ISSN: 2354-5917

PROCEEDINGS of INTERNATIONAL SEMINAR ON CHEMICAL ENGINEERING

IN CONJUNCTION WITH

SEMINAR TEKNIK KIMIA SOEHADI REKSOWARDOJO (STKSR) 2017

Clean-Sustainable Process and Product Technology

2-3rd October 2017
East Hall and West Hall
Institut Teknologi Bandung

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PROCEEDING

International Seminar on Chemical Engineering
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"Clean-Sustainable Process and Product Technology"

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2nd-3rd October 2017
West and East Hall
Institut Teknologi Bandung
Jl. Ganesha 10 Bandung INDONESIA

Organized by

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Faculty of Industrial Technology
Institut Teknologi Bandung

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ISSN: 2354-5917

MESSAGE

Welcome to all honorable keynote speakers, presenters, and participants in the International Seminar on Chemical Engineering in conjunction with Seminar Teknik Kimia - Soehadi Reksowardojo (STKSR) 2017. This annual seminar has been an event of research dissemination and knowledge sharing for chemical engineering community in Indonesian, as well as neighboring countries.

Chemical engineering concern to produce, transform, transport, and properly use of chemical, material, and energy. This field of engineering is therefore closely related to industry development in a country. Process design and analysis of technology, chemical reaction engineering, and safety analysis are the main object of chemical engineering. Chemical engineering has also significant role to fulfill one of millennium development goals, i.e. to ensure environmental sustainability. With limit on resources and increasing environment effect due to industries, we need to move toward a clean-sustainable processing technology.

We encourage youth and motivated professional to develop and share their innovation in the clean-sustainable product and process technology through this seminar. Hopefully, the seminar will bring a productive and fruitful discussion. Lastly, we greatly thanks all sponsors and contributors to support this seminar.

Prof.Dr.Ir. Kadarsah Suryadi, DEA.

Rector of Institut Teknologi Bandung (ITB)

ISSN: 2354-5917

MESSAGE

Dear Colleagues,

On behalf of the Organizing Committee of the International Seminar on Chemical Engineering, I am gladly welcome you all to Institut Teknologi Bandung, Bandung, Indonesia. This year, the Seminar which is held in conjunction with Seminar Teknik Kimia - Soehadi Reksowardojo (STKSR) 2017 raises the topic of 'Clean-sustainable Process and Product Technology'. Through this topic, we are promoting an awarness on global warming issues and sustainable production.

Those topics will be addressed in several categories, i.e. bionergy, chemurgy, alternative energy, fossil energy and mineral processing, process technology, and advance science in plenary lectures and parallel sessions. Here, we encourage young and inspiring keynote speakers to share their energy and experiencies. In end of seminar, we invite speakers in a workshop session who will share their industrial/field experiences.

We have prepared social (get-together) event, so that delegates may meet and communicate one another. Finally, the committee gratefully addressed all sponsors and ChemEng-ITB Alumni for funding and supports. We also thank all International/Technical Committee members, all the plenary and invited speakers and all oral/poster presenters for their kind efforts and contributions in making this conference a success.

Thank you

Hary Devianto, Ph.D.

Chairman of STKSR 2017

ISSN: 2354-5917

ACKNOWLEDGEMENT

The completion of this undertaking could not have been possible without the participation and assistance of so many people whose names may not all be enumerated. The contributions are sincerely appreciated and gratefully acknowledged. However, we would like to express our especially deep appreciation and gratitude to the following.

1. Institut Teknologi Bandung, Faculty of Industrial Technology, Department of Chemical Engineering.
2. Lembaga Penelitian dan Pengabdian kepada Masyarakat Institut Teknologi Bandung (LPPM ITB)
3. PT. Petrokimia Gresik
4. Medco Foundation
5. Ir. Rauf Purnama, IPU
6. Biomass Gasification Research Group Department of Chemical Engineering Institut Teknologi Bandung

for their support toward STKSR 2017. We sincerely hope that our good cooperation can extend to other opportunities in the future.

