Process design and economic evaluation of green extraction methods for recovery of astaxanthin from shrimp waste

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Abstract

Sunflower oil (SF) and its methyl ester as well as supercritical fluid (SC-CO2+ 5 wt% EtOH) have recently been shown as potential green solvents which could substitute traditional organic solvents. This study investigates the economic feasibility of using these green solvents to extract astaxanthin (ASX) from shrimp processing waste. The feasibility of commercial use of the green solvents under plausible process conditions is compared to extraction with a mixture of hexane: isopropanol (Hex:IPA). The process flowsheets describing these processes were modelled by means of SuperPro Designer and Aspen Plus. The highest ASX extraction yield was achieved using Hex:IPA (26.4 kg/year), the lowest yield using SC-CO2+ 5 wt% EtOH (12.8 kg/year). The cost of producing pure ASX for these processes was about 0.6 and 0.82 $/mg of ASX, respectively. The concentration of ASX obtained by the extraction processes with SF or the methyl ester of SF (ME-SF) was 2.5 and 153 ppm with a production cost of 0.06 and 0.16 $/mg of ASX, respectively. In addition, shrimp feed production was considered as a feasible application of the low concentration ASX obtained by SF extraction. A combination of ASX extracted with SF and synthetic ASX yielded a shrimp feed
production cost comparable to the current market price. The calculated feed price based on the ASX production cost of the other green processes, ME-SF and SCFE, resulted in a significantly higher production cost.

*Keywords:* Shrimp processing waste, Astaxanthin, SuperPro Designer, Aspen Plus, Economic evaluation, Shrimp feed application

1. Introduction

Despite the fact that marine sources are limited, harvested fish and marine crustacean are not optimally utilized. A major portion is either discarded as waste or used for low value products (e.g. silage, fishmeal or mince) resulting in a low profit for the fishery industry (Kim, 2014). Among different seafood sources, shrimp is considered the economically most important internationally traded fisheries commodity. However, the economic importance of shrimp needs to be reconciled with considerable concern about the environmental impacts of shrimp fisheries (Gillett, 2008). During the shrimp processing, depending on the species, size, and shelling procedure, about 40–50% of the raw material weight is discarded as non-edible parts. These residues still contain valuable nutrients and functional compounds such as mineral salts, proteins, chitin, and lipids as well as pigments, mainly ASX (Higuera-Ciapara et al., 2006). As shown in Table 1, total ASX content regardless of the shrimp species, varies between 3.1 and 8.4 mg/100 g wet basis. ASX with an estimated global market value of about US$257 million (März, 2008), is used as feed additive for shrimp, salmon and other farmed fish, for human consumption, as well as in cosmetics. Therefore, developing a full utilization scheme of the shrimp catch by identification and extraction of this natural compound can improve the economy of the
fishing industries, replace synthetic ASX and minimize the pollution potential and environmental impact made by shrimp residue.

The extraction efficiency of ASX depends on the solvent used, its polarity, and the solubility of ASX in the extraction solvents. Traditional processes are based on the use of fossil-derived organic solvents and characterized by being expensive, inflexible, potentially harmful and time consuming due to the multiple extraction steps required. Government restrictions (NIOSH, 1987) on the use of organic solvents (e.g. limits on solvent exposure and environmental emission and/or effects on workers’ health and safety), combined with the simultaneous increase of consumer demand for natural-derived products instead of synthetic compounds, have led to a growing interest in applying more environmentally friendly techniques both in the ASX production (Haque et al., 2016) and recovery steps. Due to the oil solubility of ASX (Sachindra and Mahendrakar, 2005), one promising alternative to the traditional processes is to substitute the organic solvents with edible oils. Apart from being environmentally friendly and a sustainable extraction method, oil plays a barrier role against oxygen and consequently retards the oxidation time and degradation rate of the ASX extract (Pu et al., 2010). In addition, vegetable oils contribute as an energy source in aquaculture feed and the use of pigmented oil in feed formulations thus can serve the dual purpose of pigment carrier as well as a source of lipid energy. Among common vegetable oils, sunflower oil (SF) was applied for extraction of carotenoids, but due to its high viscosity the extraction yield was low even at high temperatures (Sachindra and Mahendrakar, 2005; Razi Parjikolaei et al., 2015a). Therefore, beside the SF, its methyl ester (ME-SF) was introduced and applied as an alternative solvent (Razi Parjikolaei et al., 2015a). ME-SF is a renewable, non-toxic and biodegradable solvent (Reiser et al., 1956) which has lower viscosity and higher solubility for ASX and hence enhances the extraction yield.
Table 1: Astaxanthin content in various shrimp species residue measured after non-green organic solvent extraction

