Abstract

Australia is the world's largest producer of lobster after the USA and Canada with annual production around 10,000 tons, valued at approximately $400 million. The Australian lobster processing industry annually produces about 3,000 tons of by-products including heads, shells, and livers not only costing about $500,000 for disposal treatments, but also considering environmentally unfriendly. Continued production of lobster processing by-products (LPBs) without any attempt for efficient utilisation will represent both financial and environmental challenges to the Australian lobster processors. However, analysing chemical composition of Australian LPBs showed these biomaterials are rich in proteins (43.5, 41.1, and 29 % in heads, livers, and shells respectively), chitin (25 and 19.8 % in shells and heads), lipids (24.3 % in livers), and minerals (36 and 31.6 % in shells and heads). These components could be economically recovered for applications in food and nutraceutical products by developing appropriate processes using emerging technologies. As there is the global demand for lobster products while the lobster extracts have a wide range of applications in several aspects, utilisation of Australian LPBs for production of functional and nutraceutical ingredients would not only generate economic benefits but also reduce the waste problems.

Although lobster livers contain a high proportion of protein and lipids, utilisation of this material faces a significant challenge due to its Arsenic (240 mg/kg) and Cadmium (8 mg/kg) content over the regulatory limits for fishery products (2 mg/kg). However, using supercritical carbon dioxide (SC-CO_2) extraction for recovery of lipids from lobster livers has shown significant advantages. Nearly 94 % of the lipids in lobster livers were recovered by the SC-CO_2 extraction at 35 MPa, 50 ^oC, in 4 hours. The extracted lipids contained approximately 31.3 % polyunsaturated fatty acids (PUFAs) in which long chain ω-3 fatty acids (DHA, EPA) accounted for 58 %. As compared with the lipids extracted by the Soxhlet method, PUFAs in the SC-CO_2 lipids was fourfold higher (31.3 vs 7.8 %) while this value for ω-3 fatty acids were six fold (18 vs 3.1 %). Moreover, the SC-CO_2 lipids were rich in carotenoids (astaxanthin 41.6 μg/mL, β-carotene 70.4 μg/mL). Particularly, inorganic Arsenic and Cadmium contaminants of the SC-CO_2 lipids were very low compared with the regulatory limit of Australian New Zealand Food Standard (ANZFS) (0.05 and under 0.01 mg/kg vs 2 and 0.5 mg/kg, respectively). Total amount of Arsenic in the SC-CO_2 lipids was fourteen fold lower than that in the Soxhlet lipids (2.2 vs 31 mg/kg) whereas this figure for

Cadmium was twenty-seven fold. With very low heavy metal contaminants, the extracted lipids could be used for food and nutraceutical applications.

Several available techniques could be applied for protein recovery from lobster heads but isoelectric solubilisation and precipitation (ISP) coupled with ultrasound performed as a highly effective method. For protein recovery by the ISP method, cold-base extraction (4 ^{o}C) is usually preferable but extraction protein recovery (EPR) obtained in this study was relatively low (63.2 %). Although hot-base extraction could improve with a significant increase in EPR from 63.2 to 85.1 %, the harsh conditions of the hot extraction (85 ^{o}C) could degrade protein quality. Ultrasonic extraction exhibited its high efficiency with a significantly high EPR compared with the cold-base extraction (63.2 vs 90.5 %) and the ultrasonic EPR was equivalent or even higher than that of hot extraction (85.1 vs 90.5 %). Ultrasonic extraction was considerably affected by water ratio indicated by the fact there was a significant difference in the EPR between water ratio of 6 and 8 mL/g. High EPR (99 %) could be even achieved in very short time (5 minutes) as water ratio of 8 mL/g was used. Over 82 % protein in the extracted solution was efficiently recovered by isoelectric precipitation at the pH 3.5. Adding chitosan with dose of 200 – 250 mg/L could improve precipitation protein recovery (PPR, 86.6 %). Protein recovered by the ultrasonic extraction contained more protein than by the hot-base extraction (83.2 vs 78.6 %) whereas essential amino acids (EAAs) of ultrasonic-extraction protein was significantly higher than hot-extraction protein (38 vs 30.4 %). Moreover, digestibility of the protein extracted by ultrasound was significantly higher than that of the hot-extraction protein (78.4 vs 58.4 %), which was comparable to that of egg protein (88.1 %).

In contrast to protein in lobster heads, proteins in lobster shells are tightly associated with chitin intensified by mineralisation for a strong shell structure. Since lobster shells contain high chitin with several excellent functional properties and versatile biological activities which have many useful applications in agriculture, food, cosmetics, pharmaceuticals, and biomedicine, production of chitin from lobster shells has become a great interest. Although several approaches could be applied for removal of protein and minerals from lobster shells, chemical deproteinisation and demineralisation is the most common method. However, this method has several drawbacks such as potential negative impacts to the environment, negative effects on physicochemical properties of final products, not allowing the recovery of food compatible protein and minerals. In this study, protein in lobster shells was efficiently removed by microwave-intensified enzymatic deproteinisation with alcalase to shells ratio 1 %, 55 ^{o}C, and pH 8.0 for 90 minutes. High efficiency

of the microwave over the conventional process was indicated by its high weight loss (30.3 vs 24.6 %) and deproteinisation degree (85.8 vs 58.03 %) but low residual protein in deproteinised shells (65.4 vs 96.4 mg/g). Moreover, protein recovered from the microwave process had good functionalities (solubility over 85 %, water binding 2.5 fold higher than that of egg protein, fat binding 2.3 mL/g, emulsification 51.3 % and foaming capacity 91.3 %), high nutritional quality (74 % protein, 34 % EAAs, low lysine/arginine ratio: 0.7), which could be used as a functional or nutrient ingredient in food products. In addition, the generation of enzymatically deproteinised shells (EDPS) with low protein residues could facilitate a sequential demineralisation step.

