FOR CRAB-SHELL WASTE VALORIZATION

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Purpose

This report examines the commercial viability and exploitation potential for the valorisation of crab shell waste streams in the context of Ireland.

Background

According to BIM (Irelands Seafood Development Agency) report of 2021, Carb was the top three landed species of Irish vessels.[1] The crab catch was 7300 tonnes with strong growth of 49%.[1] Of those crabs, 5200 tonnes are exported by Irish crab processors with a trade value of €45M.[1] The processors are able to extract only 20% to 30% of meat during crab processing, depending on species. The rest of the material consists of shell and connective tissue.[2] In the case of Spider Crab, the extracted meat is only 15 to 20%, according to John Browne, General Manager at De Brún Iasc Teo, a crab processing company located at Co. Kerry, Ireland. So, it can be estimated that around five thousand tonnes of crab waste are produced by the processing facilities of Ireland.

Composition of Crab Side-stream

Crab processing discards consist of crab's internal organs, meat residues attached to the shell, and other external bodies that may be attached to the shell during harvest. It is essential to know that any ash component and heavy metal contamination does not exceed the set limit of European COMMISSION REGULATION (EC) No 1881/2006 for feed purposes and composting upper limit composition of the relevant authority. As crabs are bottom feeders, it is very likely that heavy metals like cadmium deposit into the crab organs over time. The current limit of cadmium contamination is 0.5mg/kg for feed use and 1.5 mg/kg for final compost material. So it is important to know both the nutrient composition of crab side steam for relevant application purposes and the content of major ash components, including heavy metals. The nutritional composition and ash content, including heavy metals of mixed crab processing discards as a whole is already being reported in Table 1 and Table 2.[3]

Table 1 Composition of crab processing discards.

Components	Composition
Moisture content (%)	42.5
Crude protein (% dry wt)	19.08
Lipid (% dry wt)	0.85
Ash (% dry wt)	30.68
Chitin (% dry wt, deproteinised shells)	29.6
Carotenoids (ųg/g)	139.9
Flavorants (% of protein)	1.4

Table 2 Details of the composition of cleaned and crushed crab shells.3

Components (mg/kg unless Composition otherwise stated)	Composition
Moisture content %	26.4
Calcium as Ca%	27.4
Calcium as CaCO3	68.5

Copper	14.4
Lead	4.8
Zinc	52.7
Cadmium	0.58
Arsenic	14.4
Nickel	1.9
Chromium	26.9

To find out the individual contribution of both nutrients and heavy metals in the crab offals and shells SYMBIOMA project has decided to investigate compositional content and heavy metals in both crab offal and shell. De Brún Iasc Teo kindly provided us with some offals and crab shells of Spider Crab to investigate for the purpose. They have also provided us with a four year mature content of Brown Crab compost of their own formula before bulking with sand to reduce any negative impact of heavy metal in the final compost on the sale for the market. The nutritional composition of Spider Crab offal and Shell is shown in Table 4. The ash and heavy metal content of Spider Crab offal, Spider Crab Shell and a five-year manure compost with brown crab & bulking agent are shown in Table 4.

Table 3 Nutritional composition of Spider Crab offal and Shell

Spider Crab	**Crab Offal**	**Crab Shell**
Energy in kcal	51 kcal/100g	57 kcal/100g
Energy in kilo Joules	216 kJ/100g	238 kJ/100g
Protein	9.4	8.6
Nitrogen	1.51 g/100g	1.38 g/100g
Fat	1.3 g/100g	0.4 g/100g
of which-saturates	0.4 g/100g	0.1 g/100g
Dietary Fibre (AOAC)	1.1 g/100g	9.4 g/100g
Sodium	0.20 g/100g	0.29 g/100g
Salt	0.49 g/100g	0.72 g/100g
Ash	4.37 g/100g	29.96 g/100g
Moisture	84.0 g/100g	54.4
Carbohydrate (by diffrn.)	ND < 0.5 g/100g	ND < 0.5 g/100g
-sugars	ND < 0.5 g/100g	ND < 0.5 g/100g
-fructose	ND < 0.5 g/100g	ND < 0.5 g/100g
-glucose/galactose	ND < 0.5 g/100g	ND < 0.5 g/100g
-sucrose	ND < 0.5 g/100g	ND < 0.5 g/100g
-lactose	ND < 2.0 g/100g	ND < 2.0 g/100g
-maltose	ND < 2.0 g/100g	ND < 2.0 g/100g

