

## Research Article

### Improving the Quality of Fish Oil from Fat Viscera of Striped Catfish (*Pangasiushypophthalmus*) Processing By-Product with Neutralization and Bleaching

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**Abstract:** This study aimed to obtain refined catfish oil by purification with neutralization and bleaching. NaOH alkaline purification treatment used 12, 14 and 16<sup>o</sup>Be. The best semi-refined oil then purified using adsorbents magnesol XL in various concentrations as many as 0, 1, 3 and 5% then stirred using a magnetic stirrer for 10, 20 and 30 min. The oil analyzed by several parameters such as yield, free fatty acids, acid value, peroxide value, p-anisidine value, total oxidation value and clarity test. The results showed that the best semi-refined oil was conducted by treatment 16<sup>o</sup>Be NaOH and refined oil was conducted by combination treatment 1% Magnesol XL and 10 minutes stirring. The whole parameters result in this combination were under International Fish Oil Standard (IFOS).

**Keywords:** Bleaching, neutralization, purification, striped catfish oil

## INTRODUCTION

Catfish is one of the main aquaculture commodities in Indonesia that the production and utilization continuously increase. Catfish production increases around 70% annually. Catfish production in Indonesia reached 31,490 tons in 2006 and increased significantly to 651,000 tons in 2012. The production of catfish in 2013 amounted to 1.1 million tons and 1.8 million tons in 2014 (KKP, 2015). As a result of a high demand for catfish, the government developed catfish aquaculture centers which is spread in 10 provinces. Some types of catfish that are developed in Indonesia are Jambal Catfish (*Pangasiusdjambal*), Striped Catfish (*Pangasiushypophthalmus*) and Pasupati Catfish (*Pangasius* sp.) (Roesfitawati, 2013). Striped catfish (*Pangasiushypophthalmus*) is the most widely cultivated in Indonesia because they have advantages over other types of catfish, it has high fecundity and good resistance to poor water conditions (Ariyanto and Utami, 2006). In addition to having good taste, catfish flesh has high nutrient content. Catfish contains 68.6% protein, 5.8% fat, 3.5% ash and water 59.3% (Kordi, 2010).

Catfish is commonly processed into fillets, smoked fish and fish meal (Roesfitawati, 2013). Fillet catfish processing produced 65% of by-product in form of head, viscera, bones and fat (Dadang *et al.*, 2009). The by-

products is commonly utilized to produce fish meal and the oil is taken as it has high content of fat (Tobuku, 2008). Research on by-product of catfish potential as a source of fish oil has been done. Thammapat *et al.* (2010) stated that the biggest lipid content of catfish was found in the viscera as many as 93.32%. All this time, the catfish oil are commonly used for non-food, for example in the manufacture of biodiesel (Widianto and Utomo, 2010), whereas catfish oil is potential as a source of omega-3 (EPA and DHA) (Luc *et al.*, 2013). Panagan *et al.* (2012) stated that catfish had EPA, DHA and ARA content as many as 0.21-2.48%, 0.95-9.96% and 0.394-1.105%, respectively which can be utilized for food and health. Omega-3 is Polyunsaturated Fatty Acids (PUFA) which is useful to maintain a healthy heart and vascular system, in the long term will reduce Low Density Lipoprotein (LDL) cholesterol and increase High Density Lipoprotein (HDL) cholesterol. It is also important for infant brain and eyes development, improve immune function, anticoagulants, resolve peripheral arterial disease and Alzheimer's (Swanson *et al.*, 2012).

The production of fish oil include extraction and purification processes (Estiasih, 2009). Once extracted, fish oil is purified to the standards of IFOS (2011). Purification aims to eliminate non-lipid impurities such as fat-soluble flavor, pigments, sugars, amino acids, short-chain peptides, inorganic salts and urea (Shahidi

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and Wanasundara, 2008). Fish oil purification is done chemically using alkaline or acid solution and physically by using adsorbents or centrifugation treatment (Suseno and Saraswati, 2015). Estiasih and Ahmadi (2012), Feryana *et al.* (2014) and Fuadi (2015) used neutralization (alkali refining) method for purifying fish oil. The amount of alkali required is calculated based on the value of free fatty acids from fish oil to be purified (Sathivel *et al.*, 2003). Purification of salmon oil with an adsorbent chitosan, neutralization and both combination had been done by Huang and Sathivel (2010), while Ortiz *et al.* (2011) used solid adsorbent. Suseno *et al.* (2011) conducted a sardine oil purification using magnesol XL adsorbents; Suseno *et al.* (2012) used magnesol XL adsorbents to improve the color quality of sardine oil in the refining process. This study aimed to obtain refined catfish oil by oil refining with alkali NaOH and adsorption using magnesol XL adsorbents.

