# Thermostability and Photostability of Shrimp Waste Oil Based on Sun Protection Factor Value, Erythema Transmission, Pigmentation Transmission and Free Fatty Acid Content

## Deri Agustiawan<sup>1</sup>, Winda Rahmalia<sup>1\*</sup>, Andi Hairil Alimuddin<sup>1</sup>, Dwi Imam Prayitno<sup>2</sup>, Endah Sayekti<sup>1</sup>

<sup>1</sup>Department of Chemistry, Faculty of Mathematics and Natural Science, Tanjungpura University <sup>2</sup>Department of Marine Science, Faculty of Mathematics and Natural Science, Tanjungpura University JI. Prof. Dr. H. Hadari Nawawi, Pontianak 78124, West Kalimantan, Indonesia Email: winda.rahmalia@chemistry.untan.ac.id

#### Abstract

The high production of shrimp is accompanied by an increase in by-products (cephalothorax, carapace, and tail), which are discarded as waste. Therefore, a solution is needed to convert shrimp waste into economic value products like shrimp waste oil (SWO). SWO contains fatty acids and astaxanthin, which have antioxidant activity to scavenge free radicals, so it can prevent skin damage such as wrinkles and dryness. Due to its fatty acids and astaxanthin content, SWO can be applied as a sunscreen. However, heating and irradiation can degrade bioactive compounds that are beneficial for health. Thermostability and photostability tests are needed to determine the best storage conditions for SWO based on sun protector factor (SPF) values, erythema transmission (%Te), pigmentation transmission (%Tp), and free fatty acid (FFA) content. The yield of SWO obtained was 2.569% from 100 grams of dry shrimp waste weight. Analysis by using FTIR showed the presence of astaxanthin content in SWO, while GC-MS showed that the SWO contains up to 32.66% of hexanoic acid. SWO thermostability and photostability tests showed a decrease in SPF values and an increase in %Te and %Tp as heating and irradiation time increased. This is due to the photobleaching effect. There was no significant change in the FFA value, indicating that SWO is quite resistant to heating and irradiation.

Keywords: erythema transmission, free fatty acid, pigmentation transmission, shrimp waste oil, sun protection factor

#### INTRODUCTION

Shrimp is one of commodities that is liked by many people. Shrimp production worldwide reaches 6 million metric tons (MMT) (Food and Agriculture Organization of the United Nations, 2018a). Based on data from the Food and Agriculture Organization of the United Nations (2018b), world shrimp exports in 2017 reached 19.3 billion US dollars. High shrimp production is accompanied by an increase in by-products in the form of cephalothorax, carapace, and tail, which are discarded as waste (Sinthusamran *et al.*, 2020). According to Islam *et al.* (2016), shrimp waste can reach 40-50% of the weight of whole shrimp. Disposal of shrimp waste has caused problems for the environment, even though shrimp waste contains bioactive components such as proteins/peptides (Liu *et al.*, 2021), chitin/chitosan (Reshad *et al.*, 2021), pigments (Fitriani *et al.*, 2023), lipids (Rahmalia *et al.*, 2022), minerals (Gómez-Estaca *et al.*, 2019) and vitamins (Nair *et al.*, 2017). Therefore, we need a way to convert shrimp waste into economic value products, such as shrimp waste oil (SWO).

Shrimp waste can be processed by extraction to produce SWO, which contains fatty acids and the carotenoid astaxanthin (Phadtare *et al.*, 2021). Fatty acids and astaxanthin have antioxidant activity. They can scavenge reactive oxygen singlet (ROS) and prevent skin damage (Dini & Laneri, 2021). The antioxidant activity of astaxanthin is ten times higher than other carotenoids (Azman *et al.*, 2021). Free fatty acids play an important role in photoaging of human skin (Kim *et al.*, 2010). Based on research conducted by Davinelli *et al.* (2018), astaxanthin can inhibit collagenase, inflammatory mediators, and ROS induction, resulting in anti-wrinkle effects. Apart from that, astaxanthin can also prevent immunosuppression due to UV rays. Toxicological tests on astaxanthin prove that this compound is safe for consumption. The high antioxidant activity of astaxanthin can provide benefits for skin health, such as preventing various diseases caused by UV radiation, and can be applied as a sunscreen (Ito *et al.*, 2018; Rahmalia *et al.*, 2022). The effectiveness of sunscreen preparations can be categorized based on the value of sun protection factor (SPF), percent transmission of erythema (%Te), and transmission of pigmentation (%Tp). The SPF value is a value that describes the level of protection of a material against UV rays. %Te describes the amount of sunlight that enters the skin after being exposed to sunscreen, causing erythema (burning of the skin). Meanwhile, %Te describes the amount of sunlight that enters the skin after being exposed to sunscreen, which can cause pigmentation (darkening of the skin). These three parameters can be determined in-vitro using a UV-Vis spectrophotometer (Abdassah et al., 2015; Eff et al., 2018; Rahardhian et al., 2019; Sami et al., 2021).

Oil resistance to heat exposure and irradiation is an important factor that must be determined for commercialization purposes. Heating and radiation can degrade bioactive compounds that are beneficial for health and can increase the free fatty acid (FFA) content (Istyami *et al.*, 2018). FFA is one of the parameters that influence oil quality (Xie & Wang, 2021). FFA is produced from hydrolysis reactions in oil (Istyami *et al.*, 2018; Lebeck & Brock, 2021; Martin *et al.*, 2019; Nitbani *et al.*, 2020). High FFA content causes oil to become rancid (Li *et al.*, 2021). Thermostability and photostability tests are needed to determine the best storage conditions for SWO. This provides additional information for the public and researchers for further SWO processing. Therefore, this study tested the thermostability and photostability of shrimp oil based on the SPF value, %Te, %Tp, and FFA content.