Table 4 Ash and heavy metal content of Spider Crab Offal, Spider Crab Shell and a five-year manure compost with brown crab & bulking agent.

Determinant on a DM basis unless otherwise indicated	**Spider Crab Offal**	**Spider Crab Shell**	**Brown Crab Compost (five year mature)**
pH 1:6 [Fresh]	7.15	8.33	7.74
Oven Dry Matter	21.4	43.9	85.0
Total Nitrogen	7.14	3.48	1.43
Ammonium Nitrogen	11045	2822	22.2
Nitrate Nitrogen	<10	<10	2706
Total Phosphorus (P)	1.94	1.98	1.33
Total Potassium (K)	0.344	0.152	0.160
Total Magnesium (Mg)	1.02	1.80	1.40
Total Sulphur (S)	0.674	0.270	0.278
Total Copper (Cu)	45.2	8.21	23.6
Total Zinc (Zn)	90.0	26.3	81.7
Total Sodium (Na)	0.753	0.696	0.731
Total Calcium (Ca)	109713	216717	274062
Equivalent field application rate			______
Conductivity 1:6 [Fresh]	3215	2510	3669
Total Iron (Fe)	456	132	555
Total Molybdenum (Mo)	0.501	<0.2	<0.2
Total Manganese (Mn)	123	101	196
Total Lead (Pb)	<1	<1	<1
Total Cadmium (Cd)	5.14	0.456	3.96
Total Mercury (Hg)	0.209	<0.1	0.172
Total Nickel (Ni)	2.56	1.48	1.68
Total Chromium (Cr)	2.70	2.83	<2
Organic Matter LOI	64.4	33.8	18.2
Lime Equivalent as CaCO3	19.1	55.6	58.7
Fluoride [100:1 H2S04 Soluble]	276	212	105
Total Arsenic (As)	32.1	6.68	17.4
Total Selenium (Se)	2.00	0.226	0.706
Total Boron (B)	21.6	30.4	12.1
N. V. as CaO equivalents	10.7	31.2	32.9

It can be noted from the above tables that the mixed crab side streams compositional content and level of heavy metal contamination is different than only offal content and shell content. It is also noticeable that the heavy metal and nutritional composition of composting material could be altered by changing the bulking agent and as it matured over time.

Current and prospective utilisation routes and values

Disposal

Crab waste must be managed as “Category 3 Animal By-Product Waste,” which entails high costs for waste management. At present, most of those wastes are disposed of in Ireland. The industrial recovery cost licence with a capacity of ten tonnes per day is ten thousand euros, and the renewal cost is 6,000 euros in Ireland.[4]

Composting

This approach is relatively low-tech and is less reliant on large economies of scale than other processes. However, it still brings a disposal cost rather than an income for the waste producer. Although some processors like De Brun Iasc Teo, produce a soil conditioner mixed with another biomass, those products attract only a small return or avoid only disposal costs, and the processing requires a huge industrial space, pieces of machinery, buying/collecting bulking agents and labour cost. Recently Lu Zhang *et al.* have studied the use of crab shell powder (25%) and bean dregs (a by-product of soybean) (45%) in green waste for composting. The two-stage optimisation has cost $573 per ton of compost product. A techno-economic study of composting by using a 2:1 ratio of wood chip/sawdust and crab processing waste was reported in 2002.[5] In this report, the crab processing waste scenario was in Maine, USA, and they were to identify a cost-effective landfill alternative. They have used three different economic models, namely Ag-Bag-1, Ag-Bag-2, and windrowing. The annual average costs for Ag-Bag 1, Ag-Bag 2, and windrowing were $62,903, $73,796 and $55,533, respectively. Windrowing results in the smallest loss of -$0.066/kg (-$63.08/tonne) across all economic models analysed (Table 5), despite the fact that none of the examined methods is profitable. To determine how much additional throughput would need to be utilised to generate a profit, a sensitivity analysis was conducted. This analysis determined that the windrow system is the only system capable of ever generating a profit, with a total throughput of greater than 1,000 tonnes per year. In our knowledge, most of the Irish crab processing SMEs’ waste throughput is under one thousand tonnes per year.