## MATERIALS AND METHODS

The main material of this research is fat viscera by-product from Striped catfish (*Pangasius hypophthalmus*) processing. Chemical used were aquadest, sodium hydroxide (NaOH, Merck), potassium hydroxide (KOH, Merck), chloroform (CHCl<sub>3</sub>, Merck), Natrium thiosulphate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, Merck), Iso-octane (Merck), n-hexane (Merck), acetic acid (CH<sub>3</sub>COOH, Merck), p-Anisidin solution (Sigma Aldrich), phenolphthalein indicators, starch solution, ethanol 95% and Magnesol XL (Dallas) as adsorbent.

Tools used were digital scales (Quattro), stirrer, centrifuge, beaker glass (Iwaki Pyrex), burret (Iwaki Pyrex), Erlenmeyer (Iwaki Pyrex), pipette volumetric (Iwaki Pyrex), spectrophotometer UV-VIS (Agilent 8453).

The purification process was conducted in two steps, neutralization and bleaching. NaOH alkaline purification treatment used 12°, 14° and 16° Baume (°Be). Crude oil weighed and heated to 60°C, then added a number of alkaline solution which was heated as well as 60°C. The mixture was stirred at 60°C, 800 rpm for 10 min. Then added hot distilled water of 70°C as much as 5% of the weight of oil, let it stand 15 min to form three layers: water, oil and soapstock. The semi-refined oil was separated from water and soapstock and the yield was calculated. Furthermore, the oil analyzed by several parameters such as free fatty acids and acid value (AOAC, 2005), peroxide value (AOAC, 2005), p-anisidine value (Watson, 1994), total oxidation (Perrin, 1996) and clarity test (AOAC, 1995). The best semi-refined oil then purified using adsorbents magnesol XL in various concentrations as many as 0, 1, 3 and 5% then stirred using a magnetic stirrer for 10, 20 and 30 min and then centrifuged at 10,000 rpm for 10 min at a temperature of 10°C. Refined oil separated from the precipitation and analyzed as well as semi-refined oil parameters.

## RESULTS AND DISCUSSION

**Neutralization:** Neutralization is a process designed to remove free fatty acids and impurities from crude oil using caustic soda and produce semi-refined fish oil (Huang and Sathivel, 2010). The crude catfish oil was neutralized by caustic soda NaOH at 12°Be, 14°Be and 16°Be. The quality of oil was analyzed by several parameters such as free fatty acid, acid value, peroxide value, p-anisidine value, total oxidation value and clarity that can be seen in Fig. 1.

The decrease average of NaOH concentration differences was 3.76% and showed no significant differences ( $p > 0.05$ ). Caustic soda solution mixed with oil in neutralization will form soap (saponification). The soap is dispersed in the liquid phase together with phospholipids, pigments and other components thus lowering the yield of fish oil during oil separation with soapstock (Kirk and Othmer, 2005).

In line with free fatty acid content and acid value, different concentrations of NaOH did not give significant differences ( $p > 0.05$ ) but the addition of NaOH in could oil could reduce the levels of free fatty acids and acid value compared with untreated ( $p \leq 0.05$ ), Alkali refining process can reduce the levels of free fatty acids and acid value as the free fatty acids saponified by NaOH and precipitated soap stock (Estiasih and Ahmadi, 2012).

The effect of different concentrations of NaOH showed no significant differences in peroxide ( $p > 0.05$ ) but it appeared that the neutralization process could reduce peroxide. The reduction of peroxide value in the neutralization caused in free fatty acids contained peroxide-bound fraction, thus when the free fatty acid precipitated through the saponification process, some peroxide precipitated as well (Aisyah *et al.*, 2010). This non significant results was caused by the main purpose of the neutralization process is to reduce the levels of free fatty acids (Huang and Sathivel, 2010). Similarly, the value of secondary oxidation parameters p-anisidine had no significant differences by the different concentrations of NaOH ( $p > 0.05$ ).

