Proceeding

ISBN 978-979-18845-2-5

THE 3rd SRIWIJAYA INTERNATIONAL SEMINAR ON ENERGY SCIENCE AND TECHNOLOGY 2010 (SISEST - 2010)

Theme :
"New and Renewable Energy Development for Solving Energy Crisis"

PALEMBANG, 3 - 4 NOVEMBER 2010

SRIWIJAYA UNIVERSITY

SOUTH SUMATERA - INDONESIA

Organized by:

The National Strategic Prime Research (New & Reneweble Energy Development) Rusnas PEBT Sriwijaya University

Sponsored by:

ISBN :978 – 979 18845 – 2 – 5

PROCEEDING
THE 3rd SRIWIJAYA INTERNATIONAL SEMINAR ON ENERGY SCIENCE AND TECHNOLOGY 2010 (SISEST 2010)

3-4 NOVEMBER 2010
SRIWIJAYA UNIVERSITY
PALEMBANG, SOUTH SUMATERA
INDONESIA

Organized by :

Lembaga Pengelola Riset Unggulan Strategis Nasional (RUSNAS) Pengembangan Energi Baru dan Terbarukan Universitas Sriwijaya (The National Strategic Excellence Research New and Renewable Energy Development Sriwijaya University)

THE 3rd SRIWIJAYA INTERNATIONAL SEMINAR ON ENERGY SCIENCE AND TECHNOLOGY (SISEST 2010)

Palembang, 3 – 4 November 2010

24. Prof. Dr. Ir. Kaprawi, DEA
25. Ir. Hawaria, M.Si.
26. Ir. Darmawan, M.Sc.
27. Hermansyah, S.Si, M.Si, Ph. D
28. Lia Cundari, ST, MT
29. Ir. Sariman, MS
30. Dr. Oo Abdul Rosyid
31. Ir. Slamet Rahardjo, M.Sc
32. Dr. Ir. Tri Kurnia Dewi, M.Sc
33. Dr. Dedy Setiabudidaya, M.Sc
34. Al Antoni Akhmad, S.T. M.T
35. Amir Arifin, S.T. M.Eng
36. Ir. Dhani Avianto
37. Astri Pertiwi, ST
38. Imron Masfuri, ST
39. Asyeni Miftahul jannah, ST
40. Hendra
41. Mariamah
42. Frinaldo Sidebang
43. Bangun Sugito
44. Ir. Nurdi, MT
45. Ir. Rr. Harminuke Eko Handayani, MT
46. Tuti Indah Sari, ST., MT
47. Barlin Oemar, ST., M.Eng
48. Wulan Erna Komariah, ST
49. Ir. Abdullah Saleh, MS, MSc
50. Ir. Rosdiana Moeksin
51. Irmawan, ST, MT
52. Ir. Sutopo
53. Pratiwi, ST
54. Ir. A.R. Fachri, M. Eng.
55. Bakti Yudo Suprapto, ST, MT
56. Drs. Dedi Rohendi, M. Si
57. Ir. Pramusito
58. Ir. Djulil Amri, MT
59. Ir. Mulkan Hambali
60. Bochori, ST.
61. Anisa, A. Md.
62. Dedi
63. Ari Sartika Sari , A.Md. AK
64. Suyatno
65. Nina Haryani, ST,MT
66. Sukirman
67. Deni Chairuddin, ST
68. Destri Yunita, S.Si
69. Renalsi Melaty, S, ST
70. Fitria Heny Widyastuti, AMd
71. Ir. Faisol Asip
72. Destri Yunita, S.Si
73. Eddy Kantosa

CONTENTS

Evaluation of Color Stability in Palm Oil Catalytic Hydrogenation

Susila Arita[1], Leily Nurul K[1], Fitri Hadiah[1], Baikuni Eris Prianda[2]
[1] *Jurusan Teknik Kimia Fakultas Teknik Universitas Sriwijaya*
Peneliti RUSNAS Pengembangan Energi Baru Terbarukan UNSRI
Jl. Raya Prabumulih KM 32 Inderalaya Sumsel

[2] *PT. Sumiasih Oleochemicals,*
Jl. Raya Bekasi Jatimulya Bekasi Timur Jawa Barat

Abstract

Applications of fatty oils (triglycerides) in food industry and wax (candles) based on palm oil is dependent on the quality of color and color stability of the product (heat stability). Commercially, in addition to the desired color is more pale palm oil, palm oil quality parameters that are not less important is the stability of color. Heat Stability is an indication of the stability of the color of palm fatty oil after heating. The color change is likely to occur due to oxidation after the stage of the process such as hydrogenation, as it passes through stages of storage, transportation or other factors.