<table>
<thead>
<tr>
<th>Shrimp species</th>
<th>Common name</th>
<th>Astaxanthin (mg/100 g of WB by-product)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parapeneaopsis stylifera</td>
<td>Kiddi shrimp</td>
<td>8.4</td>
<td>Pu (2010) for each species</td>
</tr>
<tr>
<td>Metapeneaues dobsoni</td>
<td>Kadal shrimp</td>
<td>8.4</td>
<td></td>
</tr>
<tr>
<td>Penaeus indicus</td>
<td>Indian shrimp</td>
<td>8.3</td>
<td>Razi Parjikolaei et al. (2015a)</td>
</tr>
<tr>
<td>Penaeus monodon</td>
<td>Giant-tiger shrimp</td>
<td>7.5</td>
<td>Guillou and Khalil (1995)</td>
</tr>
<tr>
<td>Pandalus borealis</td>
<td>Northern shrimp</td>
<td>3.7</td>
<td>Razi Parjikolaei et al. (2015a)</td>
</tr>
<tr>
<td>Pandalus borealis</td>
<td>Northern shrimp</td>
<td>3.1</td>
<td>Sindhu and Sherief (2011)</td>
</tr>
<tr>
<td>Aristeus alcocki</td>
<td>Arabian red shrimp</td>
<td>8.7</td>
<td>Sachindra et al. (2006)</td>
</tr>
<tr>
<td>Penaeus indicus</td>
<td>Indian shrimp</td>
<td>4.1</td>
<td>Sánchez-Camargo et al. (2011)</td>
</tr>
<tr>
<td>Farfantepeaues paulensis</td>
<td>Red-spotted shrimp</td>
<td>5.3</td>
<td>Sánchez-Camargo et al. (2011)</td>
</tr>
<tr>
<td>Penaeus monodon</td>
<td>Giant-tiger shrimp</td>
<td>5.0&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Babu et al. (2008) for each species</td>
</tr>
<tr>
<td>Penaeus indicus</td>
<td>Indian shrimp</td>
<td>3.7&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Metapeneaues monoceros</td>
<td>Brown shrimp</td>
<td>3.4&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Astaxanthin extraction was assisted by enzymatic treatment; WB: wet basis

Moreover, supercritical fluid extraction (SCFE) is a common green separation technique in the field of food, nutraceutical, and pharmaceutical applications (Casas et al., 2009; Straccia et al., 2012). By means of SCFE, it is feasible to selectively extract desired compounds without leaving toxic residues in the extracts and reducing the risk of degradation of labile compounds like ASX. In addition, according to several studies (Maciás-Sánchez et al., 2008; Corrêa et al., 2012), and as evident from previous lab scale experiments (Razi Parjikolaei et al., 2015b) when 5 wt% EtOH was employed as a polar modifier or as co-solvent, it changes the polarity of the supercritical fluid (SCF) and consequently it has a significant effect on increasing the ASX extraction yield.
Although little information about scale up criteria and cost of manufacturing is available for SCFE processes (Prado et al., 2010; Prado et al., 2012; Fiori et al., 2014), vegetable oils and/or their ME extraction processes have been studied in laboratory scale only and no information is available on the processes’ economic and environmental aspects. Consequently, their scale-up and commercialization feasibility are unknown. As a result, a study comparing different alternatives, which might lead to an identification of more suitable processes, is essential. Computer-aided process design and simulation tools such as SuperPro Designer and Aspen Plus can facilitate development, scale-up, and cost analysis of different scenarios for the ASX extraction processes. In addition, process simulators offer the opportunity to compare different processes through integrated material/energy balances, equipment sizing, utility requirements as well as environmental assessment (Kawachale and Kumar, 2011; Misailidis et al., 2009).

