

FFA ANALYSIS OF RICE BRAN OIL

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CALOFIC - Vietnam



A. FFA of vegetable oils

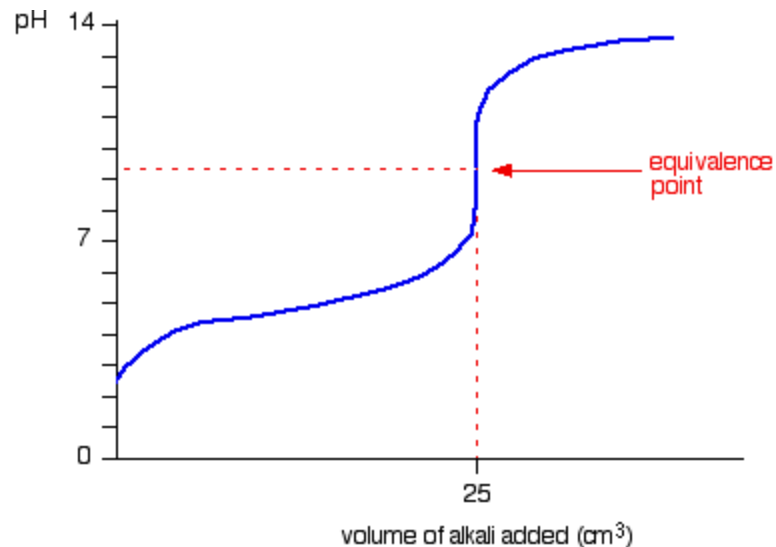
1. **Free fatty acids (FFA) or Acid value** is one of the most critical quality parameters of vegetable oils. High FFA will lead to hydrolytic rancidity and affect quality of vegetable oils in term of flavor, smoke point... Moreover, FFA is also catalyst to oxidation reaction which results in formation of free radicals- beginning of many serious diseases such as cardiovascular, cancer, aging process etc.
2. **FFA standard of vegetable oils in the world**

No	Organization/ Country	FFA (%)	Acid value (mg KOH/g)	Apply for
1	Codex	0.3 max	0.6 max	Refined vegetable oils
2	China	1.5 max	3 max	Refined vegetable oils
3	India	0.25 max	0.5 max	Refined Rice bran oil
4	Korea	0.3 max	0.6 max	Refined vegetable oils
5	Thailand			
6	Vietnam			

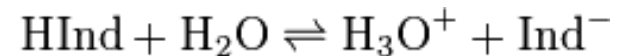
A. FFA of vegetable oils

3. Standard FFA testing methods

No	Organization	Method	Indicator
1	American Oil Chemists' Society (AOCS)	AOCS Ca 5a - 40	Phenolphthalein
2	International Standard Organization (ISO)	ISO 660:2009	Phenolphthalein
3	International Union of Pure and Applied Chemistry (IUPAC)	IUPAC 2.201	Phenolphthalein



- Principles: acid-base titration
- Mechanism of pH indicator:



A. FFA of vegetable oils

Table 1: Some popular indicators and its pH transition range

Indicator	Low pH color	Transition low end	Transition high end	High pH color
Bromothymol Blue	yellow	6.0	7.6	blue
Phenol Red	yellow	6.4	8.0	red
Neutral Red	red	6.8	8.0	yellow
Cresol Red	yellow	7.2	8.8	reddish-purple
Phenolphthalein	colorless	8.3	10.0	fuchsia
Alkali Blue 6B	Blue	9.0	14.0	colorless
Thymolphthalein	colorless	9.3	10.5	blue



Is phenolphthalein suitable for testing FFA of Rice Bran Oil?

B. Rice bran oil

- Rice bran oil is a vegetable oil, extracted from bran of the rice seed.
- Rice bran oil has been using widely in many Asian countries such as China, Japan, Korea, India and Vietnam and now is becoming more popular in Western countries due to its health benefits coming from minor components such as vitamin E, phytosterols and especially γ -oryzanol, which is exclusively found at high concentration in rice bran oil.
- Some health benefits of rice bran oil: lowering cholesterol, prevent heart disease, beauty care, anti-oxidation, etc.