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POSTER PRESENTATION SESSION

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Factorial Design Analysis applied to Bleaching of Rice Bran Oil

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Abstract
Rice bran contains edible oil which is rich in anti oxidants but, however, it has problems during storage, due to the activity of lipase enzyme. The most popular stabilization method is extrusion cooking. The extrusion cooking of rice bran, however, results in dark oil. This research is aimed to study the bleaching of rice bran oil from extrusion cooked rice bran. The experiments were carried by a full 2k factorial design with bleaching earth-to-oil ratio, temperature, and time as factors. The color of rice bran oil was measured by spectrophotometer. It was found that all main factors have significant effects on the color of rice bran oil. Among the interaction factors, only the interaction between temperature and bleaching earth-to-oil ratio has significant effect. The best result was obtained at temperature of 110°C, time of 30 minutes, and bleaching earth-to-oil ratio of 10%. In addition, rice bran oil de-acidified by solvent extraction was found to be more difficult to bleach than that by neutralization.

1. Introduction

Rice bran is a byproduct of rice milling. Rice mills generally separate rice into three fractions, i.e., white rice, rice husk, and rice bran. These fractions contribute about 70%, 20%, and 10%, respectively, of rice weight. Rice bran consists of 15~18% fat/oil, 0.4~1.5% wax, 5~8% protein, 40~50% soluble carbohydrate, and 5~8% fiber[1,2]. Rice bran oil is a healthy edible oil, containing vitamins, antioxidants, nutrients and trans fat free. It can help lower cholesterol, fight diseases, enhance the immune system, fight free radicals and more. Rice bran oil is vastly superior to traditional cooking oils and can be considered a nutraceutical (food as medicine) oil that is perfect for healthy cooking needs. The unique components, such as oryzanol or tocotrienol, have been drawing people's attention. Numerous studies show rice bran oil reduces the harmful cholesterol (LDL) without reducing good cholesterol (HDL). In those studies, oryzanol is reported as the key element responsible for that function[3]. Tocotrienol, on the other hand, is highlighted as the most precious and powerful vitamin E existing in nature and is said to have an anti-cancer effect[3]. It has been suggested to suppress production of reactive oxygen species more efficiently than tocopherols. As a vitamin-E source, rice bran oil is rich not only in alpha tocopherol but also has the highest amount of tocotrienol in liquid form vegetable oils.

Indonesia is the third largest rice producer in the world after China and India. The annual rice production of Indonesia achieved 50-60 million tones. This means that Indonesia produces rice bran of 5-6 million tons per year. However, it is not utilized for edible oil production. Rice bran is generally utilized for animal feeds and sometimes left near rice millers as waste. In certain countries, notably India, China, and Japan, however, rice bran oil makes a significant contribution to the edible oil supply.

It is well known that raw rice bran contains an extremely active lipolitic enzyme (lipase) which hydrolyses the triglycerides and releases free fatty acids. The major impediment to the development of rice bran oil industries in Indonesia has been the high free fatty acid content of the extracted oil due to the action of this enzyme. Lipase mixes with rice bran after milling and become very active on contact with air. High free fatty acids are not acceptable for edible oil refining since removal of the acidity leads to considerable losses of neutral oil. Free fatty acid levels can rise to 20 per cent in a matter of days[4]. Without stabilization process, storage of several days causes the extraction of rice bran oil becomes uneconomic.