Based on previous experiments reported by Razi Parjikolaei et al.(2015a, 2015b), SF, ME-SF, and SCFE (SC-CO2+ 5 wt% EtOH) were chosen as promising alternative solvents offering attractive advantages compared to traditional non-green organic solvent extraction. In the present study, using the commercial simulation software SuperPro Designer and Aspen Plus, a conceptual design of industrial scale processes for the green extraction of ASX using the mentioned three green solvents is performed. As a base case, extraction using the non-green organic solvents Hex:IPA is considered for evaluating the economic implications of the suggested green process designs. At the end, possible applications of the final products from the suggested process designs, in particular in shrimp feed formulation, will be discussed.
2. Process description

Four different extraction processes were simulated in SuperPro Designer v8.0 (Intelligen Inc., MIT) to evaluate a large scale production of ASX from shrimp processing waste:

1. Extraction with a fossil based organic solvent mixture (Hex: IPA, 60:40 v/v)
2. Extraction with sunflower oil
3. Extraction with sunflower oil methyl ester
4. Supercritical fluid extraction (SC-CO$_2$ + 5% wt EtOH).

In all cases, the amount of shrimp processing waste (*Pandalus borealis*) was set to 830 tons/year based on production information from Launis Fiskekonserves A/S (Aalbæk, Denmark). The extraction
processes is to be added to the existing process facilities and the waste stream therefore is considered free of charge. Further, the flowsheets were simulated and designed based on the optimum conditions found in laboratory scale experiments reported by Razi Parjikolaei, et al. (2015a, 2015b).

2.1. Non-Green Organic Solvent Extraction

The ASX extraction process using Hex:IPA is modeled as a batch process as shown in Fig. 1. The first process step is a grinder (GR-101) which reduces the waste particle size from 2.5 to 0.6 mm (Razi Parjikolaei et al., 2015a). The ground waste(S-109) is mixed with Hex:IPA (60:40 v/v) at a solvent to waste ratio of 5:1 at ambient conditions. The extraction is carried out in the agitated extraction vessel R-101. The extract (S-104) is then separated from the solid residue (S-103) by the centrifugeDS-101. The solid residue S-103 is recycled to the extraction vessel in order to complete the ASX extraction. According to the lab scale experiments (Razi Parjikolaei et al., 2015a), four batch extractions with fresh organic solvents are necessary to extract all the ASX contained in S-109. The combined ASX extracts from each batch are collected in the agitated vessel R-102 where IPA is removed from the extract by washing with an equal volume of 0.1% NaCl solution (Razi Parjikolaei et al., 2015a; Sachindra and Mahendrakar, 2006). Salt water and IPA(S-123) is separated in the decanter and ASX along with the hexane are collected as the supernatant (S-122). The aqueous IPA solution can either be sent to the water treatment section or recycled inside the process. In the latter case, the presence of the IPA-water azeotrope limits the maximum IPA purity to 87.9 wt% when ordinary distillation is used as separation method. To overcome the azeotrope composition, more complex purification steps, including azeotropic distillation or membrane separation has to be used in order to recycle pure IPA in the process. Since in the present work, the interest in the non-green extraction process is limited and used only as a base case, the feasibility of IPA recovery and/or reuse is not considered.
In order to recover the ASX from the stream S-122, hexane has to be evaporated. The recovery step is simulated as a combination of three unit operations: evaporation, spray drying, and condensation. This reduces the environmental effect of this hazardous solvent and reduces the production costs. Evaporation of hexane (nearly 80%) from ASX is done at 30 °C in EV-101 followed by a spray dryer (SDR-101) where the inlet/outlet temperatures of air are 180/110 °C (Raposo et al., 2012). Hexane recovery is done by condensation (HX-102) at 5°C. The product (S-133) is taken to be ASX with 100% purity. It should be noted that based on the lab scale experimental data, about 13% of the hexane and IPA was absorbed by the shrimp waste during the extraction step while the remaining hexane (S-105) is expected to be recovered with a minimal loss after the evaporation/condensation units and returned to the extraction section (S-108).