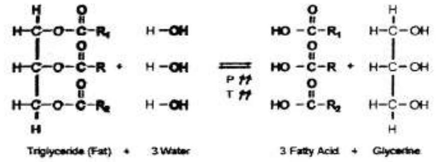
Hydrogenation process aims to reduce the number of iodine (IV) which is an indication of a double bond or the saturation level of triglycerides in palm oil compounds. Hydrogenation is the process of termination or replacement carbon double bond group (unsaturated compounds) into a single bond carbon clusters (compound saturated) fat oil by reacting with hydrogen. The process of hydrogenation which is maintained in this experimental study took place in an autoclave (reactor), where the vacuum pressure and temperature of 150-200 °C, This reaction is using Nickel as a catalyst. The oil color and color stability (heat stability) measured by a calorimeter or Lovibond Cell, which reads color in units of red and yellow (R / Y). Hydrogenation of fatty oils in this study provide the initial color (R / Y = 1.5 / 9.6), from the initial conditions (R / Y = 1.92 / 1.19). Cooling process is added at the end of phase hydrogenation of palm oil is able to provide the same quality oil colors, but has a value of better color stability (R / Y = 3.8 / 25.7), compared to the hydrogenation process without cooling (R / Y = 4.2 / 29.1). In order to meet the specification of heat stability and for export commodities as well as storage for a long time, the process should be continued with the holding stage filtration using adsorbents (activated carbon and citric acid). The test of palm oil's stability after this stage shows that the heat stability of the adsorbent filter with citric acid showed the better stability of oil color.

Key words : ***heat stability, hidrogenasi katalitik, initial color, iodine value, Lovibond Cell***

1. INTRODUCTION

Palm oil (Crude Palm Olein and RBD Palm Olein), like most other vegetable oils are compounds that are insoluble in water, whereas the main constituent parts are non-triglycerides and triglycerides.

Triglycerides on palm oil as with fats and other oils, consists of molecules which is a triglyceride ester of glycerol with three molecules of fatty acids or fatty acid by the reaction as follows:



Fatty acids are hydrocarbon chains, which each carbon atom binds one or two hydrogen atoms, except the terminal carbon atom binds three atoms of hydrogen, carbon atoms while the other terminal carboxyl group binding. Fatty acids contained in the hydrocarbon chain

is called the double bond unsaturated fatty acids, and if there is no double bonds in their hydrocarbon chain is called saturated fatty acids.

The more saturated fatty acid molecule in a triglyceride molecule, the higher the freezing point or melting point of the oil. So at room temperature are usually located on the solid phase. Conversely the unsaturated fatty acids in the triglyceride molecule, the lower the melting point of oil, so at room temperature is in the liquid phase. Palm Coconut oil is semi-solid fat that has a fixed composition.

Tabel 1. Palm Oil Compositions

No	Component	Quantity
1	Density, g/ml 50°C	0.8896 – 0.8910
2	Refraction Indeks, n_D 50	1.4544 – 1.4550
3	Saponification Value, mgKOH/g minyak	190 – 202
4	Fatty Acid Composition, (wt % metil ester)	
	C12:0	0.1 – 0.4
	C14:0	1.0 – 1.4
	C16:0	40.9 – 47.5
	C16:1	0 – 0.6
	C18:0	3.8 – 4.8
	C18:1	36.4 – 41.2
	C18:2	9.2 – 11.6
	C18:3	0 – 0.5
	C20:0	0 – 0.8
5	Iodine Value(Wijs)	50.1 – 54.9
6	Melting Point, °C	33.0 – 39.0
7	Total Carotenoid (βcarotene), mg/kg	500 – 1000

[*Source*: World oil Seeds]

2. COLORS IN OIL

Colors in the palm oil is one factor that gets special attention in order to meet commercial specification of products.