The difference of NaOH concentration 12 and 14° Bedid not give significant differences to the total oxidation value (totox) ( $p > 0.05$ ) to untreated oil, totox is a determinant of whole oil oxidation parameters (Feryana *et al.*, 2014). Data showed that the concentration of NaOH 16°Be obtained the lowest value and had significantly different value from other concentrations of NaOH ( $p \leq 0.05$ ). Unlike the physical parameters clarity, concentration differences did not give significant differences on the value of clarity ( $p > 0.05$ ). Nevertheless, the neutralization process could increase the clarity level of crude oil, this is due to the impurities precipitation in neutralization process that brighten semi-refined oil (Sathivel and Prinyawiwatkul, 2004). Based on the seven parameters

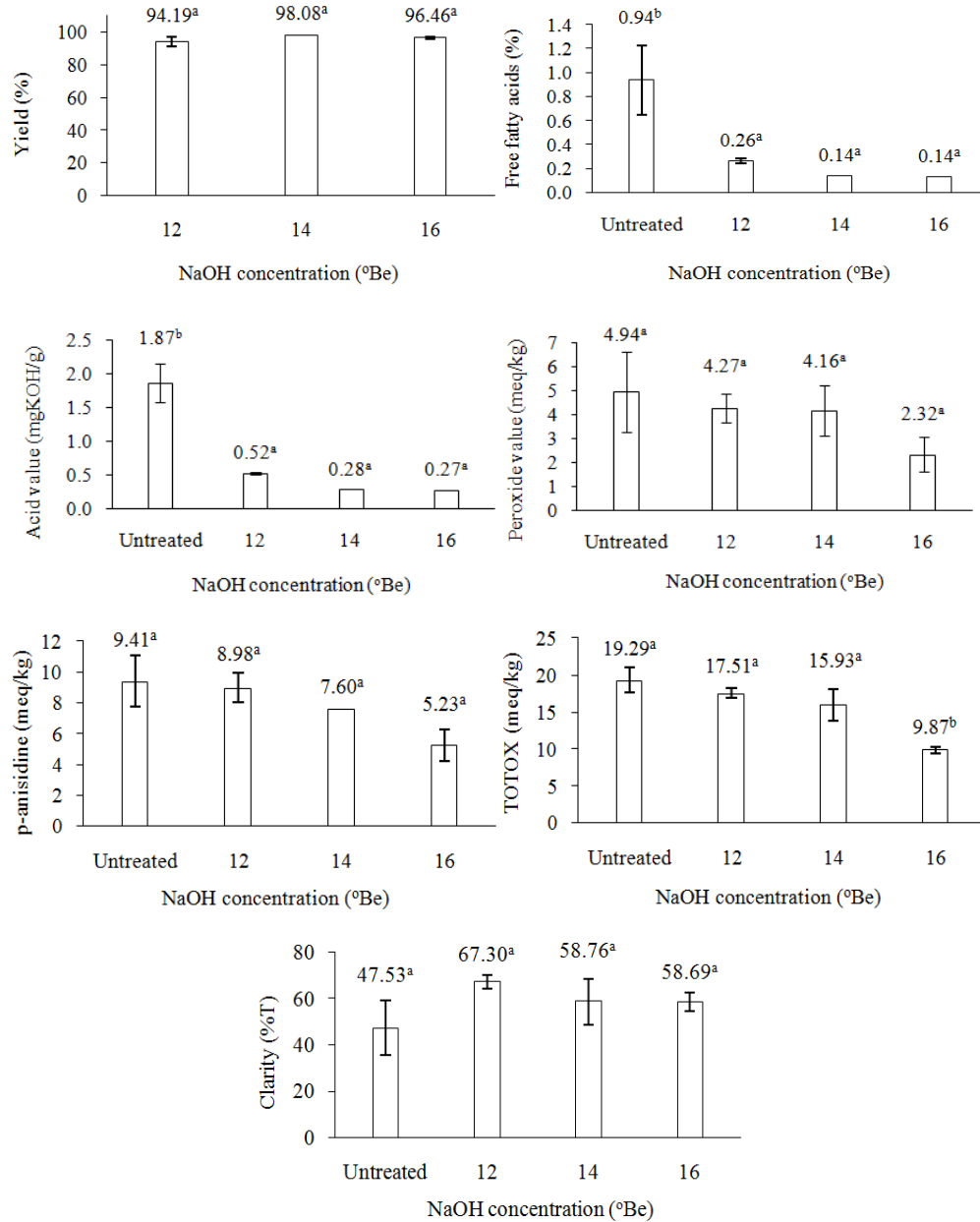


Fig. 1: Quality parameters of semi-refined fish oil

above, particularly at the primary oxidation characteristic, it can be concluded that the best concentration obtained from 16°Be NaOH concentration, the concentration was continued to a bleaching process.