#### MATERIALS AND METHODS

This research was conducted at the Chemistry Laboratory, Faculty of Mathematics and Natural Sciences, Tanjungpura University, Pontianak, West Kalimantan. The tools used in this research are burette, hot plate (Ika C-Mag HS 7), clamp and stative, condenser, two-neck round bottom flask, 500 W halogen lamp (Panasonic), heating mantle, water pump, sieve, hose, set of distillation apparatus, UV-Vis spectrophotometer (Shimadzu UV-2600), soxhlet, solar power meter (SM206-Solar), analytical balance, thermometer, vacuum drying (Agrowindo). The materials used in this study are distilled water (H<sub>2</sub>O), oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) (Merck), phenolphthalein indicator (C<sub>20</sub>H<sub>14</sub>O<sub>4</sub>) (Smart-Lab), filter paper, n-hexane (C<sub>6</sub>H<sub>14</sub>) (Fulltime), sodium hydroxide (NaOH) (Merck) and shrimp waste.

#### **Prearation of Shrimp Waste**

Shrimp waste was cleaned with water then dried at  $50^{\circ}$ C for  $\pm 5$  hours using the vacuum drying method. The dried shrimp waste was then ground using a blender and ready for further testing (Rahmalia *et al.*, 2022).

#### Extraction and Characterization of Shrimp Waste Oil (SWO)

A total of 100 g of finely dried shrimp was put into a thimble and then placed in a Soxhlet extractor. The n-hexane solvent was poured into a two-neck flask with a round bottom that had been installed in a Soxhlet extractor. The soxhlet was equipped with a condenser to avoid loss of solvent. The soxhlet was then placed on a temperature-controlled heater. The temperature was measured with a thermometer inserted into one of the necks of the round bottom flask. After extraction was complete, the oil trapped in the solvent was separated using distillation at a temperature of 65°C and followed by drying with N<sub>2</sub> gas. The SWO obtained after separation with the solvent is weighed and then calculated using the following equation (Rahmalia *et al.*, 2022).

SWO yield = 
$$\frac{\text{Mass of oil extracted}}{\text{Mass of dried shrimp}} \times 100\%$$

The SWO obtained was then characterized using Fourier Transform Infra-Red (FTIR) and Gas Chromatography-Mass Spectroscopy (GC-MS) instruments.

#### Determination of Sun Protection Factor Value, Erythema Transmission, and Pigmentation Transmission

0.05 g of SWO was dissolved in n-hexane solvent to a total volume of 5 mL. The absorbance of the solution was then measured every 5 nm interval in the wavelength range 290-320 nm using a UV-

Vis spectrophotometer to determine the Sun Protection Factor (SPF) value. Determination of the percentage transmission value of erythema (%Te) was carried out in the wavelength range 292-317 nm, while the percentage transmission value of pigmentation (%Tp) was in the wavelength range 322-372 nm. The SPF value is calculated using the following equation (Rahmalia *et al.*, 2022):

SPF = CF x 
$$\sum_{290}^{320}$$
 EE ( $\lambda$ ) x I ( $\lambda$ ) x Abs ( $\lambda$ )

where CF is correction factor (10), EE is erythema effect spectrum, I is light intensity spectrum, and Abs is absorbance. The EE x I value is a constant shown in Table 1 below.

Before calculating the %Te and %Tp values, the absorbance values obtained are first converted into percent Transmittance (%T) values following the equation (Rahardhian *et al.*, 2019).

$$T(\%) = (10^{-A}) \times 100\%$$

Where T is transmittance (%) and A is absorbance.

The transmittance results obtained were then used to calculate the %Te and %Tp values by following the equation (Sami *et al.*, 2021).

Te (%) = 
$$\frac{\sum(T \times Fe)}{\sum Fe}$$
  
Tp (%) =  $\frac{\sum(T \times Fp)}{\sum Fp}$ 

where Te is transmission of erythema (%), Tp is transmission of pigmentation (%), T is transmittance (%), Fe is flux of erythema, and Fp is flux of pigmentation.

The values of Fe and Fp are constants as shown in Table 2.

#### **Determination of Free Fatty Acid Content**

Determination of FFA levels was carried out using the acid-base titration method, where the SWO solution was titrated with a 0.01 N NaOH solution, which had previously been standardized using a 0.01 N oxalic acid solution. SWO was weighed at 0.05 grams then 0.25 mL of isopropanol was added and heated for 10 seconds. After that, 3-5 drops of phenolphthalein indicator are added to the SWO solution, then titrated hot with NaOH solution until the endpoint is pink. The FFA content was calculated as hexanoic acid using the following formula (Purnaningtyas, 2022).

 $FFA Content (\%) = \frac{Volume of NaOH x Molarity of NaOH x Molecular weight of hexanoic acid}{Mass of shrimp oil x 1000} x 100\%$ 

Wavelength (nm)	EE x I (Normalization)
290	0.0150
295	0.0817
300	0.2874
305	0.3278
310	0.1864
315	0.0837
320	0.0180

Table 1. Normalization Function Used in SPF Calculation (Rahmalia et al. (2022))

#### Shrimp Waste Oil (SWO) Thermostability Test

The SWO thermostability test was carried out by modifying the method of Zhang *et al.* (2022). SWO was tested for thermal stability by heating at a temperature of 60; 90 and 120°C for 8 hours where the SPF, %Te and %Tp values and FFA levels were measured every 2 hours. The SWO thermostability test was carried out in 3 repetitions (triplo).