One of popular stabilization methods is extrusion cooking. Stabilization of rice bran by extrusion cooking results in dark crude rice bran oil. The bleaching of rice bran oil becomes more difficult compared to other edible oils. Bleaching of edible oils is usually done by adsorption using bleaching earth. The bleaching performance of a bleaching earth is influenced by the quality of oil, bleaching earth-to-oil ratio, temperature, and time. In addition, the darkness of rice bran oil from extrusion cooked rice bran was affected by cooking condition, quality of rice bran, and perhaps the variety of rice. Although numerous researches on rice bran oil have been published, experimental results on bleaching of rice bran oil are limited. O'Brien et al[5] found the best bleaching condition at temperature range of 70 to 110°C and time range of 15 to 30 minutes. Caustic refining was found to give lighter rice bran oil compared to solvent refining and steam refining[6]. Treating rice bran oil miscella by silica gel was found to improve oil color but the slow flow rate of miscella through silica gel bed was found to be a problem[7]. Sayre et al[8] found that the extrusion of rice bran at 130°C did not affect the bleached oil color using acid activated clay. Strieder et al[9] studied bleaching in combination with winterization and found that the use of 1% (w/w) of adsorbent in relation to the mass of oil and 8% (w/w) activated carbon in relation to the total mass of adsorbent were the best conditions, which resulted in a removal of 83% of primary oxidation products and of 57% of carotenoids content. A comprehensive study on the effects of bleaching operation has not been done.

This research is aimed to study the bleaching of rice bran oil from extrusion cooked rice bran by 2^k factorial design. Bleaching earth-to-oil, temperature, and time are selected as experimental factors. The color of rice bran oil was measured by spectrophotometer. Recently, solvent extraction was found to be promising as a substitute for neutralization in removing the free fatty acid content of rice bran oil. This research, therefore, is also proposed to compare the bleaching of rice bran oils from solvent refining and neutralization.

2. Experiment

2.1 Materials

Freshly milled raw rice bran, containing an average of 12% oil and moisture of 14%, was obtained from a local rice mill. The rice bran was collected within one hour after milling. Normal hexane of technical grade was used for extracting rice bran oil. The bleaching earth used was an optimum proprietary product of a bleaching earth corporate in West Java, Indonesia. Methanol and caustic soda was used for removing free fatty acid by solvent extraction and neutralization, respectively. All chemical utilized for analysis were of pure grade.

The rice bran accepted was first cooked using an extrusion cooker with 3 dies (3 mm ID x 25 mm length opening), which was designed according to a previous literature[10]. The raw bran was fed directly into the extruder. Our previous result showed that the heat developed was sufficient to achieve a cooking temperature of 110 to 130°C[11]. The extruded hot bran was cooled in a sieve wire-air cooler to 40°C. Moisture contents of the sample brans were adjusted by conditioning in an atmosphere, and samples were then packed in polyethylene bags to prevent moisture adsorption until extraction were completed. The extruded rice bran was then contacted with normal hexane in an extractor of 50 liters capacity to extract rice bran oil. Normal hexane was removed by distillation under vaccuum to obtain crude rice bran oil. The crude rice bran oil was dewaxed and degummed by aqueous calcium chloride, settling and centrifugation. Free fatty acids were removed from dewaxed rice bran oil by two methods, i.e, solvent extraction using methanol and neutralization using caustic soda. Bleaching experiments were carried in a stirred glass using 30 grams of rice bran oil. The experiments were design using a full 2^k factorial design. Three factors were studied, i.e., bleaching earth-to-oil ratio, temperature, and time as main factors. Activated carbon, 5% of bleaching earth, was also added in all bleaching runs. Table 1 shows the levels used.

Oil color was measured by a spectrophotometer (an HP 8452A model) with automatic wave length scanning and recording. Cuvettes with 1 cm light path were used and absorbance at wave lengths of 190-800 nm was recorded.

Table 1: Factor levels.

Factor	Level	
	-1	+1
Bleaching earth-to-oil ratio (%)	1	10
Temperature (^oC)	70	110
Time (minute)	15	30

3. Results and Discussion

3.1 Interpretation of absorbance curve

Fig. 1 shows typical spectra of rice bran oils, before and after bleaching, in which free fatty acids were removed by neutralization. Two spectra for bleached rice bran oils represent the best and the worst bleaching, respectively. The spectra of neutral rice bran oil exhibits maxima at 496, 538, 560, 610, and 672 nm. The absorbance peaks at 538, 610, and 672 nm are characteristics of red, blue, and green respectively. As can be seen, these three peaks were removed after bleaching at the best condition but just shortened after bleaching at the worst condition. In other words, the performance of bleaching depends on bleaching condition.