**Bleaching:** Semi-refined oils which had been neutralized using NaOH concentration 16°Be then bleached by combination treatment of stirrer time and concentration of adsorbent. As semi-refined oil, the quality of refined oil analyzed by yield, levels of free fatty acids, acid value, peroxide value, p-anisidine value, total oxidation value and clarity that can be seen in Fig. 2.

Different combinations of time and adsorbent concentration did not give effect to the yield ( $p > 0.05$ ). Disaggregation by descriptive, the higher the temperature and adsorbent were added, the yield of fish oil was lower. Suseno *et al.* (2014) stated that the higher the adsorbent concentration was given, the more impurities were absorbed, while Rahayu and Purnavita (2014) stated that the longer the heating time, the kinetic energy of the molecules to collision would be greater so that the ability of the adsorbent to adsorb was higher.

Different combinations of time and concentration of adsorbent did not give effect to the free fatty acid content and acid value ( $p > 0.05$ ). Free fatty acid and

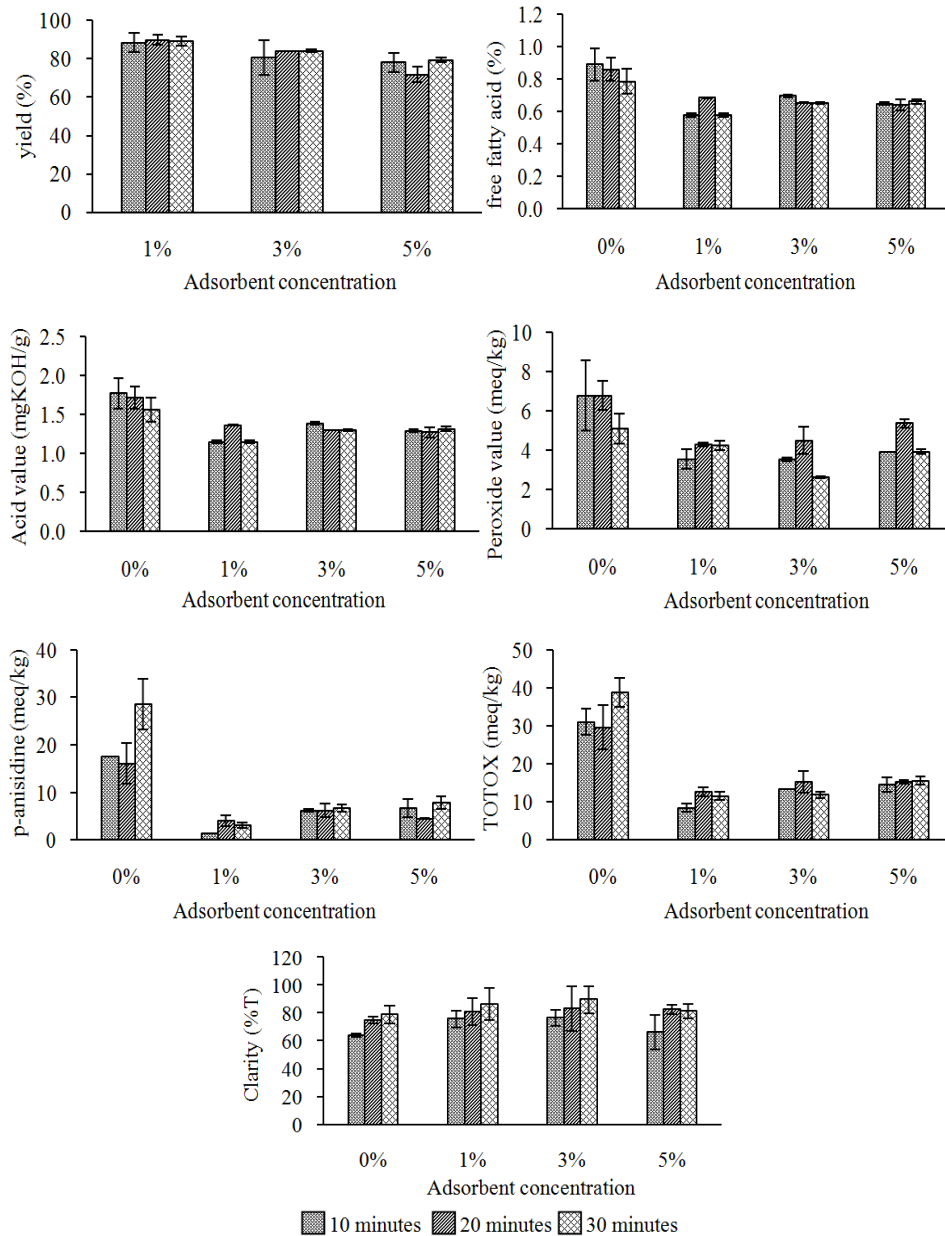


Fig. 2: Quality parameters of refined fish oil

acid value tends to have a higher value than the semi-refined oil. This is presumably because of formation of free fatty acids is due to the hydrolysis and oxidation of oil the caused by the presence of free radicals and decomposition of the double bond during heating (Paul and Mittal, 1997). The longer the time stirrer the higher the temperature received by refined oil thereby led the damage of oil in which free fatty acids were reformed and the value tend to increase by increasing heating time (Rahayu and Purnavita, 2014). However, the value of the fatty acid and the acid value obtained were below standard IFOS (2011) which should be  $\leq 1.13\%$  and  $\leq 2.25$  mg KOH/g, respectively.

Different combinations of time and concentration of adsorbent did not give effect to the peroxide value ( $p > 0.05$ ). Peroxide value of refined oil was higher than semi-refined oil. According to Suseno *et al.* (2014) a high concentration of adsorbent allowed the absorption of impurities occurred maximally, but it caused the natural antioxidants contained in pigments absorbed thus that it could affect the stability of oxidation of fish oil. According Rahayu and Purnavita (2014) oil processing at high temperatures with a long period of heating could led the reformation of peroxide compound, the value will increase with the increasing heating time.