#### Shrimp Waste Oil (SWO) Photostability Test

The SWO photostability test was carried out by modifying the method of Zhang *et al.* (2022). SWO was irradiated at an intensity of 300 W/m<sup>2</sup> for 6 hours where the SPF, %Te and %Tp values and FFA levels were measured every 1 hour. The shrimp oil photostability test was carried out with 3 repetitions (triplo).

#### **RESULT AND DISCUSSION**

#### Extraction and Characterization of Shrimp Waste Oil (SWO)

Extraction is a chemical separation process using a solvent to separate a component from its analyte based on the level of polarity (Didion *et al.*, 2023). The method used in SWO extraction in this research is soxhlation. Extraction was carried out using shrimp waste that had been cleaned with water and dried at 50°C for ± 5 hours using vacuum drying. The working principle of vacuum drying involved vacuum pressure and low temperature. This vacuum pressure lowers the boiling point of the water in the sample (low temperature) so that it does not destroy the desired bioactive compounds (Raj & Dash, 2020; Sun *et al.*, 2019). Drying was carried out to reduce the water content in shrimp waste so that during extraction, the compound withdrawal process can take place optimally (Zambrano *et al.*, 2019). The dried shrimp waste was then ground using a blender. Grinding aims to increase the surface area of the sample. The greater the surface area, the contact between the sample and the solvent will also increase so that the extraction process can take place more quickly and optimally (Oyinloye & Yoon, 2020).

Wavelength (nm)	Flux of Erythema (Fe)	Flux of Pigmentation (Fp)
290-295	0.1105	-
295-300	0.6720	-
300-305	1.0000	-
305-310	0.2008	-
310-315	0.1364	-
315-320	0.1125	-
320-325	-	0.1079
325-330	-	0.1020
330-335	-	0.0936
335-340	-	0.0798
340-345	-	0.0669
345-350	-	0.0570
350-355	-	0.0488
355-360	-	0.0456
360-365	-	0.0356
365-370	-	0.0310
370-375	-	0.0260

 Table 2. Flux of Erythema and Pigmentation (Rahardhian et al. (2019))

The yield of shrimp oil obtained was 2.569% of 100 grams of weight of dry shrimp waste. This result was higher compared to research conducted by Roy *et al.* (2020) where the oil yield obtained was 2.05% using n-hexane solvent and the supercritical CO<sub>2</sub> extraction method. However, research conducted by Raju *et al.* (2021) obtained a greater oil yield of 3.2% using the solvent n-hexane:isopropanol (1:1). Differences in yield values are influenced by several factors such as genetics, sex, size, salinity, temperature, season, food and habitat (Karnila *et al.*, 2021). The extraction method and solvents used also influence the yield SWO results.

SWO was characterized using a Fourier Transform Infra-Red (FTIR) instrument. FTIR analysis was carried out to identify functional groups contained in SWO samples. FTIR results showed the presence of astaxanthin compounds in SWO. This is proven by the presence of a peak at the absorption wave number 3385 cm<sup>-1</sup> which indicates O-H stretching vibration, 2922 cm<sup>-1</sup> which shows C-H stretching vibration of cyclic, 1738 cm<sup>-1</sup> which shows C=O stretching, 1574 cm<sup>-1</sup> which shows C-H stretching vibration C=C stretching of cyclic, 1464 cm<sup>-1</sup> which shows C=C aliphatic stretching vibration, 1057 cm<sup>-1</sup> which shows C-O hydroxyl stretching vibration and 968 cm<sup>-1</sup> which shows C-H aliphatic bending vibration (Kaczor *et al.*, 2011; Mahaffy *et al.*, 2011; Withnall *et al.*, 2003; Yuan *et al.*, 2012). The structure of astaxanthin can be seen in Figure 3.



Figure 1. Shrimp Waste (Left) and Shrimp Was Oil (Right)



Figure 2. FTIR Spectra of Shrimp Oil

The SWO was also characterized using a Gas Chromatography-Mass Spectroscopy (GC-MS) instrument to identify chemical substances based on volatility (Baccolo *et al.*, 2021). The results of the GC-MS analysis of shrimp oil can be seen in Table 3. Based on Table 3, the highest content in SWO is hexanoic acid at 32.66%. This is also in line with research conducted by Kannan *et al.* (2020) who reported that hexanoic acid is the fatty acid that is most abundant in shrimp waste. Hexanoic acid has many applications in the food and cosmetics industries due to its organoleptic characteristics (Kim *et al.*, 2022). According to Shen *et al.* (2023), hexanoic acid plays a role in reducing insulin levels.

Mass spectroscopy is used to determine the relative molecular weight and fragmentation patterns of compounds to identify the structure of the compound of interest (Gathungu *et al.*, 2020). The hexanoic acid compound has a molecular weight of 158 m/z with the molecular formula C9H18O2. The compound undergoes McLafferty rearrangement and then forms other fragments due to bond breaking. The peaks that appeared in the fragmentation of this compound were 158, 143, 74, and 42 m/z (McLafferty & Turecek, 1993). The possible fragmentation patterns that occur in these compounds are presented in Figure 4.