Colour stability is one of the criteria in evaluating the quality of oil. It is sometimes complained that palm derived soaps tend to be slightly off-color during storage. Some studies on the factors affecting the color stability will be described here. Some of the effects are temperature, and presence of unsaturated compounds and minor components.

According to Ketaren. S, dye in palm oil consists of two groups, namely:

- natural dyes.
- the dye from natural degradation

Natural Dyes

Natural dyes means color that has a pigment found naturally in palm oil, and their extraction with the oil extraction process. These dyes, include α-carotene, β-carotene, xanthopil, kloropil and anthocyanins. These substances cause the oil color is yellow, brownish yellow, greenish and reddish - reddish.

Yellow pigment carotene is caused by soluble in oil. Carotene is an unsaturated hydrocarbon compound, and if hydrogenated oil, so carotene also follows hydrogenated so that the yellow color intensity decreases. Caretonoid is not stable in acid (5.9), and high temperature and if the oil flowing hot steam, then the yellow color will disappear, and karetonoid also be asseptor protons.

Color Due to Chemical Oxidation and Degradation of components contained in oil.

Dark Color

Dark color is caused by oxidation to the tocopherol (vitamin E). If oil comes from green plants, then the substance chlorophyll, the green part with the oil extracted, and the chlorophyll is difficult to separate from oil. This dark color may occur during processing and storage, due to several factors:

1. Heating temperature is too high at the time of pressing by means of hydraulic or expeller, thus partially oxidized oil.

Besides, the oil contained in an ingredient in hot conditions will extract the dyes contained in the material.

2. Pressed materials containing oil with a high temperature will produce oil with a darker color.
3. Oil extraction using organic solvents, such as a mixture of petroleum solvents - benzene will produce oil with redder colors than the oil extracted with solvent trichlor ethylene, benzol and hexane.
4. Metals such as Fe, Cu and Mn would give an undesirable color in oil.
5. Oxidation of the fractions do not saponificated in oil, especially oxidation and chroman 5.6 tokopherol qoinon produce brownish color.

Brown

Brown pigment is usually only found in oils derived from material that has been rotten or bruised. This can happen because the carbohydrate molecules react with reducing agent such as aldehyde groups and amine groups of protein molecules and that caused by the activity of enzymes such as phenol oxidase, poliphenol oxidase etc.

Yellow Color

The yellow color is caused by the presence of *carotenoids* in addition to the natural dyes can also occur due to absorption processs in unsaturated oils. This color arises during storage and the intensity of color varies from reddish yellow to reddish purple.

Generally color arising from the degradation of natural dyes is very hard to remove, the emergence of these colors can identified, where there has been damage to the oil (6.9). So to prevent this, the process is generally added anti-oxidant substances, while palm oil contains a substance that itself has anti-oxidant, although in small amounts.

Color Measurement

For the purposes of industrial and general use, the measurements performed by means of Lovibond color - Tinto meters. Red and yellow color of palm oil is adjusted with glasses of red and yellow Lovibond instrument, with 5.25 inch cell. Glasses of red and yellow standardized with "The National Bureau of Standards in terms of color scale Priest Gibson" N ".

Tabel 2.
Crude Palm Olein Specifications

PARAMETER	UNITS	STANDARD
- Free Fatty Acid	%	5,0 max
- Unsaponifiable Matter	%	0,5 max
- moisture+Impurities	%	0,25 max
- Peroxide Value	meg/kg	15 max
- Colour Lovibond 51/4" cell	Red	6,0 max
	Yellow	60,0 max
- Melting Pint	oC	24 max
- Composition:		
* Caproic acid (C6)	%	Trace
* Caprilic acid (C8)	%	Trace
* Capric acid (C10)	%	Trace
* Lauric acid (C12)	%	1,0 max
* Myrictic acid (C14)	%	2,0 max
* Palmitic acid (C16)	%	38 – 45
* Stearic acid (C18)	%	3 – 6
* Oleic acid (C18:1)	%	38 – 45
* Linoleic acid (C18:2)	%	9 – 15
* Arachidic acid (C20)	%	1,0 max

Source : PORAM

Progress in the palm oil industry to encourage industry-tintometer Lovibond tool-making, so that in time they arise manufacture glass of red and yellow-galas from Lovibond tool that deviates from the former color gradually. For curb this then the Americans Oil Chemist's Society (AOCS), adjust the color of the glass-tintometer Lovibond color is measured by spectrophotometer.