Table 5 Investment and annual operating costs for windrow system. [5]

Item		Units	Total cost ($)
Investment Costs	Turner	1 unit	$15,000
	Shredder	1 unit	23,275
	Total investment cost		$38,275
	Total annual investment cost		$5,091
	Bulk Material	600 tons	$12,374
	Labor	2 workers	25,040

Annual Operating Costs			
	Tractor	1 unit	8,200
Equipment	Repair and maintenance cost		1,925
	Taxes and insurance cost		300
	Fuel	10125 L	603
Total annual operating cost			$48,442
Equivalent annual cost			$53,533

If it is considered the composting scenario of Ireland, the investment and other costs like labour need to take into account in both regional and historical contexts. The only Technoeconimc scenario reported here is twenty years ago. So even if it takes very moderate inflation over time, the equivalent annual cost for composting would not be less than €95,000. It is also needed to be considered that an investment of €95,000 would remain without return for a further two years before the final product is on sale in the market. So a further interest on investment would be needed to be counted, and a labour cost during maintenance of the compost bulk. Including bank interest and maintenance costs would be no less than €120,000. It will also need to account for renting two standard industrial until rent for composting space of €15,000 each. The final investment would cost €150,000.

For a 300 tons average crab catch of a processor in a year (which is a typical crab processing volume of SMEs in Ireland), the waste stream volume would be about 240 tons a year. By applying a 2:1 bulking agent, the initial composting volume would be 720 tons. On average, the crab waste mix (guts 20% and shells 44%) produces 30% dry matter. So the final contribution to the compost mass of crab residue would be 72 tons. The bulking agent added by De Brun consists of about 20% moisture. So the bulking agent would be reduced to 384 tonnes as dry mass. The total mass would be around 456 tonnes depending on batch by batch moisture contents. The mass would be broken down during composting, and the final mass would be further reduced. A moderate 350 tonnes final volume can be assumed in this case over a two years period of decomposition. The current market price of crab soil conditioner is 50 cents a kilo. So, the final return will be 175,000 Euro per year before tax.