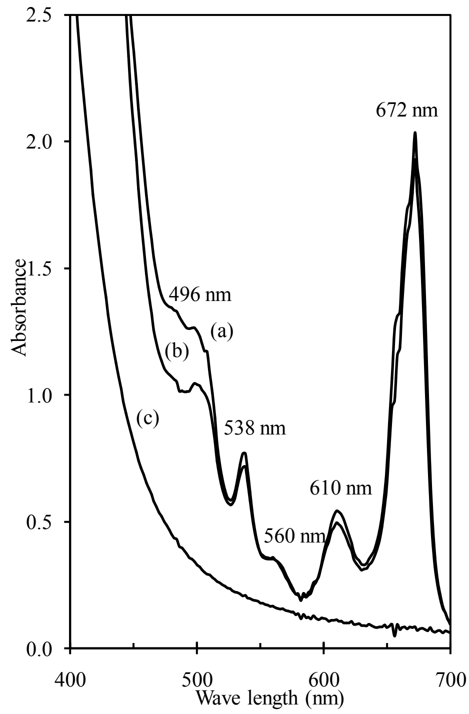

Figure 1: Spectra of rice bran oils (a) after neutralization, (b) after bleaching at %BE = 1%, T = 70 °C, t = 30 min, and (c) after bleaching at %BE = 10%, T = 110 °C, t = 30 min.

3.2. Removal of free fatty acid

As noted previously, bleaching was done after de-acidification. Neutralization by caustic soda is conventionally applied and solvent extraction by alcohol is recently considered as a promising substitute for neutralization[12,13]. Both methods were applied here to study their effects on the bleaching performance. The acid number of crude rice bran oil was 30.0 mg KOH/g. Neutralization was carried in the excess caustic soda of 1% resulting neutral oil with acid number of 2.6 mg KOH/g. The alcohol selected as solvent is methanol. Six stages of extraction reduce the acid number of oil to only 9.1 mg KOH/g.

Fig. 2 shows the spectra of oils before and after bleaching for both de-acidification methods. The absorbance peaks of bleached oil from neutralization are lower than those of oil from solvent extraction. Previously, Kim et al[6] also found that solvent extraction darkened rice bran oil. In this study, it was also found by visual that the crude rice bran oil de-acidified by neutralization was lighter than that by solvent extraction. It means that neutralization not only remove free fatty acids but also decolorized rice bran oil. It is due to the formation of soap in neutralization which could adsorb colors although the adsorption is not as good as bleaching earth. On the other hand, solvent extraction merely reduced free fatty acid content and could not reduce the color. As can be seen, the absorption spectra of crude rice bran oil is not significantly different to that after solvent extraction. Moreover, the free fatty acid content of rice bran oil could not be reduced to a value lower than 9.1 mg KOH/g. The free fatty acid left is known to add difficulty in bleaching process.