2.2. Green Solvent Extraction

2.2.1. Sunflower oil

The industrial scale ASX extractions using the green solvents, SF and ME-SF, are designed based on the one-step experimental results in lab scale of Razi Parjikolaei, et al. (2015a). It should be noted that in both solvents, the highest ASX content was achieved at a temperature of 70°C and a solvent to waste ratio of 9:1 (Razi Parjikolaei et al., 2015a). Similar to the organic solvent extraction, the SF extraction process reported in Fig. 2 consists of a grinder (GR-101) to reduce the waste particle size, a stirred extractor (R-101) and a centrifuge (DS-101). The extraction consists of: charge of shrimp waste: SF, 1:9 w/w, soaking period of 2 h, heating to 70°C, and extraction under agitation at 70°C for 30 min. It has been evaluated that about 20% of the applied SF was absorbed by the shrimp waste (S-105). Further, SF extracts about 60% of the total ASX (Razi Parjikolaei et al., 2015a) contained in the shrimp waste in S-102.
Fig. 2. Process flowsheet for the full scale ASX extraction process using sunflower oil. The processes in the box refer to the shrimp feed production application.

The concentration of ASX in the final product is 2.5 ppm. The low concentration obtained could limit its direct application since it is difficult to identify a possible market for this product. Oil enriched in ASX though could represent a resource for the production of food and aquaculture.

If the possibility of an additional concentration step is considered, according to the best knowledge of the authors, possible processes successfully applied for concentration of carotenoids from oils, are: adsorption chromatography (Baharin et al., 1998), membrane filtration (Darnoko and Cheryan, 2006), and molecular distillation (Batistella et al., 2002). In the first process, organic solvents (mostly Hex and IPA) are involved and hence the process cannot be labelled green and does not represent an alternative to the Hex:IPA process. On the other hand, in the latter two cases, the high viscosity of the sunflower oil limits the efficiency of the separation. To overcome this problem, another green solvent for the ASX extraction process, ME-SF, is introduced and designed based on the previous study of Razi Parjikolaei, et al. (2015a).
2.2.2. Methyl ester of sunflower oil

As shown in Fig. 3, the extraction process using ME-SF is similar to the SF extraction process except that the recovery of ASX achieved in S-106 is 80%. Moreover, due to lower viscosity of ME-SF compared to SF, the amount of solvent retained by the solid waste was evaluated to be 15%. In order to concentrate the ASX in the final product, ordinary distillation could be considered as the first choice because of its separation efficiency (Kiss, 2014). However, in the case of natural products, ordinary distillation is not a suitable method due to the risk of degradation of natural compounds that are exposed for a long time to high temperatures. To circumvent this drawback, molecular distillation appears to be the most appropriate method for the separation of high molecular weight compounds with low vapor pressures. However, despite the high number of applications reported in the literature (Solaesa et al., 2016; Borgarello et al., 2015; Posada et al., 2007), the modeling of molecular distillation apparatus still represent a challenge.

Two main approaches have been reported; the former is based on balance equations (Li and Xu, 2014; Micov et al., 1997), the latter uses process simulators (Durán et al., 2010; Mallmann et al., 2009). The
last approach was chosen in the present work and Aspen Plus v8.6 was used as the process simulator. Molecular distillation is not included as a stand-alone unit operation and the simulation is built up following the three step procedure introduced by Durán, et al. (2010). The first step includes the creation of a property database for the compounds not included in the simulator, in this case the ASX. Besides the physico-chemical properties of ASX obtained by the Aspen Plus, the estimation method proposed by Nannoolal, et al. (2008), based on group contributions and interaction between functional groups, was selected to estimate the ASX vapor pressure. In the second step, the molecular distillation was implemented in Aspen Plus as a distillation column with a single stage (Durán, et al.; 2010). The rigorous distillation model RadFrac was selected, the operative pressure was set to 1000 Pa to prevent compound degradation (Rao et al.; 2007). Using the sensitivity analysis tool implemented in the simulator, the distillate flowrate was optimized to obtain a final product with a concentration of 153 ppm of ASX. The UNIQUAC thermodynamic model (Durán, et al.; 2010) was selected and a separation efficiency of 90% was used to take into account the deviation from the ideal stage behavior. When the optimization was computed, a residue mass flowrate of 0.25 kg/min with the required ASX purity was obtained. For completion, also the third step of the procedure of Durán, et al. (2010) should be applied. This step includes the comparison between the simulated and the experimental data. In this case, experimental data are not available but the results obtained are comparable to the cited cases of separation of natural products (e.g. thymol, tocotrienol, and omega 3 polyunsaturated fatty acids) by molecular distillation (Solaesa et al., 2016; Borgarello et al., 2015; Posada et al., 2007).

