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Synthesis and Characterization of Maleinized Rice Bran Oil Fatty Acids

Dr. Deepti Shikha
Associate Professor, Department of Chemistry, Brahmanand College Kanpur, Uttar Pradesh, India

ABSTRACT

Ricebran oil has higher percentage of free fatty acids which accounts for its use in various industries. In the present work rice bran fatty acids have been used for maleinization. In rice bran fatty acids maleic anhydride reacts with oleic acid without loss of unsaturation in the acid and formed succinic anhydride type adduct. Hydration of the maleinized product is performed to overcome from a number of technological difficulties such as increase in the product viscosity, abrupt and uncontrollable drop of the acid number and also gelation. Inspite of its high free acid content and dark colour, rice bran oil can be conveniently used in laundry soaps directly, but conversion of oil into distilled fatty acids provides various avenues for value added products. The absence of linolenic acid in rice bran fatty acids has an excellent advantage in providing non-yellowing characteristics. This property of rice bran fatty acids opens avnues for coating industries.

Keywords : Rice Bran, Maleinization

I. INTRODUCTION

Rice bran oil (RBO) is a polymerized semidrying oil. Rice bran (Oryza sativa) forms 8% of milled rice contains 15-20% oil,0.4-1.5% wax, 8% protein, 40-50% carbohydrates, 5-8% fibre1. The latest study provides a detailed insight into the global rice bran oil market. India represents the world's largest producer accounting for the majority of the total global production. India is followed by China and Japan. Majority of the total rice bran oil is used for edible purposes, while the rest is consumed for industrial applications.2

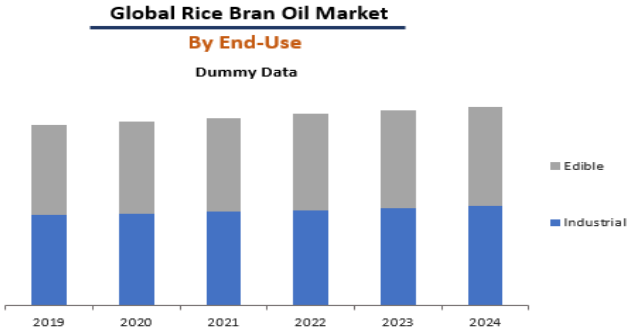


Fig.1: Global Rice Bran Oil Market

Rice bran oil is invariably high in fatty acids. The rice bran oil fatty acids used represent a mixture of saturated acids (15-20%) and unsaturated fatty acids (80-85%). Palmitic, oleic and linoleic fatty acids constitutes more than 90% of the rice bran fatty acids portion of glycerides.

The stereo specific analysis indicates [3] that $C_{16:0}$ is exclusively at the 1 and 3 positions while $C_{18:1}$ occurs on all three positions and $C_{18:2}$ predominantly occupies the 2-positions.The structures and properties[4] of these three major fatty acids present in RBO are as follows:

Table-1. Structures and properties of three major fatty acids

Fatty acid	Scientific name	Structure	Empirical formula	Mol. wt.	MP (°C)
Palmitic	Hexadecanoic	$CH_3(CH_2)_{14}COOH$	$C_{16}H_{32}O_2$	256.5	63
Oleic	9-Octadecenoic	$CH_3(CH_2)_7CH=CH(CH_2)COOH$	$C_{18}H_{34}O_2$	282.5	13.4
Linoleic	9,12-Octade-Cadienoic	$CH_3(CH_2)_4CH=CH-CH_2-CH=CH(CH_2)_7COOH$	$C_{18}H_{32}O_2$	280.5	-5

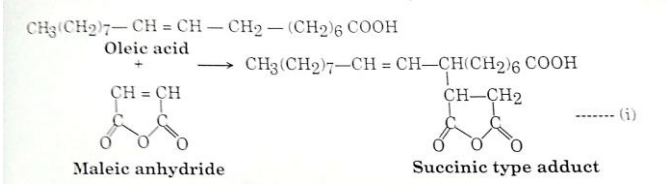
The selection of oils or fatty acids are made depending on the final use of the resin e.g. whether the resin will be used as film forming materials or as plasticizing materials, like linseed oil used as a drying oil; soybean oil, which do not form satisfactory films at normal temperature, used as a semidrying oil in air drying alkyd resins is suitable for baking finishes; castor oil, rap seed, cottonseed and coconut oils are non-drying oils, they can not form films under air drying or baking conditions; hence they are used as plasticizers. In the present work, fatty acids derived from rice bran oil i.e. polyunsaturated semi-drying oil are taken as film former, plasticizer as well as to provide reactive sites for further modification. Besides this we can compare the fatty acid composition of rice bran oil with other natural oils which are generally used in paints, varnishes and oil-modified resins as follows[5].