Table 2 and Table 3, indicates that the Initial Colour-color analysis on Crude Palm Olein RBD Palm Olein after a decrease of R / Y 6.0 / 60 max to R / Y 3.0 / 30.0 max, this shows that for applications using the product of fat / palm oil quality from the color-Initial colour is very tight.

Tabel 3.
RBD Palm Olein Specifications

PARAMETER	UNITS	STANDARD
- Free Fatty Acid	%	0,5 max
- Unsaponifiable Matter	%	0,05 max
- Moisture+Impurities	%	0,1 max
- Peroxide Value	meg/kg	10 max
- Colour Lovibond 51/4" cell	Red	3,0 max
	Yellow	30,0 max
- Melting Pint	oC	24 max
- Composition:		
* Caproic acid (C6)	%	Trace
* Caprilic acid (C8)	%	Trace
* Capric acid (C10)	%	Trace
* Lauric acid (C12)	%	1,0 max
* Myrictic acid (C14)	%	2,0 max
* Palmitic acid (C16)	%	38 – 45
* Stearic acid (C18)	%	3 – 6
* Oleic acid (C18:1)	%	38 – 45
* Linoleic acid (C18:2)	%	9 – 15
* Arachidic acid (C20)	%	1,0 max

Source : PORAM

Damage Colors In Oil

Generally, oxidative damage occurs in unsaturated fatty acids, but when oil is heated at 100 ° C or more, saturated fatty acids can be oxidized. Oxidation on heating to a temperature of 200 °C, It damages easier on oil with a high degree unsatuated, while hydrolysis occur in oil with long chain saturated fatty acids.

3. HIDROGENATION OF OIL

The process of hydrogenation is the process of replacing or eliminating carbon double bond group (unsaturated compounds) into a single bond carbon clusters (saturated compounds) by reacting or substitution with hydrogen. Hydrogenation process that occurs produces more amount of saturated fat.

This hydrogenation process using a device called an autoclave, where the tool is operating at high pressures (17-21 bar) and high temperatures (150-165 oC). To accelerate the reaction, nickel catalysts are used. This process is executed in batch system.

The process of hydrogenation of oils and fats will change the physical-chemical properties of oils and fats such as isomerization of the geometry, position isomerization, conjugation and hydrogenation. Hydrogenation process illustrated as follows:

- Hydrogenation of double bonds in unsaturated fatty acid chains
- Isomerization of geometry, namely a change in the cis isomer into trans unsaturated fatty acid chains
- Conjugation, the formation of the unsaturated bond conjugated system is more than one, is a special form of position isomerization.
- Positional isomerization of the change of unsaturated bonds in unsaturated fatty acids.

The process of hydrogenation is a process of modifications that is necessary to increase the added value of oil. In terms of quality, the hydrogenation process would change melting point and solid fat content is higher, while the number of iodine (Iodine Value, IV) is lower. The process of hydrogenation of oils and fats can be done partially and totally. Partial hydrogenation is a process that changes the most unsaturated fatty acids, and potentially produces trans fatty acids. While the total hydrogenation is a process that transforms all unsaturated fatty acids into saturated fatty acids (Basiron, 2000).

In the process of hydrogenation or saturation reactions occur theoretically be explained as a reaction to convert the double chain hydrocarbon compounds into a single chain. Some are calling this reaction as "hardening" or compaction due to the product of this process has a higher melting point. This reaction is run in exothermic that the rising temperatures will affect the product.

The reaction is run in exothermic can be used to raise the temperature of the reactants in this case an unsaturated oil to the desired reaction temperature. Theoretically, this reaction produces energy of 7.1 J or 1.7 cal per gram of C_{18} is reduced as much as one number IV or by 30 Kcal per mole of product per IV or 1400 Kcal per ton per unit Iodine Value (IV) which can raise the temperature of the product by 1.58 °C.