Figure 3. Chemical Structure of Astaxanthin (Villaró et al., 2021)

Table 3. Results of GC-MS Analysis of Shrimp Oil

Name of Compound	Chemical Formula	RT	SI	Content (%)	
Hydroxylamine, O-(2-methylpropyl)-	C <sub>4</sub> H <sub>11</sub> NO	4.98	827	0.01	
Hydroperoxide, heptyl	C7H16O2	19.58	841	1.70	
Oxalic acid, allyl heptyl ester	$C_{12}H_{20}O_4$	24.43	822	0.56	
Hexanoic acid, 3-ethyl-, methyl ester	C9H18O2	27.41	741	32.66	
(2S,3S)-(-)-3-Propyloxiranemethanol	C6H12O2	25.23	669	0.02	
1-Propanol, 2-methyl-	$C_4H_{10}O$	32.76	738	2.40	
Oxalic acid, allyl octyl ester	C13H22O4	28.82	778	0.98	
Oxirane, (3-methylbutyl)-	C7H14O	33.24	759	0.77	
Heptane, 1-nitro-	C7H15NO2	32.60	757	17.73	
Allyl methallyl ether	C7H12O	34.94	749	7.00	
1,5-Hexadien-3-ol	C6H10O	31.87	707	1.14	
Oxirane, [(tetradecyloxy)methyl]-	C17H34O2	33.67	726	0.28	
2-Furanol, tetrahydro-2,3-dimethyl-, trans-	C6H12O2	36.15	693	4.34	
Hydroperoxide, pentyl	$C_5H_{12}O_2$	50.45	769	0.37	
Z-1,9-Dodecadiene	C12H22	34.71	746	1.04	
Heptane, 1-nitro-	C7H15NO2	46.97	772	3.85	
2,4,6,8-Tetramethyl-1-undecene	C15H30	39.85	801	1.27	
1,2:4,5:9,10-Triepoxydecane	C10H16O3	39.21	751	9.81	
1,6-Octadiene, 3,7-dimethyl-	C10H18	40.84	703	10.05	
Z-1,9-Hexadecadiene	C <sub>16</sub> H <sub>30</sub>	38.30	729	2.06	
5,10-Dioxatricyclo[7.1.0.0(4,6)]decane	$C_8H_{12}O_2$	41.28	739	0.36	
1,6-Bis(2-propyn-1-yloxy)hexane	C12H18O2	39.33	723	0.07	
2,6-Nonadien-1-ol	C9H16O	40.70	713	0.34	
2,3-Epoxyhexanol	C6H12O2	48.24	713	0.26	
Oxirane, (2,2-dimethylpropyl)	C7H14O	53.13	690	0.93	
Total (%)					



Figure 4. Fragmentation of Hexanoic Acid

### Thermostability and Photostability Test Based on SPF Value, %Te, %Tp, and FFA Content

The thermostability test is carried out to determine the stability and duration of the compound's protective effect against heating. SWO was tested for thermal stability by heating at temperatures of 60, 90, and 120°C based on the SPF value, %Te, %Tp, and FFA content. The photostability test was carried out to determine the stability and duration of the compound's protective effect against irradiation, especially UV radiation. The results of the thermostability and photostability test for shrimp oil based on the SPF value are shown in Table 4.

Based on Tables 4 and 5, the SPF value decreases as heating and exposure time increases. The decrease in the SPF value is due to the photobleaching effect where there is a decrease in the absorption value after heating and irradiation. According to Liu *et al.* (2015), the photobleaching effect can occur due to irreversible modification (breaking) of covalent bonds caused by the transition of electrons from the singlet/<sup>1</sup>S state to the triplet/<sup>3</sup>S state by fluorophores (compounds that can undergo fluorescence). The electrons will be excited and then react with hydrogen atoms to form active oxygen species which then form singlet oxygen in an excited state (<sup>1</sup>O<sub>2</sub>). After that, a reaction occurs between radical oxygen species and singlet oxygen, causing a photobleaching effect.

Temperature (°C)	Heating Time (Hour)	SPF ± SD	Protection Category
	0	8.827 ± 0.133	Maximum Protection
	2	7.525 ± 0.004	Extra Protection
60	4	5.420 ± 0.010	Moderate Protection
	6	4.959 ± 0.065	Moderate Protection
	8	3.609 ± 0.099	Minimum Protection
	0	8.565 ± 0.037	Maximum Protection
	2	6.437 ± 0.103	Extra Protection
90	4	5.306 ± 0.043	Moderate Protection
	6	4.757 ± 0.042	Moderate Protection
	8	2.707 ± 0.146	Minimum Protection
	0	8.224 ± 0.201	Maximum Protection
	2	6.241 ± 0.013	Extra Protection
120	4	5.135 ± 0.019	Moderate Protection
	6	4.092 ± 0.202	Moderate Protection
	8	1.420 ± 0.145	-

#### Table 4. Shrimp Oil Thermostability Test Based on SPF Value

Table 5. Photostability Test of Shrimp Oil Based on SPF Value

on Category
n Protection
rotection
rotection
e Protection
e Protection
e Protection
e Protection

Table 6. Shrimp Oil Thermostability Test Based on %Te and %Tp  $% \mathcal{T}_{\mathcal{T}}$ 