Table-2. Comparative Chart of Fatty Acid Composition of Rice Bran Oil with other Natural Oils (percent of total acids)

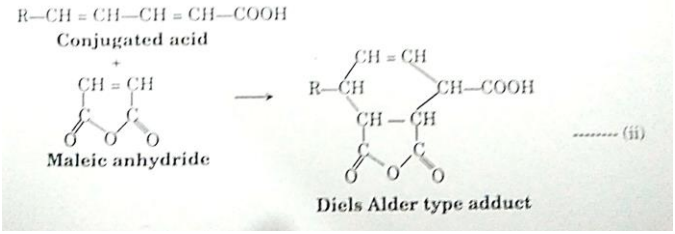
Acids	Chemical formula	Vegetable Oils							
		Ricebran	Tall	Tung	Safflower	Soybean	Sunflower	Linseed	Castor
Myristic	$C_{14}H_{28}O_2$	0.47	-	-	0.1	0.1	-	-	-
Palmitic	$C_{16}H_{32}O_2$	18.87	7	4	4.5	8	4	5.5	2
Stearic	$C_{18}H_{36}O_2$	2.15	-	1	2	4	3	4	1
Arachidic	$C_{20}H_{40}O_2$	2.07	-	-	0.4	0.6	0.6	0.3	-
Lignoceric	$C_{24}H_{48}O_2$	-	-	-	-	-	0.4	0.2	-
Unsaturated acids									
Myristoleic	$C_{14}H_{26}O_2$	-	-	-	-	0.1	-	-	-
Palmitoleic	$C_{16}H_{30}O_2$	0.29	1	-	-	0.2	-	-	-
Oleic	$C_{18}H_{34}O_2$	43.68	44	8	20	28	33	22	7
Linoleic	$C_{18}H_{32}O_2$	31.87	37	4	70	54	59	17	3
Linolenic	$C_{18}H_{30}O_2$	0.6	-	3	3	5	-	51	-
Eleostearic	$C_{18}H_{30}O_2$	-	-	80	-	-	-	-	-
Ricinoleic	$C_{18}H_{34}O_3$	0	-	-	-	-	-	-	87

Chemistry of Maleinized Rice Bran Oil Fatty Acids

In rice bran oil fatty acids maleic anhydride reacts with one mole of oleic acid without loss of unsaturation in the acid and formed succinic anhydride type adduct by transfer of a hydrogen atom[5] from the fatty acid chain to the maleic anhydride as follows



A Diels-Alder type of addition is entirely possible for oil with conjugated unsaturation.



II. METHODS AND MATERIAL

Materials used: The materials/chemicals used in this research work have been mentioned here below:

i. Rice bran oil fatty acids: color lovibond tintometer - R=5,Y=3; acid value-177 mg KOH/g, iodine value(wijs) - 90, refractive index at 32^{0}C- 1.4655

ii. Maleic anhydride- m.w.-98.06%, minimum assay(acidimetric)-97%,m.p. - 52-55^{0}C, S.D.Fine-Chemicals

iii. Ethyl Alcohol- m. w.- 46,b.p.-78to79^{0}C,distilled in the laboratory

iv. Phenolphthalein, LR- m. w.- 318.33, pH range - 8.3 to 10.0, m.p.- 258 to 261^{0}C, BDH Chemicals

v. Potassium hydrogen phthalate - minimum assay- 99.9%, m.w.-204, Ranbaxy Laboratories

vi. Potassium hydroxide, LR-m.w.-56.11,minimum assay- 85.0%, Ranbaxy Laboratories

vii.Sodium thiosulphate - m. w.- 248.18, minimum assay- 99%,Qualigens Fine Chemicals

viii. Sodium hydroxide, Pellets, LR- m.w. - 40.00, minimum assay- 96.0%, Samir Tech-Chem

ix. Starch -S.D.Fine Chemicals

Methods Employed

A number of techniques were employed for the analysis of raw material and synthesized maleinized Rice Bran Fatty acids. The methods are discussed here under:

(i) Color

It was determined by Lovibond Tintometer[6] using 1/4" Lovibond cell. The colour of the sample was reported using following relationship.