As a result, as shown in Fig. 3, a molecular distillation unit operation (V-102) is included and the concentration and distribution of the compounds is chosen based on the data obtained by the Aspen Plus simulator. The pigmented ME-SF from each extraction batch is collected in a storage tank (V-101) to be charged to V-102. A continuous distillation is carried out at a pressure of 1000 Pa with a
temperature of 140°C and a feed flow of nearly 12.7 kg/min. ME-SF is collected as the distillate and returned to the extractor (S-109). This reduces the amount of fresh solvent needed for each batch extraction. The distillation unit increases the concentration of ASX in the product stream (S-110) from 3.04 to 155 ppm which is suitable as feed and food diet additives (Torrissen and Christiansen, 1995; Yamada et al., 1990).

Fig. 4. Process flowsheet for the full scale ASX extraction process using supercritical fluid extraction (SC-CO2+ 5% EtOH)
2.2.3. **Super critical fluid solvent**

The semi-continuous extraction process of ASX on an industrial scale, using a mixture of SC-CO\(_2\) and EtOH (5%wt), is modeled based on the optimum conditions found in laboratory scale experiments reported by Razi Parjikolaei, et al. (2015b) and shown as Fig. 4. Since moisture represents almost 87% of the shrimp wastes weight and interferes with the effectiveness of the SCFE process, drying is a necessary step prior to extraction (Sun and Temelli, 2006). Therefore, shrimp waste is dried using a tray dryer (TDR-101) operated at 40°C for 5 h and then homogenized to maintain the constant particle size (0.6 mm) in all the batches using GR-101. In each batch, the dried ground shrimp waste is sent to the extractor (V-101). SC-CO\(_2\) and EtOH are mixed continuously after passing through a pump (P-102 and PM-101, respectively) and then heated (HX-102) to reach the optimum operating conditions found in a previous lab-scale study (SC-CO\(_2\)+ 5%wt EtOH; Pressure 400 bar; Temperature 55°C) (Razi Parjikolaei et al., 2015b). The solvent flow rate was calculated to be 125.5 kg/min using the same ratio of solvent to feed mass (S/F) as used in the lab scale. A cyclone separator (V-102) at ambient operating conditions was included to allow periodic discharge of the ASX extracted during the process (S-104).

In order to concentrate the ASX from this stream, EtOH has to be evaporated. Similar to the non-green solvent process design, the evaporation and crystallization step is simulated as two extra unit operations: evaporation and recovery. EtOH is recovered from the ASX stream using a process similar to the non-green organic solvent recovery section, combining an evaporator (EV-101) with a spray dryer (SDR-101) followed by a condenser at 5°C (HX-101). The final product (S-113) is taken to be ASX with 100% purity. Nearly 3% of EtOH is assumed to be absorbed by the shrimp waste during the extraction step while a 2% CO\(_2\) loss is also considered mainly due to depressurization of the supercritical extractor at the end of each batch extraction (Prado et al.; 2012). The recovered EtOH (S-
110) and CO₂ (S-101) are recycled to the extraction section after reaching the required operating conditions.