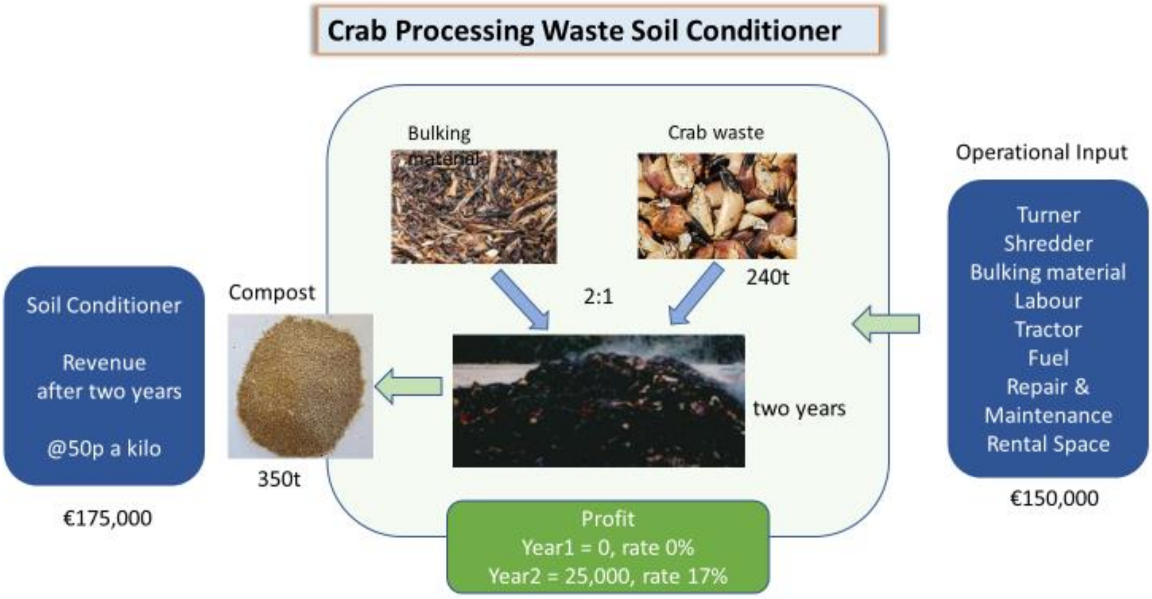

Figure 1 The investment, return and profit analysis of crab waste processing.

Chitin Extraction

Chitin, Poly(beta-(1–4)-N-acetyl-D-glucosamine), is a polymeric component of the outer support yarn of arthropods, such as crustaceans and bony fish scales (Figure 2). The majority of commercial chitin is derived from the shells of shrimp, crayfish, and crab. Industrial chitin is extracted from crustaceans through a two-step chemical process: removal of calcium carbonate with dilute HCl and removal of proteins with dilute NaOH. If necessary, hydrogen peroxide, potassium permanganate, or oxalic acid are used to bleach raw chitin.[6, 7]

Figure 2 Chitin from crab shell and shrimp processing waste.

Chitosan is produced by partially deacetylating chitin, typically with NaOH at elevated temperatures. Chitin and chitosan's low solubility and high viscosity at neutral pH limit their use in food and drug applications. However, their functional properties and solubility can be enhanced by enzymatically or chemically cleaving them into oligomers.[8] Chitin and chitosan can also be produced through the use of proteolytic enzymes (proteases) or fermentation via new alternative methods.

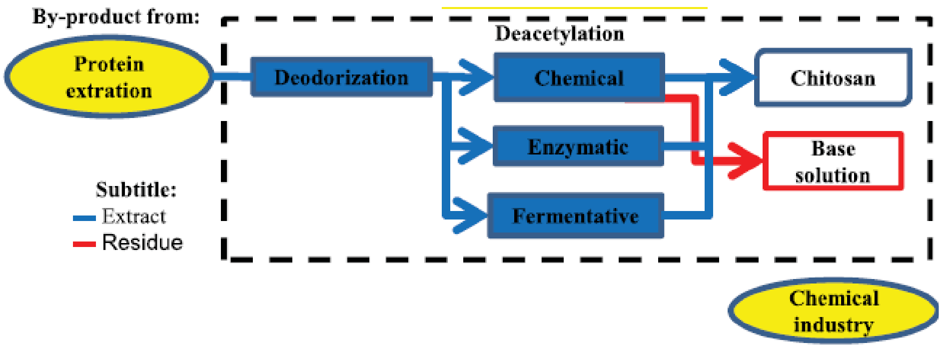

Figure 3 Process flow diagram for chitin extraction from the by-product.[10]

Chitin and its derivative, chitosan, have a wide range of applications in foodstuffs, cosmetics, biomedicine, pharmaceutical drugs, agriculture, and the environmental sector.[13-15] Numerous properties of chitin and chitosan (film-forming ability, antimicrobial activity, biocompatibility, biodegradability, high adsorption, and nontoxicity) permit their use in a variety of biomedical applications, including wound healing, tissue engineering, cancer diagnosis, and drug delivery.[16] Recently, chitosan and its derivatives have gained interest as a possible component in health-promoting and therapeutic products. Chitosan possesses anti-inflammatory, anticoagulant, antidiabetic, antiallergic, anti-obesity, and antihypertensive properties.[18] Their antimicrobial properties are also utilised in a variety of film materials used for food packaging.[19]