Color reading (1/4"cell) = (aY + 5bR)

where , a= the sum total of the various yellow (Y) slides used

b= the sum total of the various red (R) slides used

(ii) Refractive Index

The refractive index of samples was determined[6] by using Abbe refractometer. It was calculated at desired temperature as given below

$R = R' + K (T' - T)$

where,

R' = the reading of the refractometer reduced to the specific temperature, T^{0}C

K = constant 0.000365 for fats

T = the specified temperature

(iii) Acid Value

0.1-0.2grams of sample was weighed accurately in a 250 ml conical flask. To this 100ml of ethanol[6] was added in a sample of oil, shaked and warmed if necessary to dissolve and then this solution was titrated against a standard solution of potassium hydroxide to the pink end point using phenolphthalein as indicator. The acid value was calculated as given below:

Acid value = 56.1V N/w

where,

V = volume in ml of standard alcoholic potassium hydroxide solution used

N = normality of standard potassium hydroxide solution

w = weight in grams of the material taken for the test

(iv) Iodine Value

The iodine value (wijs) was calculated[7]as

Iodine value = 12.69 (B-S) N/ w

B= volume in ml of standard sodium thiosulphate solution required for the blank

S = volume in ml of standard sodium thiosulphate solution required for the sample

N= normality of the standard sodium thiosulphate solution

w= weight in grams of the material taken for the text

(v)Unreacted Maleic Anhydride Content

The maleic anhydride content is determined[8] by titrating the material with standard sodium hydroxide solution using phenolphthalein as an indicator and deducting the maleic anhydride content equivalent to maleic acid content.

Reagent

1. Potassium hydrogen phthalate (previously dried for 2 hours at 120^0C)

2. Phenolphthalein indicator (0.1 gram per 100 ml ethanol)

3. Standard sodium hydroxide solution (0.5 N) standardized as follows:

4gram of potassium hydrogen phthalate was weighed and transferred to a 500ml conical fiask.To this 120 ml of water was added to dissolve by warming on a water bath and titrated hot with standard sodium hydroxide solution (0.5N) to the first pink colour using phenolphthalein as an indicator. The factor F for 0.5 N standard solution will be :

$F = M_1 / (0.2042 x V_1)$

Where,

M_1= mass in grams of potassium hydrogen phthalate

V_1 = volume in ml of standard sodium hydroxide solution

1 gram of sample was weighed accurately into a 250-ml conical flask. To this 35 ml of standard sodium hydroxide solution from a burette and 35 ml of water was added, and warmed gently to dissolve the sample then this solution was completely neutralized with standard sodium hydroxide solution using phenolphthalein as an indicator until the pink colour was obtained.

Calculation:

Unreacted Maleic anhydride content = 4.902 V x F/ M - 0.845A

Where

V = volume in ml. of standard sodium hydroxide solution

F = Factor for standard sodium hydroxide solution

A= Maleic acid content, present by mass

M= Mass in grams of the material taken for the test

(vi) Fourier Transform Infrared Spectroscopy (FTIR)[9]

Fourier Transform Infrared Spectra (υ max in cm^{-1}) were recorded on a Bruker Vector 22 spectrophotometer. Liquid samples were examined as thin films, obtained by squeezing a drop between a pair of infrared transmitting plates or as solution in solvent which are reasonably transparent to infrared radiation and good solvating properties.

3.Synthesis of Maleinized Rice Bran Oil Fatty Acids

For the maleinization of rice bran oil fatty acids, weighed quantity of fatty acid was taken in a three neck round bottom flask, fitted with a thermometer pocket having thermometer, mechanical stirrer and water condenser. it was heated to 90^0C with constant stirring. The calculated amount of maleic anhydride was added slowly within 20-30 minutes. After the complete addition of maleic anhydride, temperature was raised to 180-210^0C depending on the percentage of maleic anhydride. The temperature was maintained till the desired acid value is obtained. The samples were withdrawn at different intervals to check the acid value and untreated maleic anhydride content.