3. Cost Analysis and Economic Evaluation

Since definitive information is not available for the market of ASX concentrated in SF and ME-SF, the goal of the cost analysis is to determine the cost of ASX production with the green techniques and to evaluate if the cost is sufficiently low, that the creation of a market for green production of ASX is feasible compared to the traditional organic solvent extraction process. Moreover, as the quality and the concentration of ASX in the final products are different so are their potential final applications. Thus a direct comparison between the SF or ME-SF processes with the two processes using either SCFE or an organic solvent mixture could not be done with absolute certainty. However, it is feasible to perform a full economic analysis of each of the four process scenarios that includes both economic and qualitative indexes. For the economic part capital and operative costs along with the total annual cost and the product unit cost are considered. The quality parameters include the process yield, the products’ phase and ASX concentration, and the annual production capacity.

3.1. Economic Parameters Evaluation

To perform the economic evaluation, all the simulations were set in design mode, where SuperPro Designer determined the size of the equipment based on the input streams and would select more than one piece of equipment based on physical limitations. The characteristic equipment dimensions have been used for the evaluation of the purchase cost (PC) according to prices from the Matche database (www.matche.com). According to Eq. (1), the PC was increased by 20% to take into account the minor equipment that are not listed in the simulation flowsheet.
Table 2: Capital cost assumptions used to estimate the capital cost for the four ASX extraction process designs

<table>
<thead>
<tr>
<th>Direct Cost (DC)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Installation</td>
<td>0.3 PC*</td>
</tr>
<tr>
<td>Installation unlisted equipment</td>
<td>0.5 (0.3 PC)</td>
</tr>
<tr>
<td>Piping</td>
<td>0.35 PC</td>
</tr>
<tr>
<td>Instrumentation</td>
<td>0.40 PC</td>
</tr>
<tr>
<td>Insulation</td>
<td>0.03 PC</td>
</tr>
<tr>
<td>Electrical facilities</td>
<td>0.10 PC</td>
</tr>
<tr>
<td>Buildings</td>
<td>0.45 PC</td>
</tr>
<tr>
<td>Yard improvements</td>
<td>0.15 PC</td>
</tr>
<tr>
<td>Auxiliary Facilities</td>
<td>0.40 PC</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Indirect Cost (IC)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Engineering</td>
<td>0.25 DC</td>
</tr>
<tr>
<td>Construction</td>
<td>0.35 DC</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Other Cost (OC)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Contractor’s fee</td>
<td>0.05(DC+IC)</td>
</tr>
<tr>
<td>Contingency</td>
<td>0.10(DC+IC)</td>
</tr>
</tbody>
</table>

PC: Purchase cost

\[
P_C = \sum_{i=1}^{N_{equipment}} PC_i + \text{unlisted equipments} = 1.2 \sum_{i=1}^{N_{equipment}} PC_i
\]  

Since the purchase cost takes into account only the vendor’s selling price, the total capital investment (TCI) was evaluated to include the contribution of installation, piping, instrumentation, building, etc. The different contributions were grouped in three categories; direct costs (DC), indirect costs (IC), and others (OC) according to Eq. (2). The single term contributions are reported in Table 2.

\[
TCI = PC + \text{installation} + DC + IC + OC
\]  

For the supercritical extraction process the equipment’s PC was corrected with the appropriate pressure coefficient as reported by Peters et al, (2004).
The construction year was assumed to be 2015 and consequently the prices were updated to 2015 prices using the published chemical engineering index (Chemical Engineering, 2015). A payback time of 5 years was considered to annualize the total capital investment.

For the evaluation of the operative costs the equipment occupancy was set for 24 h assuming the plant to be operated in three daily shifts for 330 days, which represents a total of 7920 h of operation per year. Thirty days were considered for plant maintenance each year. For the organic solvent extraction the treatment cost related to the aqueous IPA stream was evaluated in 0.056 $/m³ according to Turton et al. (2003). Table 3 shows the basis used for estimating the operating costs, categorized as raw materials, utilities, labour requirements, facility-dependent and miscellaneous costs.

As a global economic index, the total annual cost (TAC) evaluated according to the Equation (3):

$$ TAC = \text{operative cost} + \frac{TCI}{\text{payback time}} $$

(3)
3.2. Qualitative parameters calculation

The first parameter considered is the ASX recovery or the process yield, defined as the ratio of the amount of ASX in the final product and the ASX in the waste feed. The annual production capacity gives an indication of the process potential and was evaluated as kg of product on annual basis. The product purity and the physical phase were also included among the qualitative parameters.