Temperature	Heating		Protection	MIN + SD	Protection
(°C)	Time (Hour)	%IE ± 3D	Category %1P±3D		Category
	0	13.617 ± 0.319	Fast Tanning	33.009 ± 0.531	Sunblock
	2	20.524 ± 0.139	-	42.929 ± 0.866	Extra Protection
60	4	26.572 ± 0.620	-	44.795 ± 0.999	Extra Protection
	6	29.358 ± 0.329	-	48.862 ± 0.404	Standard Suntan
	8	43.736 ± 0.130	-	76.622 ± 0.549	Fast Tanning
	0	17.492 ± 0.438	Fast Tanning	44.738 ± 0.960	Extra Protection
	2	21.975 ± 0.352	-	50.222 ± 0.907	Standard Suntan
90	4	28.514 ± 0.205	-	50.448 ± 0.252	Standard Suntan
	6	31.303 ± 0.362	-	54.542 ± 0.164	Standard Suntan
	8	49.303 ± 0.148	-	72.374 ± 0.496	Fast Tanning
	0	19.067 ± 0.870	-	45.811 ± 0.172	Standard Suntan
120	2	22.900 ± 0.684	-	48.329 ± 0.225	Standard Suntan
	4	30.158 ± 0.140	-	51.496 ± 0.118	Standard Suntan
	6	37.704 ± 0.950	-	51.758 ± 0.116	Standard Suntan
	8	71.171 ± 0.924	-	75.340 ± 0.890	Fast Tanning

#### Jurnal Kelautan Tropis Juni 2024 Vol. 27(2):247-260

The SPF value obtained is lower compared to the research results of Rahmalia *et al.* (2022) where the SPF value obtained was  $15.17 \pm 0.092$ . According to Mbanga *et al.* (2014), several factors can influence the SPF value such as differences in solvents, the type of emulsion used, as well as the effects and interactions of other components such as esters and emulsifiers used in the formulation. Apart from SPF, the SWO thermostability and photostability tests are also based on %Te and %Tp, the results of which can be seen in Table 6.

Based on Tables 6 and 7, the %Te and %Tp values increase with increasing heating and irradiation time. This is because the longer the heating and irradiation time will reduce the absorption value and increase the transmittance percentage so that %Te and %Tp will also increase. The sunblock category is the best because it can protect the skin completely against UV A and UV B rays. This category prevents the skin from erythema and pigmentation. The extra protection category can protect the skin from erythema by absorbing less than 85% of UV B radiation and preventing pigmentation. The standard suntan category is able to absorb most of the UV B rays and absorb a little of the UV A rays, causing pigmentation without erythema. Standard sunbathing can prevent erythema in normal people's skin or non-sensitive skin. The fast-tanning category can darken the skin quickly without causing erythema so that it can provide a maximum darkening effect (Lolo *et al.*, 2017).

SWO thermostability and photostability tests were also determined based on the free fatty acid (FFA) content. Thermostability test results based on FFA content obtained at a temperature of 60°C for 8 consecutive hours of heating were 4,951; 5,161; 5,056; 5,161; and 5.056%. FFA content at 90°C

Irradiation Time (Hour)	%Te ± SD	Protection Category	%Tp ± SD	Protection Category
0	11.750 ± 0.169	Standard Suntan	27.515 ± 0.436	Sunblock
1	18.087 ± 0.752	Fast Tanning	33.297 ± 0.949	Sunblock
2	22.007 ± 0.429	-	35.459 ± 0.728	Sunblock
3	25.799 ± 0.097	-	40.589 ± 0.653	Extra Protection
4	30.372 ± 0.484	-	43.004 ± 0.264	Extra Protection
5	33.572 ± 0.359	-	44.615 ± 0.242	Extra Protection
6	35.630 ± 0.919	-	44.643 ± 0.270	Extra Protection

Table	7. Shrimp	Oil Photo	stability	Test Bo	used on	%Te	and %Tp
	••••	0	o. o. o. o ,			/0.0	



#### Triglycerides

Fatty Acid

Glycerol

Figure 5. Hydrolysis of Triglycerides into Fatty Acids and Glycerol (Martin et al., 2019)



Figure 6. Shrimp Oil Thermostability Test Based on FFA Content



Figure 7. Shrimp Oil Photostability Test Based on FFA Content

for 8 consecutive heating hours was 5,267; 5,267; 5,161; 5,267; and 5.161%. The results of FFA content at a temperature of 120°C for 8 consecutive hours of heating were 5.267; 5,161; 5,477; 5,267; and 5.372%. Meanwhile, the photostability test results for FFA content obtained during 6 consecutive hours of irradiation were 5.477; 5,161; 4,951; 5,267; 5,161; 5,267; and 4.951%. Thermostability and photostability tests based on FFA content show that shrimp oil is stable against heating and radiation. This is because the heating and irradiation carried out have not been able to hydrolyze the oil into free fatty acids. Good quality oil should contain low content of free fatty acids (Xie & Wang, 2021).

#### CONCLUSION

Shrimp waste has the potential for further use because it contains bioactive compounds such as fatty acids and astaxanthin. Use as a cosmetic can be done if viewed from the SPF, %Te, and %Tp values. Based on photostability and thermostability tests, shrimp waste oil shows good resistance.