The rice bran oil fatty acids were treated up to extent of 20% of maleic anhydride. Reaction conditions i.e. time, temperature and percentage of maleic anhydride were optimized. The details of the maleinized fatty acids and codes are given in Table -3.

Table 3. Reaction Conditions for Maleinization of RBO Fatty Acids

S.No.	Code No.	Amount of Fatty Acids(gms)	Amount of maleic anhydride(% by wt.)	Temp(0C)	Time(min)
1	S_1	100	6	200-210	225
2	S_2	100	8	200-210	210
3	S_3	100	10	200-210	180
4	S_4	100	10.5	200-210	120
5	S_5	100	11	200-210	120
6	S_6	100	12	180-190	240
7	S_7	100	15	180-190	210
8	S_8	100	20	180-190	180

4.Characterization of maleinized RBO Fatty acids

The above synthesized maleinized fatty acids were characterized for their physical and chemical properties including Fourier Transform infrared spectroscopy. The acid value and unreacted maleic anhydride of maleinized fatty acid was determined by the method described above. The value obtained have reported in Table - 4.

All the maleinized fatty acids were neutralized with triethylamine. Neutralized maleinized fatty acids were found soluble in all proportions in distilled water. Solubility of the maleinized fatty acids was observed at room temperature i.e., 32^0C. The water soluble samples were examined for hazyness or any suspended particles. It was found that all maleinized fatty acids solutions were clear and transparent. The observation have been reported in Table -4.

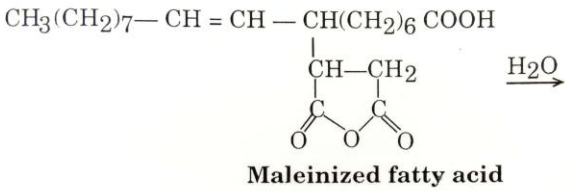
Table – 4. Characteristics of Maleinized RBO Fatty Acids

S.No.	Code No.	Acid value	Unreacted Maleic anhydride(%by Wt.)	Solubility in Water	Clarity
1	S_1	226	0.89	Soluble	Clear
2	S_2	231	1.82	Soluble	Clear
3	S_3	240	2.98	Soluble	Clear
4	S_4	242	3.23	Soluble	Clear
5	S_5	249	3.63	Soluble	Clear
6	S_6	255	5.02	Soluble	Clear
7	S_7	261	6.85	Soluble	Clear
8	S_8	279	8.98	Soluble	Clear

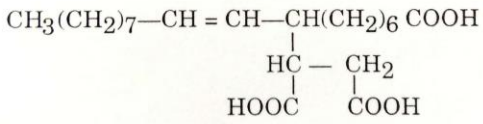
Presence of various groups in the maleic anhydride, pure rice bran oil fatty acids and maleinized fatty acids backbone were identified by various peaks obtained through Fourier Transform Infrared Spectroscopy (FTIR) technique as shown in FTIR spectrums Fig.4 to 6.

5.Hydration of maleinized rice bran oil fatty acids

Hydration of above synthesized fatty acids results in the opening of the anhydride rings.[10]



Maleinized fatty acid



Hydrated maleinized fatty acid

Hydration was carried out by boiling maleinized fatty acids in water for about one hour. The excess unreacted water was then distilled off under reduced pressure. All the samples were prepared in this manner.

III. RESULTS AND DISCUSSION

Maleinization of rice bran fatty acids was done 6 to 20% on the basis of amount of RBO fatty acids, the important factor was reaction conditions as shown in Table 3. During the synthesis, the addition reaction takes place between maleic anhydride and fatty acid and a substituted succinic anhydride was formed by the transfer of a hydrogen atom[5] from the fatty acids chain to the maleic anhydride.