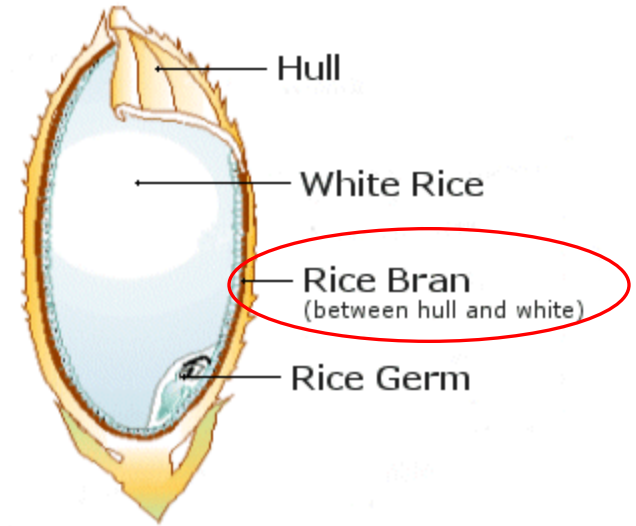


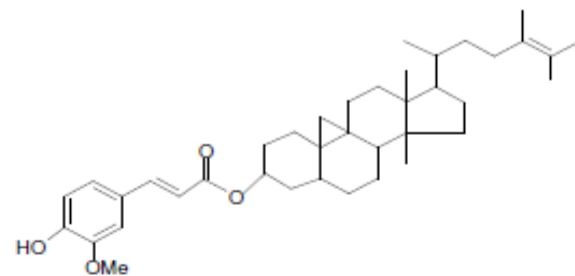
Figure 1: Structure of rice seed

B. Rice bran oil

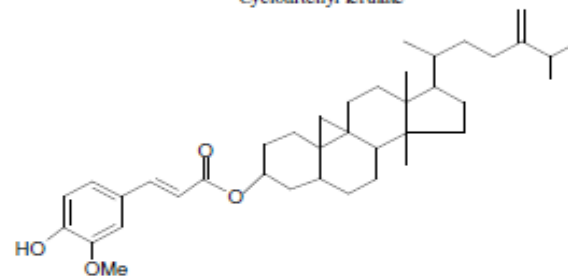
- γ -oryzanol is a mixture of ferulic acid (4-hydroxy-3-methoxycinnamic acid) esters of triterpene alcohols. It has been exclusively found in rice bran oil.
- According to A.G. Gopala Krishna et al (2006) γ -oryzanol has acidity and this value is determined by formula:

γ -oryzanol acidity (as % NaOH consumed)

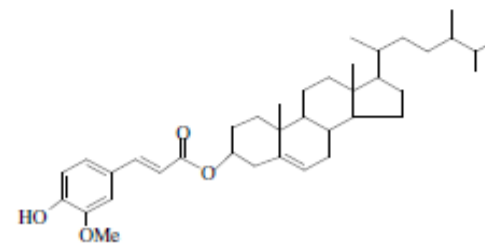
$$= V \times 0.004 \times 100/W$$



Cycloartenyl ferulate



24-methylene Cycloartenyl ferulate



Campesteryl ferulate

Figure 2: Structure of main components of γ -oryzanol

B. Rice bran oil

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Acidity of oryzanol and its contribution to free fatty acids value in vegetable oils

A. G. Gopala Krishna, K. H. Hemakumar, Sakina Khatoon

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Tested FFA of RBO

**= Real FFA of RBO + Acidity of
γ-oryzanol**



How to determine real FFA of RBO ?

Abstract

Model oil systems containing physically refined rice bran oil to which oryzanol was added were examined to determine the effects of oryzanol concentration on FFA values. When oryzanol was added to the model oils at a 0.5% level and FFA was determined, increases in FFA value were 0.28% as determined with phenolphthalein, 0.58% with thymolphthalein, and 0.07% with alkali blue 6B. Oils containing added oryzanol at 0.5–1.5% showed a proportionate increase in FFA values with an average increase of 0.413% per gram of oryzanol. A direct titration of purified oryzanol showed an acidity of 42.5% expressed as FFA. In spectroscopic studies, the phenolic group in the ferulic acid moiety of oryzanol was titrated by sodium hydroxide. Based on these data, indicator correction factors for oryzanol's acidity and a formula for calculating real FFA content of vegetable oils containing oryzanol were developed.



C. Materials & Methods

- Vegetable Oils:
 - ✓ RBD Rice bran oil: from China, Thailand, India and Vietnam
 - ✓ RBD Soybean oil: from South America (comparison purpose)
 - ✓ RBD Palm Olein: from Malaysia (comparison purpose)
- Indicator:
 - ✓ Phenolphthalein: from Merck (USA)
 - ✓ Bromothymol Blue: from Merck (USA)
 - ✓ Alkali Blue 6B: from Sigma-Aldrich (USA)
- FFA testing methods: AOCS Ca 5a – 40



D. Results

Table 2: FFA of some vegetable oil samples with different oryzanol contents

Sample	Oryzanol (ppm)	FFA (%)		
		Bromothymol Blue	Phenolphthalein	Alkali Blue 6B
RBD Palm Olein	0	0.020 ± 0.001	0.026	0.020 ± 0.001
RBD SBO	0	0.021 ± 0.002	0.040 ± 0.001	0.034 ± 0.002
RBD RBO 1	4,600	0.035 ± 0.001	0.183 ± 0.003	0.040 ± 0.001
RBD RBO 2	6,400	0.047 ± 0.001	0.289 ± 0.004	0.050
RBD RBO 3	11,000	0.039 ± 0.001	0.416 ± 0.018	0.077 ± 0.002
RBD RBO 4	14,000	0.083 ± 0.002	0.497 ± 0.016	0.101 ± 0.007



D. Results

Table 3: FFA of some vegetable oil samples calculated based on research of Krishna et al. (2006)

Sample	Oryzanol (ppm)	FFA (%)			
		Phenolphthalein		Alkali Blue 6B	
		Tested by existing method	Real content by calculation	Tested by existing method	Real content by calculation
RBD Palm Olein	0	0.026	0.026	0.020 ± 0.001	0.020
RBD SBO	0	0.033 ± 0.001	0.033	0.034 ± 0.002	0.034
RBD RBO 1	4,600	0.183 ± 0.003	-0.013	0.040 ± 0.001	-0.007
RBD RBO 2	6,400	0.289 ± 0.004	0.017	0.050	-0.015
RBD RBO 3	11,000	0.416 ± 0.018	-0.052	0.077 ± 0.002	-0.035
RBD RBO 4	14,000	0.497 ± 0.016	-0.098	0.101 ± 0.007	-0.042



E. Conclusion

- Bromothymol Blue should be used as indicator for testing FFA of RBO.
- Need to set up a specific international standard method for testing FFA of RBO.
- IARBO should make a recommendation to international standard organizations (AOCS, ISO...) to conduct research and issue standard method applicable for rice bran oil.

Thank
You