3.3. Comparison of extraction processes scenarios

The results of the economic analysis and the qualitative parameters are summarized in Table 4.

It is noted that since the simple one-step process design for SF extraction involves only three unit operations, it has the lowest total equipment cost and consequently the lowest capital investment followed by ME-SF extraction. The difference between the operating costs of the two green solvent
processes is a result of recycling ME-SF. The highest investment cost was observed for the high pressure SCFE technique. This has been considered as a limiting factor for its widespread commercial application. However, compared to the three green extraction processes, the operating cost of the process using fossil based organic solvents is the highest. This is mainly due to the large amount of solvents that have to be recovered, recycled or treated in the process and the large amount of water involved. Considering the TAC, a direct comparison between the four processes studied could be misleading due to the difference in the product specifications. In the case of the organic solvent extraction and the SCFE, the comparison is valid as in both processes the final product mass composition of ASX is 100%. As shown in Table 4, the SCFE has 47% reduction in the TAC compared to the organic solvent process. However, taking into account the difference in the annual production rate, the SCFC has an increase of about 27% in the product unit cost compared to the organic extraction.

This difference is not so impressive if the indirect environmental benefits of the green process are considered, e.g. pure ASX produced by SCFE, is free from potential solvent contaminations corresponding to a higher market appeal.

The extraction processes based on using SF and ME-SF have the lowest TAC and the highest annual product rate mainly depending on the amount of solvent used. In this case, the solvent is part of the final product and only for the ME-SF is partially removed in order to increase the ASX concentration. Once again, a comparison between these two processes is not possible since they differ in the final product concentration and the production rate. Knowing the limitations, the product unit cost was evaluated and reported in Table 4. As expected, the ME-SF process has a higher product unit cost (0.16 $/mg of ASX) but also a higher quality of the product. Therefore, the product from the ME-SF
extraction process is expected to have a wider range of possible applications and so should reach a higher market price compared to pigmented SF.

Since the production cost of ASX compared to traditional method appears reasonable, processes using these three green solvents could be further studied by looking at the size of the specific segments of the potential market.

4. Application of astaxanthin obtained by the green extraction processes

According to the BCC market research report (März, 2008), the carotenoids application market is divided into three main sectors; the feed, food and pharmaceutical sectors. While food and pharmaceutical applications account for nearly 26.6% and 14.6% of the market, respectively, feed applications take more than half of the market (58.8%). Farmed crustaceans and other aquatic animals are unable to produce ASX de novo and hence it must be available in their supplementary diet to meet metabolic nutritional requirements. Therefore, using ASX in the aquaculture industry is important not only from the standpoint of pigmentation to increase consumer demand, but also as a necessary nutrient for adequate growth and reproduction of commercially valuable species. For instance, according to Torrissen and Christiansen (1995), ASX should be added at a level above 10 mg/kg of dried fish feed to ensure the well-being of Atlantic salmon. This required dosage has been found to be around 100 ppm of ASX in the feed of the shrimp species Penaeus japonicas (Yamada et al., 1990). However, currently, the synthetic form of ASX represents the most important source for fish and crustacean farming operations (März, 2008) and hence using ASX derived according to the ecological principles is of interest. In the present work, the feasibility of applying ASX obtained from the three green solvents in formulation of shrimp feed was studied.
4.1. Shrimp feed

Shrimp feed is one of the primary factors affecting the overall economy of the shrimp farming industry (Hernández et al., 2004). Besides all the challenges regarding the quality and economic improvement of the shrimp feed used, there is also a drive to make the aquaculture a sustainable practice from an environmental standpoint. Developing a shrimp feed formulation which can be applied worldwide is not an easy task and the formulation varies from country to country based on the feed ingredient availability and costs as well as consumer preferences. In this study, to have a general overview, the main ingredients and their approximate content in the shrimp feed (in particular *Fenneropenaeus indicus*) were taken to be (www.fao.org): Carbohydrate (10 w%, wheat), protein and essential amino acids (50 w%, soybean meal), Ash (nearly 20 w%, minerals e.g. phosphorus, calcium), Fat (20 w%, sunflower oil), and pigment (100 ppm, ASX) (Yamada et al., 1990).