The rice bran oil fatty acids were maleinized only to 20% because above this percentage RBO fatty acids were gelled even at low temperature. Fig 2 & 3 depict the change in acid value and concentration of the unreacted maleic anhydride with time respectively. The concentration of the unreacted maleic anhydride decreases at prolonged process duration. Due to difficulties arising during the following stages, the reaction product should be less than 3%. The data in Fig 2&3 suggest that this condition is satisfied only when the amount of initially fed maleic anhydride ranges from 5-10%, the reaction time being 2 to 4 hours. The optimal temperature and duration of the process should depend upon the desired acid value of the product obtained. This acid value should not exceed 220 to 240 mg KOH/ gm and for this reason the reaction temperature range of 200-220^{0}C is most appropriate. Higher temperature leads to premature gelation.

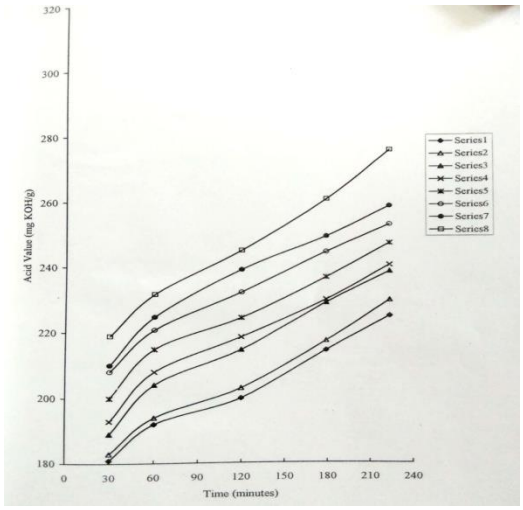


Fig.2 Change in Acid Value during Maleinization of Rice Bran Fatty Acids

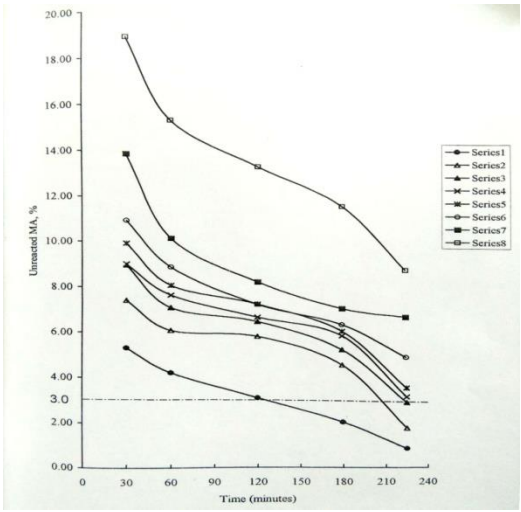


Fig. 3. Change in Unreacted Maleic Anhydride during Maleinization of Rice Bran Fatty Acids

Series 1- 6% Maleic Anhydride
Series 2- 8% Maleic Anhydride

Series 3- 10% Maleic Anhydride
Series 4- $10^{1/2}$% Maleic Anhydride
Series 5- 11% Maleic Anhydride
Series 6- 12 Maleic Anhydride
Series 7- 15% Maleic Anhydride
Series 8- 20% Maleic Anhydride

On the basis of the studies carried out, the following process conditions were established to be the optimal ones : 8% maleic anhydride based on the amount of rice bran fatty acids, reaction temperature 210 ± 10^0C and reaction time of 3-4 hours with unreacted maleic anhydride content is less than 3%. Higher maleic anhydride not only causes gelation during processing but can also reduce alkali resistance.

The solubility of all neutralized maleinized RBO fatty acids was checked in water. It was observed that all maleinized fatty acids were soluble in water and clear as shown in Table 4.

In the FTIR spectrum of the maleic anhydride, pure rice bran oil fatty acids and maleinized fatty acids, the peaks were observed as shown in Fig.4 to 6.The peaks at wave number 1782cm^{-1} is attributed to anhydride group in maleic anhydride(Fig.4) and peaks at 1710 cm^{-1} and 1282cm^{-1} (Fig.5) are attributed to C=O and C-O stretching vibration of carboxylic group present in pure rice bran fatty acids respectively. The peaks obtained at 1778-1782cm^{-1} and increase in intensity at peaks 1287cm^{-1}(Fig.6) in maleinized fatty acids confirms the incorporation of anhydride group.

