oil from reesterified rice bran oil (RRBO) and its application in varnish formulation

One hundred grams of RRBO and 0.5% lead acetate catalyst was taken and the mixture was heated slowly to raise the temperature up to 250-260°C under constant agitation. The viscosity, as a tool to monitor the reaction, was measured after every hour. The process was continued till no appreciable change was observed in viscosity. The stand oil thus prepared was mixed with 20% (w/w) rosin modified phenolic resin for application as varnish. The process was repeated with DCO taken as standard for evaluation of the performance characteristics. All products prepared as mentioned above were applied on metallic panels and the coated films were analyzed for their properties related to their performance by standard methods⁹.

3 RESULTS AND DISCUSSION

The experimental DRBO used for the reesterification process and DCO sample were analyzed for their physico-chemical characteristics and the results are shown in the

Table 1. The acid value of DRDO sample is 24.25. Other characteristics depicted in the table are within the standard values of DRBO and DCO.

The effect of the catalyst dose on reesterification with 50% excess glycerol was investigated. The reaction was carried out at 150°C, 180°C and 200°C for 5 h-duration and the results are shown in **Table 2**. The drop in acid value of RRBO was the minimum at 0.2% catalyst concentration, as shown in **Table 2**. The results clearly indicate that 0.2% catalyst concentration is the optimum dose for the reduction in FFA present in DRBO.

Further, the reaction was carried out using 50%-excess glycerol and the acid value was determined each hour. As shown in **Fig.1**, the rate of reesterification increased with temperature. The maximum drop in acid value was about 7.1 at 150°C and 19.3 at 200°C for 6 h-duration.

When the percentage of excess glycerol was increased up to 70%, the reesterification rate was faster than the ear-

Table 2 Effect of Catalyst Concentration on Reesterification¹.

Catalyst Conc. (%, w/v)	Drop in Acid Value for 6 h.		
	150°C	180°C	200°C
0.10	5.6	8.3	17.6
0.15	6.2	9.1	18.2
0.20	7.0	10.7	19.3
0.25	6.7	10.3	19.2
0.30	6.3	10.0	19.0

1: 50% excess glycerol was used

Table 1 Physicochemical Characteristics¹ of the Experimental Rice Bran Oil and Dehydrated Castor Oil.

CHARACTERISTICS	RICE BRAN OIL	DEHYDRATED CASTOR OIL
Specific gravity (30°C / 30°C)	0.920	0.9238
Acid value	24.3	4.5
Saponification value	189.4	192.6
Iodine value	95.6	124.2
Peroxide value	3.2	2.6
Refractive index	1.4670	1.4802
Color value (Iovibond tintometer, 1/4" cell)	42.1	6.0
Unsaponifiable matter (%)	4.8	0.8
Viscosity at 30°C (poise)	—	3.5

1: average of two determinations

lier case (Fig. 2). The maximum reduction in acid value was 20.2 at 200°C within 4 h. It was noticeably better than that obtained with 50%-excess glycerol at 200°C even after 7 h.

Figure 1 also shows the decrease in acid value during the reesterification process using 100%-excess glycerol. The results followed the similar trend as mentioned earlier. However, the impact of increasing the amount of glycerol is not encouraging as the maximum drop in acid value is about 20.0 after 5 h i.e. almost same as that when 70%-

excess glycerol was used.

Therefore, it can be concluded that 70%-excess glycerol, 0.2% of catalyst concentration and 200°C were the most suitable conditions for the reesterification of high FFA-containing RBO.

The RRBO was alkali neutralized (acid value = 0.42) and taken for stand oil and varnish preparation and the properties of their coated films were shown in Table 3. Also these results were compared to those obtained from DCO taken as a standard. The drying rate of both products prepared from RRBO i.e. stand oil and its varnish is slightly lower

Fig. 1 Reesterification of DRBO with 50%-Excess Glycerol (denoted by columns) & 100%-Excess Glycerol (denoted by lines), Catalyst Concentration was 0.2%.

Fig. 2 Reesterification of DRBO with 70%-Excess Glycerol. Catalyst Concentration was 0.2%.

Table 3 Performance Characteristics of Prepared Stand Oils and Varnishes from RARBO^a and DCO.

Sr.no	Stand oil/ varnishes	Viscosity (poise)	Drying properties ^b (h)			Flexibility 1/4" mandrel	Scratch hardness (kg)
			SD	HD	TFD		
1.	RRBSO	10.3	2.5	9.0	16.0	p	1.0
2.	DCSO	12.5	2.0	7.5	12.2	P	1.3
3.	Varnish from RARBSO	12.8	2.2	7.8	14.6	P	1.1
4.	Varnish from DCSO	14.0	1.8	6.5	10.6	P	1.5

^a — acid value was 0.42

^b — 2% mixed dryers(Co-octoate, Pb-octoate and Mn-octoate) were used

RARBO — Reesterified and alkali neutralized rice bran oil

RARBSO — Reesterified and alkali neutralized rice bran stand oil

DCO — Dehydrated castor oil

DCSO — Dehydrated castor stand oil

SD — Surface drying

HD — Hard drying

TFD — Tack free drying

P — Pass

than the same products obtained from DCO. However, the flexibility and scratch hardness of RRBO's samples are quite comparable to the standard one and therefore, the RRBO can be suitably used as a component in the varnish preparation.

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