#### REFERENCES

- Azman, K.A.K., Seong, F.C., Singh, G.K.S., & Affandi, M.M.R.M.M., (2021). Physicochemical Characterization of Astaxanthin-loaded PLGA Formulation Via Nanoprecipitation Technique, Journal of Applied Pharmaceutical Science, 11(6), 56–61. doi: 10.7324/JAPS.2021.110606
- Baccolo, G., Quintanilla-casas, B., Vichi, S., Augustijn, D., & Bro, R., (2021). From Untargeted Chemical Profiling to Peak Tables - A Fully Automated Al Driven Approach to Untargeted GC-MS, Trends in Analytical Chemistry, 145(116451), 1–8. doi: 10.1016/j.trac.2021.116451
- Boni, J., Aida, S., & Leila, K., (2018) Lipid Extraction Method from Microalgae Botryococcus braunii as Raw Material to Make Biodiesel with Soxhlet Extraction, *IOP Conference Series: Journal of Physics:* Conference Series, 1095(012004), 1–7.
- Chang, M.Y., Chan, E.S., & Song, C.P., (2021). Biodiesel Production Catalysed by Low-Cost Liquid Enzyme Eversa® Transform 2.0: Effect of Free Fatty Acid Content on Lipase Methanol Tolerance and Kinetic Model, *Fuel*, 283(3), 1–8. doi: 10.1016/j.fuel.2020.119266
- Davinelli, S., Nielsen, M.E., & Scapagnini, G., (2018). Astaxanthin in Skin Health, Repair, and Disease: A Comprehensive Review, Nutrients, 10(4), 1–12. doi: 10.3390/nu10040522
- Didion, Y. P., Tjalsma, T. G., Su, Z., Malankowska, M., & Pinelo, M., (2023). What is Next? The Greener Future of Solid Liquid Extraction of Biobased Compounds: Novel Techniques and Solvents Overpower Traditional Ones, Separation and Purification Technology, 320(10), 1–22. doi: 10.1016/j.seppur.2023.124147
- Dini, I., & Laneri, S., (2021). The New Challenge of Green Cosmetics: Natural Food Ingredients for Cosmetic Formulations, *Molecules*, 26(13), 1–28.
- Eff, A.R.Y., Pertiwi, R.D., Rakhmawati, I., & Utami, T.P., (2018). In-vitro and in-vivo Sunscreen Activity of Active Compounds Isolated from Fruits of Phaleria marcocarpha (Scheff.) Boerl, Journal of Young Pharmacists, 10(2), 106–110. doi: 10.5530/jyp.2018.2s.21
- Fitriani, D., Rahmalia, W., Ardiningsih, P., Usman, T., Nurbaeti, S.N., & Prayitno, D.I., (2023). Extraction of Astaxanthin from Fermented Acetes using Virgin Coconut Oil with the Glass Beads Vortex Method, Oillseeds and Fats, Crops and Lipids, 30(4), 1–8.
- Food and Agriculture Organization of the United Nations, (2018a). Fishery and Aquaculture Statistics, Food and Agriculture Organization of the United Nations, Rome.
- Food and Agriculture Organization of the United Nations, (2018b). The State of World Fisheries and Aquaculture, Food and Agriculture Organization of the United Nations, Rome.
- Gathungu, R. M., Kautz, R., Kristal, B. S., Bird, S. S., & Vouros, P., (2020). The Integration of LC-MS and NMR for the Analysis of Low Molecular Weight Trace Analytes in Complex Matrices, *HHS Public* Access, 39(1–2), 35–54.
- Gómez-Estaca, J., Alemán, A., López-Caballero, M.E., Baccan, G.C., Montero, P., & Gómez-Guillén, M.C., (2019). Bioaccessibility and Antimicrobial Properties of a Shrimp Demineralization Extract Blended with Chitosan as Wrapping Material in Ready-to-eat Raw Salmon, Food Chemistry, 276, 342–349. doi: 10.1016/j.foodchem.2018.10.031
- Islam, S.Z., Khan, M., & Alam, A.K.M.N., (2016). Production of Chitin and Chitosan from Shrimp Shell Wastes, J. Bangladesh Agril. Univ., 14(2), 253–259.
- Istyami, A.N., Soerawidjaja, T.H., & Prakoso, T., (2018). Mass Balances and Thermodynamics Study of Thermal Triglyceride Hydrolysis, MATEC Web of Conferences, 156(3), 1–5.
- Ito, N., Seki, S., & Ueda, F., (2018). The Protective Role of Astaxanthin for UV-Induced Skin Deterioration in Healthy People-A Randomized, Double-Blind, Placebo-Controlled Trial, *Nutrients*, 10(7), 1–10. doi: 10.3390/nu10070817
- Kaczor, A., Turnau, K., & Baranska, M., (2011). In Situ Raman Imaging of Astaxanthin in a Single Microalgal Cell, Analyst, 136(6), 1109–1112. doi: 10.1039/c0an00553c