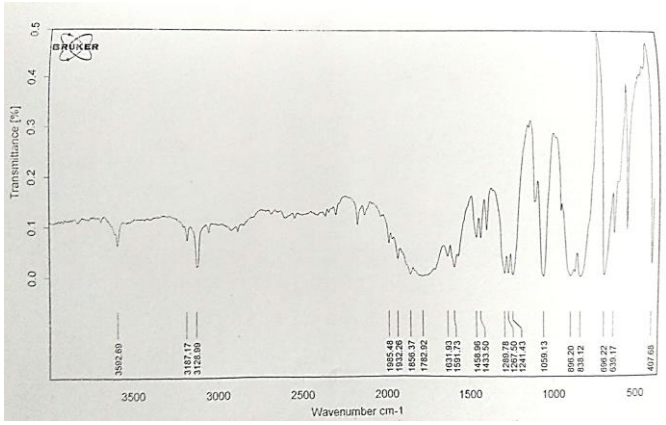


Fig 4. FTIR spectrum of Maleic anhydride

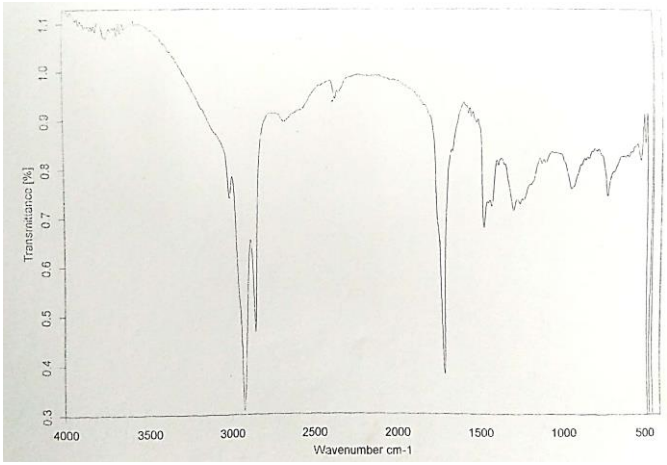


Fig 5. FTIR spectrum of Pure Rice bran Fatty Acids

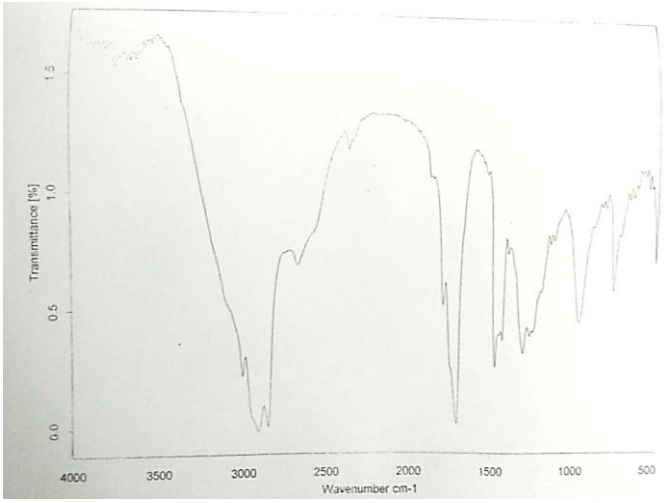


Fig 6. FTIR spectrum of Maleinized Rice bran Fatty Acids

IV.CONCLUSION

On the basis of above experiments it may be concluded that the maleinization of RBO fatty acids was safe up to 20%. Beyond this limit the probability of gelation increases. The temperature and duration of the process depend up on the desired acid value of the product obtained. The acid value and unreacted maleic anhydride should not exceed 220 to 240 mg KOH/gm and 3% respectively. Higher maleic anhydride not only causes gelation during the processing but also affect the film properties. The clarity of solutions was consistent and solubility in water was satisfactory. The increase in acid value, decrease in unreacted maleic anhydride content and FTIR spectra confirmed the incorporation of anhydride group in fatty acids.

Malenized Rice bran oils can be recommended for use in industrial finishes where good mechanical properties with mild chemical resistance are required. The fuller exploitation of rice bran oil will certainly ease the pressure on other petroleum based conventional resins if it is commercially utilized.

V. ACKNOWLEDGEMENT

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