Although demineralisation of the EDPS with strong inorganic acids has high efficiency, this process is environmentally unfriendly and harmful for chitin quality caused by deacetylation and depolymerisation. Alternatively, demineralisation of the EDPS with lactic acid intensified by microwave has indicated several significant advantages. The process was optimised at a mild condition (lactic acid to shell (LA/S) ratio of 18 mL/g, 100 ^{o}C, and 23 minutes) achieving a high degree of demineralisation (99.2 %). Chitin obtained from the optimised process had low residues of protein (1.6 %) and mineral (0.99 %), which is suitable for advanced applications. Its mineral residue was tenfold lower than that of chitin demineralised by the stirring method (0.99 vs 10 %). As compared with chitin conventionally demineralised by lactic acid with LA/S ratio of 50 mL/g, 100 ^{o}C in 60 minutes, mineral residue of lobster chitin was 3.7 fold lower (0.99 vs 3.7 %) or it was comparable to chitin demineralised by kitchen microwave with LA/S ratio of 200 mL/g, 121 ^{o}C in 30 minutes (0.99 vs 0.22 %). The chitin obtained by this demineralisation process had a chemical structure very similar with the high quality chitin based on analysis from the FTIR-spectra. Particularly, this process also allowed the recovery of minerals from lobster shells with a good mineral profile (87 % calcium) potentially useful as another value-added product.

Extracts recovered from Australian LPBs were demonstrated with high quality attributes, which show good potential for food and nutraceutical applications. Lobster chitin with high DA (89.9 %) and high binding capacity of fat and cholesterol tested on various oils (7.5 – 16.1 g/g for fat and 258.7 mg/g for cholesterol) indicates its promising application for weight loss and cholesterol management products. Fat, cholesterol binding property over its high-quality counterparts demonstrates the great potential of lobster chitin for fat blocker production. Minerals recovered from lobster shells under the form of lactate salt with a good profile (87 % calcium) show this product could be directly marketable as a food ingredient since calcium lactate has several

applications in the food industry. Moreover, high solubility and bioavailability of lobster calcium over a commercial dietary calcium supplement (60.6 vs 8.3 % and 11.3 vs 1.9 %) demonstrated its potential in the production of calcium supplements. Lobster proteins with high protein content (74 - 83.2 %), rich in EAAs (34 - 39 %), and easy digestibility (78.4 - 96.9 %) could be directly marketable as lobster protein powders (LPPs). Possessing pleasant flavours, application of LPPs for flavouring purposes was demonstrated by food panellists. LPPs (1 %) formulated with lobster lipids generated pleasant flavours in the lobster flavour blends. Strong flavour of lobster lipids showed its promising application as flavorants. Using 2 % lobster lipids for production of infused lobster oils or 4 % for salt plated with lobster lipids were demonstrated by the evaluation panel. Particularly, richness in PUFAs (31.3 %), omega-3 (18 %), carotenoids (astxanthin 41.6 μg/mL and β-carotene 70.4 μg/mL) of lobster lipids demonstrated this product could be directly marketable as a dietary supplement.

Production of functional and nutraceutical lobster extracts from Australian LPBs was found to be not only promising at the laboratory scale but also feasible at the industrial scale. Economic feasibility was analysed for production of lobster extracts from different LPBs (livers, heads, and shells) in three production scales (A, B, and C equivalent to using 30, 52.2, and 74 % of Australian LPB availability, respectively) using the commercial simulation software, Superpro Designer. The result shows production of extracts from lobster shells by the integrated process required more total capital investment (TCI) than that from other LBPs (heads or livers) in all scales (17.414 vs 6.418 and 3.379 million USD, 22.872 vs 11.010 and 3.919 million USD, 27.559 vs 13.584 and 4.412 million USD for scales of 30, 52.2, and 74 %, respectively). However, production of lobster extracts by the integrated process was found to be the most financially interesting since this process could generate the highest net present value (NPV, 37.665 vs 15.193 and 5.777 million USD, 81.637 vs 42.729 and 9.535 million USD, 126.502 vs 72.504 and 13.975 million USD for scales of 30, 52.2, and 74 %, respectively). Production at the large scale (using 74 % of LPBs) was more feasible than at the small scales (using only 30 or 52.2 % of LPBs) found in all LPBs (livers, heads, and shells). This was determined by the increases in revenues and profitability due to upscaling over the rise in its TCI and AOC (eg. TCI of lipid production increased by 16 - 30.6 % while its NPV grew by 65 – 141.9 %). Although the cost of LPBs with 1,000 USD/ton was applied for all the processes, their profitability was still high. Even in the worse scenario with only 30 % of Australian LPB availability for utilisation, these industrial productions were still feasible indicated by their positive NPVs and not-over-three-year payback time (4.608 million USD and 2.63 years, 13.270 million

USD and 2.20 years, and 36.697 million USD and 2.22 years for production extracts from lobster livers, heads, and shells, respectively). All these results reveal that investing on these lobster projects are financially attractive due to the low risk with the low TCIs and AOCs and the short payback time.