Refining technology of crude deep-sea fish oil

The content of polyunsaturated fatty acids (PUFA) in marine fish oil is abundant, among which eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) have attracted much attention [1], with various nutrition and health functions. [2], Research on prevention of cardiovascular disease [3-4], prevention of Alzheimer's disease [5], anti-tumor, anti-inflammatory [6], etc. is very extensive. The raw materials of deep sea fish oil mainly come from the pressed oil in the process of fishmeal processing, that is, the hair oil. Hair oil is generally darker, more viscous, and has a strong odor. The presence of phospholipids, proteins, trace metals and other impurities in crude fish oil has a great influence on the quality of fish oil, so it must be removed to achieve The standard of consumption.

The global ocean area accounts for 71% of the Earth's surface area and is therefore rich in marine resources. With the consumption of terrestrial resources, the development of marine resources has become a research hotspot in the new era. Marine fishery is dominated by fish, accounting for more than 80% of the world's total aquatic products. Marine fish processing products are growing rapidly, and the use of by-products from their processing to extract fish oil has become an important source of natural marine fish oil.

The crude fish oil obtained by cooking, pressing and centrifugation is used as raw materials, and is subjected to degumming, deacidification and decolorization steps to determine the appropriate addition amount of phosphoric acid, alkali liquor and activated clay, and the vacuum deodorization parameters are generally debugged during operation of the equipment. Not be considered. The change of fatty acid composition of fish oil and the physical and chemical indicators of fish oil before and after refining were tested, which provided a certain reference for the effective utilization of deep-sea fish oil.

The whole fish from the sub-fish of Mauritania with a water depth of 30~300 m. The scraps in the workshop include some fish heads (no need for squid head, squid head and sardine head), and the fish oil is extracted by cooking (80~90 °C).

Sodium thiosulfate, sodium hydroxide, potassium iodide, Wechsler reagent, glacial acetic acid, diethyl ether and absolute ethanol are all analytically pure, phosphoric acid (excellent grade); n-hexane (chromatographic grade), 37 fatty acid methyl ester standards, Methyl decanoic acid standard was purchased from Shanghai Anpu Experimental Technology Co., Ltd.; neutral activated clay, purchased from Jiangsu Junda Atta Cotta Materials Co., Ltd.

BT224S electronic analytical balance; DZF-6050 vacuum drying oven; MARS microwave digestion instrument; R250B rotary evaporator; DZKW-4 electronic constant temperature water bath; Avanti J-26x P refrigerated centrifuge, American Beckman Instrument Co., Ltd.; TRACE GC ULTRA gas phase Chromatograph (detector is FID), American Thermo Fisher; Xiangyi TG16-WS centrifuge; T960 automatic potentiometric titrator.

1.2 Experimental methods

1.2.1 Refining of crude fish oil

Referring to Crexi [8], Chew [9], He Liping [10] and other methods, some modifications were made to investigate the acidity, recovery and sensory quality of fish oil by volume fraction of phosphoric acid, excess alkali and activated clay. influences.

1.2.1. 1 Effect of phosphoric acid volume fraction on fish oil quality
Weigh a certain amount of fish oil, heat it to 70 ° C in a water bath and mix well. Then slowly add different volume fractions (85%, 80%, 75%, 70%, 65%) of phosphoric acid according to 1% of the quality of the fish oil. Stir well. Heat at 70 ° C for 1 min, then centrifuge at 10 000 r / min for 10 min, take the upper layer and weigh. The acid was deacidified with 4 mol/L, an oil base of 0.3% excess alkali and a theoretical alkali amount, and then decolorized with an activated clay of 20% oil quality.

1.2.1. 2 Effect of excess alkali on fish oil quality
Add 4 mol/L of excess alkali and theoretical alkali amount of fish oil quality of 0.5%, 1.0%, 1.5%, 2.0%, 2.5% to the degreased oil of the above optimal conditions (7.13×10-4×oil quality×acid) Value) of Na OH solution. After stirring evenly, heat to 70 ° C, keep warm for 30 min, then cool to room temperature, let stand for stratification, centrifuge at 10 000 r / min for 10 min, and remove the precipitate. Add deionized water with an oil quality of about 10% and 90 to 95 ° C. Repeat twice to aspirate the upper oil sample and weigh it. Decolorization was carried out with activated clay of 20% oil quality.

1.2.1. 3 Effect of the amount of activated clay on the quality of fish oil
The deacidified oil with the above optimal conditions was heated to 60 ° C, and the neutral activated clay was added at 5%, 10%, 15%, 20%, 25% of the fish oil mass, stirred for 30 min, and centrifuged at 10 000 r/min. Min, aspirate the upper oil sample and weigh it.

1.2.2 Sensory evaluation of deep sea fish oil and determination of physical and chemical indicators
Sensory evaluation: refer to SC/T 3502-2000; iodine value determination: refer to GB/T 5532-2008; insoluble impurities determination: refer to GB/T 15688-2008; acid value determination: refer to LS/T 6107-2012; peroxide value Determination: Refer to LS/T 6106-2012; Determination of moisture and volatile matter: refer to GB 5009.236-2016; Determination of unsaponifiable matter: refer to GB/T 5535.1-2008.