Similarly, with the peroxide value, different combinations of time and concentration of adsorbent did not give effect to the p-anisidine value ( $p > 0.05$ ), but significantly different from the untreated ( $p < 0.05$ ). Guillén and Cabo (2002) stated that the p-anisidine was not always in line with the high number of peroxide, but the high number of peroxide may cause high p-anisidine if the process given allowed the occurrence of further degradation to fish oil. Meanwhile different combinations of time and concentration of adsorbent did not give effect to totox value ( $p > 0.05$ ). This is because the total value of the oxidation was the summation of results between the two times of the number of peroxide value with the p-anisidine value (Perrin, 1996). An increase of peroxide value and totox led to increase p-anisidine values and vice versa. The total value of oxidation can be used to measure the progressivity of the deterioration process that occurs in oil and provides information on the formation of primary as well as secondary oxidation products (Hamilton and Rossell, 1986).

Clarity is the important physical parameters for fish oil products, because it will determine consumer acceptance. The higher the value of fish oil clarity, the better the product acceptance by consumers. Different combinations of time and concentration of adsorbent did not give effect to the clarity value ( $p > 0.05$ ). Refined oil clarity was better than semi-refined oil. The adsorption process for oil purification is a process to remove any impurities such as trace metals, pigments, pigment-breakdown products and primary oxidation products such as aldehydes and ketones, the loss of impurities caused higher fish oil clarity (Sathivel and Prinyawiwatkul, 2004; Proctor and Toro-Vazquez, 1996; Miki, 1991). Based on seven parameters above can be concluded that the best treatment to obtain the best refined catfish oil was combination of time and concentration of adsorbent 10 minutes and 1%, respectively. The refined catfish oil had yield  $88.16 \pm 4.91\%$ , free fatty acid content  $0.58 \pm 0.01\%$ , acid value  $1.15 \pm 0.02$  mg KOH/g, peroxide value  $3.56 \pm 0.51$  meq/kg, p-anisidine value  $1.38 \pm 0.04$  meq/kg, total oxidation value  $8.49 \pm 0.99$  meq/kg and clarity value  $75.58 \pm 6.26$  %T. The oxidation parameters value was under IFOS (2011) which is free fatty acid  $< 1.13\%$ , acid value  $< 2.25$  mg KOH/g, peroxide value  $< 3.75$  meq/kg, p-anisidine value  $< 15$  meq/kg, total oxidation value  $< 20$  meq/kg.