This process runs partially where polyunsaturated acids to monounsaturated acids changed first and then become saturated acids. This is because the polyunsaturated acid is more reactive than monounsaturated acid. Nevertheless, such as linoleic acid, if the product is not hydrogenated oleic acid but rather in the form of trans-isomers or double bonds (more linear structure) in thermodynamics is more stable than-cis-double bonds (structure bent). Trans-isomers form more like saturated fatty acids than unsaturated fatty acids.

There are several factors or variables that influence the reaction of the hydrogenation reaction:

1. Reaction temperature.

Theoretically, the optimum reaction temperature for hydrogenation reactions fat or oil is at temperature range 150-200 °C. Nickel catalyst used is not active, if the reaction occurs in temperatures less than 150 °C. On the other hand, it will causes an oil degradation if the reaction is run over a temperature of 210, these both conditions make the catalyst becomes inactive. So the reaction has been extremely slow.

2. Pressure reaction

Theoretically, the effective pressure is in range of 2.08 to 3.47 MPa. Where is the pressure below 2.08 MPa would require extra longer time to achieve the desired level of reaction. So if the pressure is set above 3.47 Mpa, it would only have a very small effect towards the reaction.

3. Agitation

Good agitation or well stirring will increase the reaction rate. This is based on the fact that the agitation will produce a perfect dispersion of hydrogen gas bubble in the fluid that would produce the optimum diffusion surface area.

Optimum level of agitation depending on the shape of the type of reactor used. Form in the autoclave affect the pattern of fluid flow in these reactors. A good flow pattern of contact will ensure the widest diffusion of reactants and catalysts.

In term of reaction, the agitation has several functions as:

- Dispersion of catalyst in a reactant
- Keeping the catalyst remains in suspension
- Maintain and control the temperature of the reactants.

4. Catalyst.

The most widely used catalyst in the hydrogenation process is Nickel. Nickel catalysts generally have high activity. In general, the addition of catalyst will accelerate the reaction in accordance with its function. But also keep in mind that the addition of a radical catalyst to cause dehydrogenation reaction.

The addition of the catalyst carried out after the reactor temperature reached in desired temperature.

4. SOME IMPORTANT PARAMETERS IN OIL

a. Iodine Values (IV)

Iodine value is a measure of unsaturated oil expressed as the number of grams of iodine bound per 100 grams of oils or fats. The lower the iodine value, the more saturated oil and have a higher degree of stability against oxidation which can damage the oil. This is because the existing double bond on carbon chain carotene will be charged atom H. Hydrogenated carotene color will grow pale.

b. Color

Determination of the color of the unit is Red (R) / Yellow (Y), APhA or Hazen. Here the unit of measurement used colors are Red (R) / Yellow (Y).

In the hydrogenation process, which takes place at high temperature conditions, the dye in the oil will be damaged, so that the resulting color will be more pale. Hydrogenation process is conducted in vacuum conditions.

c. Heat Stability

Heat stability is a measure of the level of color stability of oil after heated at a certain temperature and time of done in the oven.

Although oil has undergone a process of heating at high temperature and vacuum and has changed from unsaturated compounds into saturated compounds, it does not mean that automativally has a betterthe value of the Heat Stability.

Heat stability is important to considered, in respect of the meet the specification of palm oil products, commercially.

5. METHODOLOGY AND ANALYSYS OF RAW MATERIALS

Table 4. Oil analysis of raw materials

No	IV	Color	
		Red (R)	Yellow (Y)
01	35.02	1.9	19.0
02	35.10	1.8	18.7
03	34.38	1.9	20.1
04	34.85	2.0	19.0
05	34.93	2.0	18.7

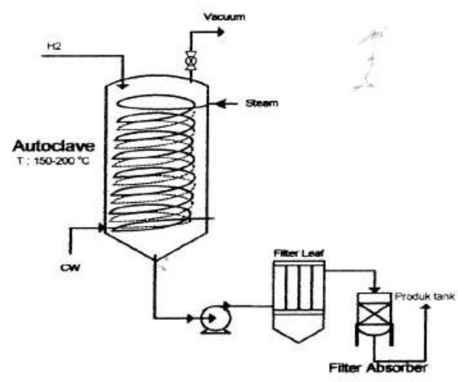


Figure 1. Set of Equipments

6. RESULT AND DISCUSSIONS

a. Color Analysis and Heat Stability of Hydrogentaion without cooling

No	IV	Initial Color		HST	
		Red (R)	Yellow (Y)	Red (R)	Yellow (Y)