- Kannan, S., Burelle, I., Orsat, V., & Raghavan, G.S.V., (2020). Characterization of Bio-crude Liquor and Bio-oil Produced by Hydrothermal Carbonization of Seafood Waste, Waste and Biomass Valorization, 11(6), 3553–3565. doi: 10.1007/s12649-019-00704-y
- Karnila, R., Hasan, B., Ilza, M., Leksono, T., & Ahmad, M.A., (2021). Astaxanthin Extraction of Vanname Shrimp (Litopenaeus vanname) Using Palm Oil, IOP Conference Series: Earth and Environmental Science, p.1–6. doi: 10.1088/1755-1315/695/1/012056
- Kim, E.J., Jin, X.J., Kim, Y.K., Oh, I.K., Kim, J.E., Park, C.H., & Chung, J.H., (2010). UV Decreases The Synthesis of Free Fatty Acids and Triglycerides in The Epidermis of Human Skin in Vivo, Contributing to Development of Skin Photoaging, *Journal of Dermatological Science*, 57(1), 19–26. doi: 10.1016/j.jdermsci.2009.10.008
- Kim, J., Kim, K.Y., Ko, J.K., Lee, S.M., Gong, G., Kim, K.H., & Um, Y., (2022) Characterization of a Novel Acetogen Clostridium sp. JS66 for Production of Acids and Alcohols: Focusing on Hexanoic Acid Production from Syngas, *Biotechnology and Bioprocess Engineering*, 27(1), 89–98.
- Lebeck, J., & Brock, B., (2021). Plasma Glycerol Levels in Men with Hypertriglyceridemia, Scandinavian Journal of Clinical and Laboratory Investigation, 81(4), 298–302. doi: 10.1080/00365513.2021. 1904282
- Li, L.W., Chen, X.Y., Liu, L.C., Yang, Y., Wu, Y.J., Chen, G., Zhang, Z.F., & Luo, P., (2021). Oil-in-water Camellia Seeds Oil Nanoemulsions via High Pressure Microfluidization: Formation and Evaluation, *LWT*, 140(8), 1–8. doi: 10.1016/j.lwt.2020.110815
- Lin, Y.J., Chang, J.J., Huang, H.T., Lee, C.P., Hu, Y.F., Wu, M.L., Huang, C.Y., & Nan, F.H., (2023). Improving Red-color Performance, Immune Response and Resistance to Vibrio Parahaemolyticus on White Shrimp Penaeus vannamei by an Engineered Astaxanthin Yeast, Scientific Reports, 13(1), 1–16. doi: 10.1038/s41598-023-29225-4
- Liu, Z., Liu, Q., Zhang, D., Wei, S., Sun, Q., Xia, Q., Shi, W., Ji, H., & Liu, S., (2021). Comparison of the Proximate Composition and Nutritional Profile of Byproducts and Edible Parts of Five Species of Shrimp, Foods, 10(11), 1–16.
- Liu, Z., Ueda, K., Kim, H.J., & Sparrow, J.R., (2015). Photobleaching and Fluorescence Recovery of RPE Bisretinoids, *PLoS ONE*, 10(9), 1–16. doi: 10.1371/journal.pone.0138081
- Lolo, W.A., Sudewi, S., & Edy, H.J., (2017). Determination Sun Protecting Factor (SPF) of Krokot Herbs Extract (Portulacaoleracea L.), Journal of Pharmaceutical Science and Clinical Research, 2(1), 1–5. doi: 10.20961/jpscr.v2i01.5230
- Mahaffy, P., Tasker, R., Bucat, B., Kotz, J.C., Weaver, G.C., Treichel, P.M., & McMurry, J.E., (2011). Chemistry: Human Activity, Chemical Reactivity, Nelson Education, Toronto.
- Martin, J.F.G., Ruiz, J.C., Garcia, M.T., Feng, C.H., & Mateos, P.A., (2019). Esterification of Free Fatty Acids with Glycerol within the Biodiesel Production Framework, *Processes*, 7(11), 1–10.
- Mbanga, L., Mulenga, M., Mpiana, P.T., Bokolo, K., Mumbwa, M., & Mvingu, K., (2014). Determination of Sun Protection Factor (SPF) of Some Body Creams and Lotions Marketed in Kinshasa by Ultraviolet Spectrophotometry, International Journal of Advanced Research in Chemical Science, 1(8), 7–13.
- McLafferty, F.W., & Turecek, F., (1993). Interpretation of Mass Spectra (Fourth), University Science Books, California. doi: 10.5702/massspec.s22-64
- Nair, S., Gagnon, J., Pelletier, C., Tchoukanova, N., Zhang, J., Ewart, H. S., Ewart, V., Jiao, G., & Wang, Y., (2017). Shrimp Oil Extracted from the Shrimp Processing Waste Reduces the Development of Insulin Resistance and Metabolic Phenotypes in Diet-induced Obese Rats, Applied Physiology, Nutrition, and Metabolism, 42(8), 841–849.
- Nitbani, F.O., Tjitda, P.J.P., Nurohmah, B.A., & Wogo, H.E., (2020). Preparation of Fatty Acid and Monoglyceride from Vegetable Oil, *Journal of Oleo Science*, 69(4), 277–295.
- Oyinloye, T.M., & Yoon, W.B., (2020). Effect of Freeze-Drying on Quality and Grinding Process of Food Produce: A Review, Processes, 8(3), 1–23.
- Phadtare, I., Vaidya, H., Hawboldt, K., & Cheema, S.K., (2021). Shrimp Oil Extracted from Shrimp Processing By-Product is a Rich Source of Omega-3 Fatty Acids and Astaxanthin-Esters, and Reveals Potential Anti-Adipogenic Effects in, *Marine Drugs*, 19(5), 1–18.
- Purnaningtyas, S.R.D., (2022). Analysis of Free Fatty Acid Levels (as Lauric Acid) Pure Coconut Oil (Virgin Coconut Oil/VCO) for Sale in Kediri City, Strada Journal of Pharmacy, 4(1), 18–22.