## CONCLUSION

Catfish by-product processing is able to be utilized as a source of fish oil. Purification process was carried out by neutralization and bleaching. The results showed that the best semi-refined oil was conducted by treatment  $16^\circ\text{Be}$  NaOH and refined oil was conducted by combination treatment 1% Magnesol XL for 10 min

stirring. The whole parameters result of refined fish oil were under international fish oil standard (IFOS, 2011).

## REFERENCES

- Aisyah, S., Y. Eny and A.F. Ghanaim, 2010. Penurunan angkaperoksidadan asam lemak bebas (ALB) pada proses bleaching minyak goreng bekas oleh karbon aktif polong buah kelor (*Moringa alifera*. Lamk) dengan aktivasi NaCl. *Alchemy*, 1(2): 53-103.
- AOAC, 1995. Association of Official Analytical Chemists. Association of Official Analytical Chemists Inc., Maryland.
- AOAC, 2005. Association of Official Analytical Chemist. Association of Analytical Chemist Inc., Arlington.
- Ariyanto, D. and R. Utami, 2006. Evaluation of growth rate, genetic variability and heterosis estimacy on interspecific crossing in pangasius catfish (*Pangasius* sp.). *J. Fish. Sci.*, 8(1): 81-86.
- Dadang, W.I., S.P. Peni, P.T. Enny, S. Yan, R. Selamet, S. Abu, 2009. *Bisnis Patin Butuh Kejelasan Pasar*. Agrina, Tabloid Agribusiness, Retrieved from: <http://www.agrina-online.com/redesign2.php?Rid=7&aid=1929>. (Accessed on: August 20, 2016)
- Estiasih, T., 2009. *Minyak Ikan: Teknologi dan Penerapannya untuk Panganan Kesehatan*. Graha Ilmu, Yogyakarta.
- Estiasih, T. and K. Ahmadi, 2012. Pembuatan trigliserida kaya asam lemak  $\omega$ -3 dari minyak hasil samping pengalengan lemuru (*Sardinella longiceps*). *J. Tek. Pert.*, 5(3): 116-128.
- Feryana, I.W.K., S.H. Suseno and Nurjanah, 2014. Pemurnian minyak ikan mackerel hasil samping penepungan dengan netralisasi alkali. *J. Pengolahan Hasil Perikanan Indonesia*, 17(3): 207-214.
- Fuadi, I., 2015. *Pemurnian alkali dan kristalisasi suhurendah dari minyak ikan hasil samping pengalengan mackerel (*Scomber japonicus*)*. M.S. Thesis, Bogor Agricultural University, Bogor, ID.
- Guillén, M.D. and N. Cabo, 2002. Fourier transform infrared spectra data versus peroxide and anisidine values to determine oxidative stability of edible oils. *Food Chem.*, 77(4): 503-510.
- Hamilton, R.S. and J.B. Rossell, 1986. *Analysis of oils and fats*. Elsevier Applied Science, London, pp: 23-32.
- Huang, J. and S. Sathivel, 2010. Purifying salmon oil using adsorption, neutralization, and a combined neutralization and adsorption process. *J. Food Eng.*, 96(1): 51-58.
- IFOS, 2011. *International Fish Oils Standard. Fish Oil Purity Standards*. Retrieved from: <http://www.omegavia.com/best-fish-oils-supplement-3/>. (Accessed on: October 4, 2016)