Considering the SF in the shrimp feed formulation, the final product of the proposed green process using SF (S-106) can be used in the feed formulation as a source of lipid energy along with ASX as a required pigment (Fig. 2, unit operations in the box). It is worth mentioning that the final product from the extraction step (S-106) is not concentrated enough to reach the final concentration of 100 ppm required in the final product. Hence, extra ASX needs to be applied as a supplementary stream (S-107), mixed with the other ingredient (MX-101), before being formed to a pellet (TB-101).

As mentioned, the common source of ASX is a synthetic form with the average purchasing cost of US$ 2.5/g (www.oilgae.com). However, considering the use of fossil-based organic solvents and other chemicals involved in the production process, to make an eco-friendly product, using natural ASX seems essential. To evaluate some alternatives for synthetic ASX in the supplementary stream, ASX
produced by extraction with the two other green solvents suggested in this paper and the shrimp feed costs were compared.

The shrimp feed production using synthetic ASX (2.5 $/g of ASX) as a supplementary stream for the SF process (stream 107, Fig. 2) costs around 0.9 $/kg of the feed which is comparable with the current cost of the feed for *Fenneropenaeus indicus*, 0.84-0.91 $/kg (www.fao.org). Considering ASX derived from the ME-SF and SCFE processes as an ASX supplementary source, based on the production unit cost of ASX for each process shown in Table 4, the final price will be 16.4 and 80 $ per kg of the shrimp feed, respectively. As expected, the price is significantly higher compared to using synthetic ASX. At present this is not economically sustainable. However, taking into account the ecological issues related to the fossil based solvents involved in other processes, using natural ASX seems essential. Therefore, further investigation should be performed in order to optimize the scenarios and evaluate the potential market size of natural ASX produced from the processing waste.

5. Conclusions

The commercial production of ASX using shrimp processing waste was investigated for four scenarios: using SF, ME-SF, and SCF as green solvents and a mixture of fossil based organic solvents as a base case. From the results obtained, a direct comparison between the processes seems in some aspects a complicated task. The main reason is the difference in the purity of the final product and the corresponding possibility of industrial applications. The reference case, using fossil-based organic solvents, is able to reach a purity of 100% with the known penalty of a high environmental impact. Hence the market of pure ASX in this case is questionable due to the use of potentially harmful solvents. Of the green solvent processes investigated, only supercritical extraction is able to produce a
pure ASX final product. Considering the sunflower oil extraction process the final product reached an ASX concentration of about 2.3 ppm which is not be sufficient for various possible applications. However, it is possible to employ this stream as feed and/or food supplements. Taking into account the limits of the SF oil extraction, mainly due to the high viscosity of the oil, the corresponding methyl ester of sunflower oil was employed. The corresponding process is able to reach a concentration of ASX of 155 ppm after the concentration step. This final product could find wider market applications as direct food and feed additives.

Comparing the processes from an economical point of view and taking into account the differences in the purity obtained, the non-green process can be directly compared to the supercritical extraction. The correspondent production cost was 0.6 $/mg of ASX and 0.82 $/mg of ASX for the solvent based and supercritical process, respectively. However, it should be emphasized that the supercritical extraction has the indisputable advantage of potential wider applications and a consequently a wider market since no risks are evidenced in its production. For the oil and methyl ester extraction processes, the comparison is more complicated since the reference market for the final product is not defined. For this reason the possibility of shrimp feed production was examined using only green-derived ASX as the supplementary stream. From the results obtained the economic sustainability of this solution seems limited since the corresponding cost is 10-80 times the cost of the feed obtained using synthetic ASX. This conclusion does not mean the sunflower oil or the methyl ester based processes cannot be made competitive or not economically valuable. The trend is for natural products to carry a much higher consumer marked price than identical or similar synthetically derived products. A final application to be considered could be as natural products applied for different purposes e.g. in a tablet or softgel capsule which is the most commonly used form of carotenoids in dietary supplements.
Nevertheless, it is evident that further process optimization is necessary in order to reach a final production price that is competitive to the price for synthetically derived ASX.

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