01	0,9	1,4	10,3	4,3	30,0
02	0,8	1,8	8,1	4,1	27,9
03	0,8	1,5	9,5	4,4	29,5
04	0,9	1,5	9,5	3,9	29,1
05	0,9	1,6	10,1	4,2	27,3

b. Color Analysis and Heat Stability of Hydrogentaion wit cooling using water

No	IV	Initial Color		HST	
		Red (R)	Yellow (Y)	Red (R)	Yellow (Y)
01	0,9	1,5	9,7	3,8	25,3
02	0,8	1,7	10,1	3,7	26,1
03	0,8	1,4	8,9	3,9	25,7
04	0,9	1,6	9,3	3,8	25,5
05	0,9	1,4	9,5	3,7	26,4

From the experiments a, b in the process of hydrogenation with the difference of the cooling process after the hydrogenation reaction showed that although from the color, it is found that there is no difference Initial Colour (Red / Yellow = 1.5 / 9.6) but in terms of product stability there are differences quite high (R / Y = 4.2 / 29.1 decreased to R / Y = 3.8 / 25.7).

It proves that the high temperature oil can still be oxidized in spite of saturated compounds (lower IV).

c. **Color Analysis and HST after hydrogenation with Cooling Water and filtration by using absorbent Active Carbon**

No	IV	Color		HST	
		Red (R)	Yellow (Y)	Red (R)	Yellow (Y)
01	0,9	1,5	10,0	2,3	18,0
02	0,8	1,6	9,1	2,4	18,3
03	0,8	1,4	9,3	2,3	19,2
04	0,9	1,6	8,7	2,5	18,5
05	0,9	1,4	9,3	2,4	19,0

From the experiments c, d in the process of hydrogenation in the presence of the cooling process and the different uses of absorbent, it showed that there is no difference Initial Colour (Red / Yellow = 1.5 / 9.6) but in terms of product stability there are differences quite high (R / Y = 3.7 / 27.8 decreased to R / Y = 2.4 / 18.6).

Variable quantity and duration of contacts citric acid or other absorbent on the hydrogenation product can be performed on the following research, so the results can be obtained HST R / Y is minimal so the quality of products in applications use fat / oil can be improved.

7. CONCLUSION

- The process of hydrogenation (vacuum conditions and high temperatures) to create color-Colour Initial products to be better than the color of raw material.

- Compounds are more saturated, IV <1 remains will be oxidized by air if stored at temperatures above 100 °C

- The use of citric acid (as cheleating agent for the hydrogenation product fat / oil to maintain color stability.

REFERENCES

Geoghegan, 1965, " Modified Color Stability Test for Fatty Acids", Book of Color Stability Test, JAOCS

Hasibuan, Hasrul Abdi., " Perolehan kembali Nikel dari Katalis Nikel terpakai Pasca Proses Hidrogenasi Minyak Sawit dengan Proses Pendian Asam Sulfat", Tesis, Universitas Sumatera Utaa, 2009

Ketaren, S. , 1986. Pengantar teknologi minyak dan lemak pangan. Jakarta : Universitas Indonesia, Jakarta: 1986, { 17 - 260).

Mark, ER, Jhon; J Mc. Ketto [and] Othmer, D. F., 1967. Bentonites in Encyclopedia of Chemical Technology ", 2nd ed, (7), 1967, (339 -358).

Pitoyo, 1988. The possibility of extraction of beta-carotene bleaching tanab waste palm oil refining process. Yogyakarta: Gadjah Mada University.

Rudi Hartono, Agus Rohmat, 2007, "Use of Citric Acid in Improving Quality of Used Cooking Oil", Proceedings of the Seminar on Development of Chemical Technology for Processing of Natural Resources of Indonesia, Chemical Engineering University of Sultan Ageng Tirtayasa, Cilegon.

Roseli Ap. Ferrari*; Vanessa da Silva Oliveira; Ardalla Scabio, " Oxidative Stability of Biodiesel From Soybean Oil Fatty Acid Ethyl Esters", *UEPG - Depto. Engenharia de Alimentos, , PR - Brasil.*