- Kirk, K.E. and V.F. Othmer, 2005. Encyclopedia of Chemical Technology. John Willey and Sons Inc., New York.
- KKP, 2015. Ministry of Marine Affairs and Fisheries. Produksi Perikanan Budidaya. Retrieved from: <http://statistik.kkp.go.id/sidatik-dev/2.php?t=15>. (Accessed on: September 23, 2016)
- Kordi, M.G.H.K., 2010. Budidayakan Patin di Kolam Terpal. Lily Publisher, Yogyakarta.
- Luc, N.T., L.H. Du and N.T. Dzung, 2013. Optimization of the smoking process of Pangasius fish fillet to increase the product quality. Adv. J. Food Sci. Technol., 5(2): 206-212.
- Miki, W., 1991. Biological functions and activities of animal carotenoids. Pure Appl. Chem., 63(1): 141-146.
- Ortiz, X., L. Carabellido, M. Marti, R. Marti, X. Tomas and J. Diaz-Ferrero, 2011. Elimination of persistent organic pollutants from fish oil with solid adsorbents. Chemosphere, 82(9): 1301-1307.
- Panagan, A.T., H. Yohandini and M. Wulandari, 2012. Analisis kualitatif dan kuantitatif asam lemak tak jenuh omega-3, omega-6 dan karakteristik asam lemak ikan patin (*Pangasius pangasius*). J. Penelitian Sains, 15(3): 102-106.
- Paul, S. and G.S. Mittal, 1997. Regulating the use of degraded oil/fat in deep-fat/oil food frying. Crit. Rev. Food Sci. Nutr., 37(7): 635-662.
- Perrin, J.L., 1996. Determination of Alteration. In: Karleskind, A. and J.P. Wolff (Eds.) Oils and Fats, Manual Vol. 2, Lavoisier Publishing, Paris.
- Proctor, A. and J.F. Toro-Vazquez, 1996. The Freundlich isotherm in studying adsorption in oil processing. J. Am. Oil Chem. Soc., 73(12): 1627-1633.
- Rahayu, L.H. and S. Purnavita, 2014. Pengaruh suhu dan waktu adsorpsi terhadap sifat kimia-fisika minyak goreng bekas hasil pemurnian menggunakan adsorben ampas pati aren dan bentonit. Momentum, 10(2): 35-41.
- Roesfitawati, 2013. Ikan patin hasil alam bernilai ekonomi dan berpotensi ekspor tinggi. Warta Ekspor, Ministry of Trade Taboid, Jakarta. Retrieved from: [http://djpen.kemendag.go.id/app\\_frontend/admin/docs/publication/8241384233598.pdf](http://djpen.kemendag.go.id/app_frontend/admin/docs/publication/8241384233598.pdf). (Accessed on: August 17, 2016)
- Sathivel, S. and W. Prinyawiwatkul, 2004. Adsorption of FFA in crude catfish oil onto chitosan, activated carbon, and activated earth: A kinetics study. J. Am. Oil Chem. Soc., 81(5): 493-496.
- Sathivel, S., W. Prinyawiwatkul, J.M. King, C.C. Grimm and S. Lloyd, 2003. Oil production from catfish viscera. J. Am. Oil Chem. Soc., 80(4): 377-382.
- Shahidi, F. and U.N. Wanasundara, 2008. Methods for Measuring Oxidative Stability in Edible Oils. In: Akoh, C.C. and D.B. Min (Eds.), Food Lipids: Chemistry, Nutrition and Biotechnology. CRC Press, New York.
- Suseno, S.H. and Saraswati, 2015. Teknologi Industri Minyak Ikan. IPB Press, Bogor.
- Suseno, S.H., A.Y. Tajul and W.A. Wan Nadiyah, 2011. Improving the quality of lemuru (*Sardinella lemuru*) oil using magnesol XL filter aid. Int. Food Res. J., 18: 255-264.
- Suseno, S.H., A.Y. Tajul, W.A. Nadiyah and A.F. Noor, 2012. Improved of color properties on *Sardinella lemuru* oil during adsorbent refining using Magnesol XL. Int. Food Res. J., 19(4): 1383-1386.
- Suseno, S.H., Nurjanah, A.M. Jacob and Saraswati, 2014. Purification of *Sardinella* sp., oil: Centrifugation and bentonite adsorbent. Adv. J. Food Sci. Technol., 6(1): 60-67.
- Swanson, D., R. Block and S.A. Mousa, 2012. Omega-3 fatty acids EPA and DHA: Health benefits throughout life. Adv. Nutr., 3(1): 1-7.
- Thammapat, P., P. Raviyan and S. Siriamornpun, 2010. Proximate and fatty acids composition of the muscles and viscera of Asian catfish (*Pangasius bocourti*). Food Chem., 122(1): 223-227.
- Tobuku, R., 2008. Lemak daging dan kinerja pertumbuhan ikan patin (*pangasius hypophthalmus*) yang diberi pakan dengan rasio karbohidrat dan lemak berbeda. M.S. Thesis, Bogor Agricultural University, Bogor, ID.
- Watson, C.A., 1994. Official and Standardized Methods of Analysis. 3rd Edn., The Royal Society of Chemistry, Cambridge.
- Widianto, T.N. and B.S.B. Utomo, 2010. Pemanfaatan minyak ikan untuk produksi biodiesel. Squalen, 5(1): 15-20.