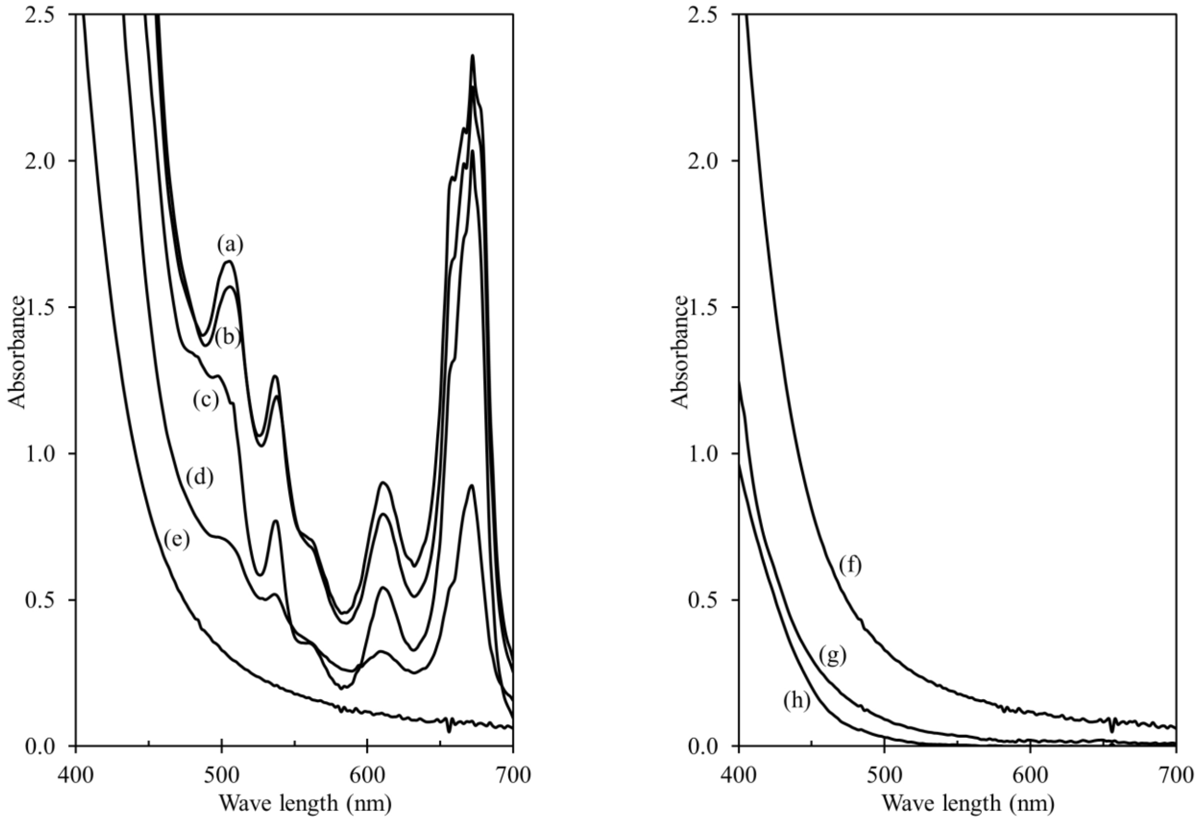

Figure 2: Spectra of rice bran oils (a) crude, (b) after extraction, (c) after neutralization, (d) after extraction and bleaching, (e) after neutralization and bleaching, (f) maximum bleached rice bran oil of this study, (g) commercial bulk refined palm oil, and (h) imported refined rice bran oil.

3.3. Analysis of factorial design

A guideline to convert absorbance spectra to bleaching performance was not found. Visual observation, however, showed that the lower the sum of absorbance peaks at the red, blue, and green color characteristics, i.e., 538, 610, and 672 nm, respectively, the lighter the oil color. The sum of the absorbance peaks at these three wave lengths was selected as a response.

Table 2: Measured responses.

Run	X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	$X_1X_2X_3$	Response			
	%BE	T	t	%BE·T	%BE·t	T·t	%BE·T·t	Y1	Y2	Y_{ave}	σ
1	-1	-1	-1	1	1	1	-1	3.033	3.243	3.13	0.1
2	-1	-1	1	1	-1	-1	1	3.153	3.126	3.14	0.0
3	-1	1	-1	-1	1	-1	1	2.348	2.231	2.29	0.0
4	-1	1	1	-1	-1	1	-1	2.533	2.762	2.64	0.1
5	1	-1	-1	-1	-1	1	1	0.616	0.666	0.20	0.0
6	1	-1	1	-1	1	-1	-1	0.664	0.549	0.25	0.0
7	1	1	-1	1	-1	-1	-1	0.528	0.140	0.12	0.2
8	1	1	1	1	1	1	1	0.389	0.468	0.40	0.0
∑ (-)	11.22	6.74	5.76	5.40	6.12	5.81	6.17				
∑ (+)	0.99	5.47	6.45	6.81	6.09	6.40	6.04				
Effect	-5.11	-0.63	0.34	0.71	-0.02	0.29	-0.06				
Coefficient	-2.56	-0.32	0.17	0.35	-0.01	0.15	-0.03				
									Average:	1.53	0.1