- Rahardhian, M. R. R., Suharsanti, R., Sugihartini, N., & Lukitaningsih, E., (2019). In Vitro Assessment of Total Phenolic, Total Flavonoid and Sunscreen Activities of Crude Ethanolic Extract of Belimbing Wuluh (Averrhoa bilimbi) Fruits and Leaves, Journal of Global Pharma Technology, 11(4), 308–313.
- Rahmalia, W., Dasilia, C., Usman, T., Prayitno, D.I., & Nurbaeti, S.N., (2022). Astaxanthin and Omega-3-rich Oil from Fermented Acetes (Cincalok) and Its Application as Bioactive Additive and Sunscreen in Lotion, Oilseeds and Fats, Crops and Lipids, 29(18), 1–8. doi: 10.1051/ocl/2022012
- Raj, G.V.S.B., & Dash, K.K., (2020). Microwave Vacuum Drying of Dragon Fruit Slice: Artificial Neural Network Modelling, Genetic Algorithm Optimization, and Kinetics Study, Computers and Electronics in Agriculture, 178(12), 1–15. doi: 10.1016/j.compag.2020.105814
- Raju, N., Gulzar, S., Buamard, N., Ma, L., Ying, X., Zhang, B., & Benjakul, S., (2021). Comparative Study of Astaxanthin, Cholesterol, Fatty Acid Profiles, and Quality Indices Between Shrimp Oil Extracted from Hepatopancreas and Cephalothorax, *Frontiers in Nutrition*, 8(803664), 1–12. doi: 10.3389/fnut.2021.803664
- Rathod, B. B., Murthy, S., & Bandyopadhyay, S., (2020) Is This Solution Pink Enough? A Smartphone Tutor to Resolve the Eternal Question in Phenolphthalein-Based Titration, *Journal of Chemical Education*, 96(3), 1–9. doi: 10.1021/acs.jchemed.8b00708
- Reshad, R.A.I., Jishan, T.A., & Chowdhury, N.N., (2021) Chitosan and Its Broad Applications: A Brief Review, Journal of Clinical and Experimental Investigations, 12(4), 1–13.
- Roy, V.C., Getachew, A.T., Cho, Y.J., Park, J.S., & Chun, B.S., (2020) Recovery and Bio-potentialities of Astaxanthin-rich Oil from Shrimp (*Peneanus monodon*) Waste and Mackerel (Scomberomous niphonius) Skin Using Concurrent Supercritical CO<sub>2</sub> Extraction, Journal of Supercritical Fluids, 159(104773), 1–10. doi: 10.1016/j.supflu.2020.104773
- Sami, F.J., Soekamto, N.H., Firdaus, & Latip, J., (2021). Bioactivity Profile of Three Types of Seaweed as an Antioxidant, UV-protection as Sunscreen and Their Correlation Activity, Food Research, 5(1), 441–447.
- Shen, C., Chen, Y., Wang, Q., Sun, Y., Lin, H., Ni, M., Chen, Y., Zhang, L., Jin, J., Ying, X., Zou, Y., Wang, X., Ye, Y., Yuan, M., Yin, N., Cao, Z., Zhang, Y., Gu, W., Wang, W., Ning, G., Wang, J., Zhao, S., Hong, J., & Liu, R., (2023). Fecal Short Chain Fatty Acids Modify Therapeutic Effects of Sleeve Gastrectomy, Frontiers in Endocrinology, 14(1277035), 1–12. doi: 10.3389/fendo.2023.1277035
- Sinthusamran, S., Benjakul, S., Kijroongrojana, K., Prodpran, T., & Kishimura, H., (2020). Protein Hydrolysates from Pacific White Shrimp Cephalothorax Manufactured with Different Processes: Compositions, Characteristics and Antioxidative Activity, Waste and Biomass Valorization, 11(5), 1657–1670.
- Skoog, D.A., Holler, F.J., & Crouch, S.R., (2018). Principles of Instrumental Analysis, Ed.7, Cengage Learning, Boston.
- Sun, Y., Zhang, M., & Mujumdar, A., (2019). Berry Drying: Mechanism, Pretreatment, Drying Technology, Nutrient Preservation, and Mathematical Models, Food Engineering Reviews, 11(10), 61–77.
- Villaró, S., Ciardi, M., Morillas-España, A., Sánchez-Zurano, A., Acién-Fernández, G., & Lafarga, T., (2021). Microalgae Derived Astaxanthin: Research and Consumer Trends and Industrial Use as Food, Foods, 10(10), 1–17. doi: 10.3390/foods10102303
- Withnall, R., Chowdhry, B.Z., Silver, J., Edwards, H.G.M., & Oliveira, L.F.C.de., (2003). Raman Spectra of Carotenoids in Natural Products, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 59(10), 2207–2212. doi: 10.1016/S1386-1425(03)00064-7
- Xie, W., & Wang, H., (2021). Grafting Copolymerization of Dual Acidic Ionic Liquid on Core-Shell Structured Magnetic Silica: A Magnetically Recyclable Brönsted Acid Catalyst for Biodiesel Production by One-Pot Transformation of Low-Quality Oils, *Fuel*, 283(118893), 1–12. doi: 10.1016/j.fuel.2020.118893
- Yuan, C., Jin, Z., & Xu, X., (2012). Inclusion Complex of Astaxanthin with Hydroxypropyl-β-cyclodextrin: UV, FTIR, 1H NMR and Molecular Modeling Studies, *Carbohydrate Polymers*, 89(2), 492–496. doi: 10.1016/j.carbpol.2012.03.033
- Zambrano, M.V., Dutta, B., Mercer, D.G., MacLean, H.L., & Touchie, M.F., (2019). Assessment of Moisture Content Measurement Methods of Dried Food Products in Small-Scale Operations in Developing Countries: A Review, Trends in Food Science & Technology, 88, 484–496. doi: 10.1016/j.tifs.2019.04.006

Zhang, S., Li, X., Ai, B., Zheng, L., Zheng, X., Yang, Y., Xiao, D., & Sheng, Z., (2022). Binding of βlactoglobulin to Three Phenolics Improves the Stability of Phenolics Studied by Multispectral Analysis and Molecular Modeling, *Food Chemistry: X*, 15(100369), 1–11. doi: 10.1016/j.fochx.2022. 100369