1.2.3 Determination of phospholipid content in fish oil

2 Results and analysis

Crude fish oil is generally more viscous, mainly because of the presence of some mucus, such as phospholipids, proteins, sugars, etc., which will seriously affect the quality of fish oil, so it must be removed. The experimental results showed that the crude fish oil had a low phospholipid content of 0.02%. Considering the production cost and the quality of fish oil, the dephosphorization is carried out by using phosphoric acid, mainly by using phosphoric acid to promote the conversion of non-hydrated phospholipids into hydrated phospholipids and the characteristics of water absorption and swelling to achieve sedimentation and removal. Phosphoric acid volume fraction for the quality of refined fish oil

It can be seen that when the volume fraction of phosphoric acid is 80%, there is a significant difference in acid value, and the acid value is the lowest at this time. When the phosphoric acid volume fraction is 85% and 80%, the color has a significant change. Considering that the acid value is a key factor affecting the quality of fish oil, a phosphoric acid having a volume fraction of 80% is selected. Li Chongchong et al. [13] added a phosphoric acid with a volume fraction of 60% of fish oil by 1% in the degumming of fish oil. The effect is better, which may be due to the difference in temperature and time of fish oil raw material and degumming. .

2.1.2 Optimization of excess alkali

More than 95% of the fats and oils are triglycerides, which are rancid to varying degrees due to exposure to air and light, and produce free fatty acids. When the free fatty acid content is too high, it will produce a pungent odor, and will accelerate the hydrolysis and rancidity of the neutral oil, and increase the solubility of the peptizing substances such as phospholipids and glycolipids and the fat-soluble substances in the oil. Free fatty acids are themselves catalysts for the hydrolysis of oils and phospholipids. Therefore, deacidification is a key process that affects grease loss and product quality in the oil refining process. The effect of excess alkali on the quality of refined fish oil is shown in Table 2.

It can be seen that with the increase of excess alkali, the acid value shows a downward trend as a whole, and the recovery rate shows a decreasing trend, which is consistent with the research results of He Liping et al. [10]. When the excess alkali is 1.5%, the acid value decreases drastically, and there is no significant difference between the acid value and the recovery rate of 2.0% and 2.5% of the excess alkali. At this time, the acid value reaches the level of refined fish oil in China's aquatic industry. standard. Considering factors such as fish oil quality, recovery rate and factory cost, 1.5% excess alkali (4 mol/L) is the most suitable deacidification condition, which is significantly lower than 4.0% excess alkali in Crexi et al. [8].

2.1.3 Optimization of the amount of activated clay added

Activated clay has a strong adsorption capacity for chlorophyll, peptized impurities, basic and polar atomic groups, and is therefore often used for oils that are difficult to decolorize. Some studies [14] found that boiled crude fish oil only needs to use white clay as a decolorizing agent. The effect of the amount of activated clay added on the quality of refined fish oil is shown in Table 3.

Effect of the amount of activated clay on the quality of refined fish oil

It can be seen from Table 3 that after decolorization, the color of the fish oil turns bright blue, which indicates that the activated clay can adsorb the pigment substances in the fish oil well, and the more the amount of activated clay, the better the adsorption effect. At the same time, with the increase of the amount of activated clay, the recovery rate of fish oil gradually decreased. When the amount of activated clay added is 20%, the acid value (KOH) is 0.32 mg/g, and the recovery rate is 72.62%. Liu Shucheng et al [15] studied the tuna oil refining process, and its refining process decolorization used 10% active clay addition, the recovery rate was 81.37%.

In summary, the optimum process conditions for fish oil refining are: phosphoric acid volume fraction of 80%, excess alkali of 1.5%, and active clay addition of 20%.

It can be seen that the quality of the deep-sea crude fish oil is good. Since the fish oil is extracted in the vicinity of Mauritania after the fish is caught, the fish oil is fresh and the transportation process is well preserved. Many indicators have reached the first-class standard of crude fish oil. The oxidation value is very low, in line with the first grade standard of refined fish oil, but the impurity content is high. After refining, the fish oil is clear and transparent, without acid odor. The acid value is an important indicator of fish oil quality, which is decreased by 94.7%. The peroxidation value of refined fish oil is 0.76 mmol/kg, indicating that the whole refining process is well controlled and the quality of fish oil is high. No oxidative rancidity occurred. The impurity content decreased from 3.66% to 0.02%, the decline rate reached 99.5%, and the iodine value did not change much. Therefore, the refining process conditions can better control the product quality, and the indexes of refining deep sea fish oil are all refined in the aquatic industry. The first grade standard of fish oil is of high quality. The physicochemical indexes such as acid value, peroxide value and iodine value after refining are slightly better than the tilapia oil obtained by the vacuum refining method of Zhao Kuo et al. [16].

2.3 Changes in fatty acid composition during fish oil refining

The fish oil was refined according to the optimal process conditions, and the crude fish oil, the crude fish oil stored at -80 ° C for 5 months, and the fatty acid composition of the fish oil during the refining process were analyzed. The results are shown in Table 5.

Note: crude fish oil 1 is fresh crude fish oil; crude fish oil 2 is crude fish oil after storage for 5 months; ND is not detected; each line of different letters indicates significant difference (p