Table 2 also shows the effects of main factors and interaction factors including the standard deviation. In general, the relation between response and all factors is given below:

$$Y = \beta_o + \beta_1 \cdot X_1 + \beta_2 \cdot X_2 + \beta_3 \cdot X_3 + \beta_{12} \cdot X_1 \cdot X_2 + \beta_{13} \cdot X_1 \cdot X_3 + \beta_{23} \cdot X_2 \cdot X_3 + \beta_{123} \cdot X_1 \cdot X_2 \cdot X_3 \quad (1)$$

where Y is response, X_1 is bleaching earth-to-oil ratio (%BE), X_2 is temperature (T), and X_3 is time (t). Considering the effects shown in Table 2, the relation between color, bleaching earth-to-oil ratio, temperature and time can be expressed as follows:

$$Y = 1.54 - 2.56 \cdot \%BE - 0.32 \cdot T + 0.17 \cdot t + 0.35 \cdot \%BE \cdot T - 0.01 \cdot \%BE \cdot t + 0.15 \cdot T \cdot t + 0.03\% \cdot BE \cdot T \cdot t \quad (2)$$

The confidence interval for the coefficients in the above equation can be expressed by the following equation:

$$CI(\beta_i) = \beta_i \pm t_{\alpha,n-1} \cdot s/\sqrt{(n)} \quad (3)$$

where β_i is the nominal value of i^{th} coefficient, $t_{\alpha,n-1}$ is t value from the student's t distribution at significance level of α and degree of freedom n-1, n is number of data, and s is standard deviation. If the limits of confidence interval of a coefficient have different signs, the effect of corresponding factor is not significant. The standard deviation found in this study was 0.11. At the confidence level of 95% and number of data of 8, the student's t value was found to be 2.84. The confidence intervals of the coefficients can be expressed as:

$$CI(\beta i) = \beta i \pm 0,11 \quad (4)$$

Considering the confidence interval of each coefficient, it can be convinced that the two interaction factors between bleaching earth-to-oil ratio and time, between temperature and time, and the three interaction factors have no significant effects on the response. In contrast, all main factors and the interaction factor between bleaching earth-to-oil ratio and temperature have significant effect. The relation between color, bleaching earth-to-oil ratio, temperature and time, therefore, can be simplified as follows:

$$Y = 1.53 - 2.36 \cdot \%BE - 0.32 \cdot T + 0.17 \cdot t + 0.35 \cdot \%BE \cdot T \quad (5)$$

3.4 Comparison to commercial edible oil

Fig. 2 also compares the spectra of rice bran oil bleached in this study and that of commercial edible oils. Two commercial oils were included, one is a local bulk refined palm oil and one is an imported refined rice bran oil. Commercial oils are lighter than the bleached oils of this study. Even the best bleached oil is still darker than both commercial oils. Visual observation also showed that both commercial oils are lighter than the bleached oils of this study. The optimum grade of the bleaching earth used could not bleach as light as the commercial oils.

4. Conclusions

The effects of bleaching earth-to-oil ratio, bleaching temperature and bleaching time in bleaching of rice bran oil extracted from extrusion cooked rice bran have been studied using a full 2^k factorial design in which bleaching earth-to-oil ratio, bleaching temperature and bleaching time were selected as factors. It was found that all main factors have significant effects on the color of bleached oils. Among two and three interaction factors, however, only the interaction factor between bleaching earth-to-oil ratio and temperature has significant effect. The best bleached oil was obtained at bleaching earth-to-oil ratio of 10%, bleaching temperature of 110 ^oC and bleaching time 30 minutes. However, the bleached oil was not as light as the commercial edible oils. It was also found that rice bran oil pretreated by solvent extraction was more difficult to bleach than that pretreated by neutralization

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