Global Chitosan Market

Global Chitosan Market size was valued at USD 1.83 billion in 2020 and is projected to expand (Figure 4) at a CAGR of approximately 14.8% from 2021 to 2027 due to product usage in a variety of end-user industries, such as water treatment, healthcare, food & beverages, and cosmetics, among others. Rapid growth in the food and beverage industry and increasing demand for advanced packaging materials with eco-friendly properties will encourage the use of chitosan-based packaging in this industry.[23]

Figure 4 Global Chitosan market and projected regional growth.[23]

Several firms are offering chitosan and its derivatives as nutraceutical medicinal and food items. Seatone® and Lyprinol®, both derived from mussels, are common examples of functional foods used in anti-arthritic and anti-inflammatory therapy.[24]

Chitin extraction process evaluation

No commercial chitin extraction facility exists in Ireland, as of our knowledge. Recently, with their project partner Nofima in Norway under a project called BlueShell, the Technical University of

Dublin has conducted an upscaling of chitin extraction using the traditional strong acid-base extraction process. But due to high effluent remediation costs and lower grade chitin production, the strong acid-based chitin processing is not becoming a viable and sustainable business case in the EU, including Ireland. It is also known that although microbial and enzymatic extraction process produces high-quality chitin, due to incomplete deproteination and longer incubation time, it is neither gaining popularity in global chitin producing industries.[3] The control of the quality of the product is also difficult as initial pH, inoculation concentration, fermentation time, agitation speed, carbon source and concentration all might affect the final product quality.[4] On the other hand, crab shell is comparatively tougher than shrimp shell and contains a higher percentage of calcium carbonate. For all those reasons, most of the global chitin supply comes from less restricted and environmentally regulated countries like China and India, using HCl and NaOH-based shrimp shells extraction while crab shells remained underutilised.[5]

The bottleneck and way to overcome

Lab-scale use of mild organic acid is also proven to preserve the functional properties of removed calcium salt, and by-products could be marketed, such as lactic acid salt as calcium lactate.[6] Although it is known that dilute acid reduces chain scission and partial deacetylation of chitin to preserve its high market value, there is a threshold limit of dilution under which the acid cannot play a role in a batch reactor.[7] The less effectiveness of moderately dilute acid on the crab shell might be due to the accumulation of calcium salt particulate on the surface of the reacted crab shell as the reaction of calcium carbonate of crab shell and acid takes place. As such, the action of dilute acid on the crab shell is reduced or stopped over time.[5] To maintain the efficacy of the batch process and stop the accumulation of salt particles on the crab shell, at least three-time washing and treatment are needed.[5] Due to salt accumulation of the crab shell, the size of the feedstock is also required to be kept under one millimetre, which means a necessity to pre-processing of crab shell as it is obtained from the crab processing facility.[5] The foaming in the conventional batch reactor is another issue that causes hindering in batch processing in terms of occupying valuable space of the reactor and processing time.[5]

Development of Microwave-assisted Biorefinery Process

Considering the dispersed location of Irish crab processing facilities and all other factors mentioned above, an in-house 500g to 1000g scale integrated chitin extraction process from crab shells was developed at Atlantic technological University. Here we have developed a mild organic acid-base chitin extraction process from crab shells by applying microwave irradiation at low temperature using a continuous solvent flow of lactic acid, as shown in Figure 5. The integrated microwave-assisted crab shell processing can systematically extract chitin/chitosan along with other valuable crab shell compounds, astaxanthin, an expensive bioderived carotenoid, at little cost and environmental effect. Furthermore, rather than traditional grinding and drying process of raw material preparation is avoided in the integrated process. This means saving time, energy, money and ecological issues relating feedstock preparation process. Moreover, the by-product of the processing is another valuable chemical, calcium lactate. As the produced calcium lactate is a bioderived compound, it will have future uses in Pharmaceutical and biological applications. The process could be safely operated at small to medium size crab processors premises.

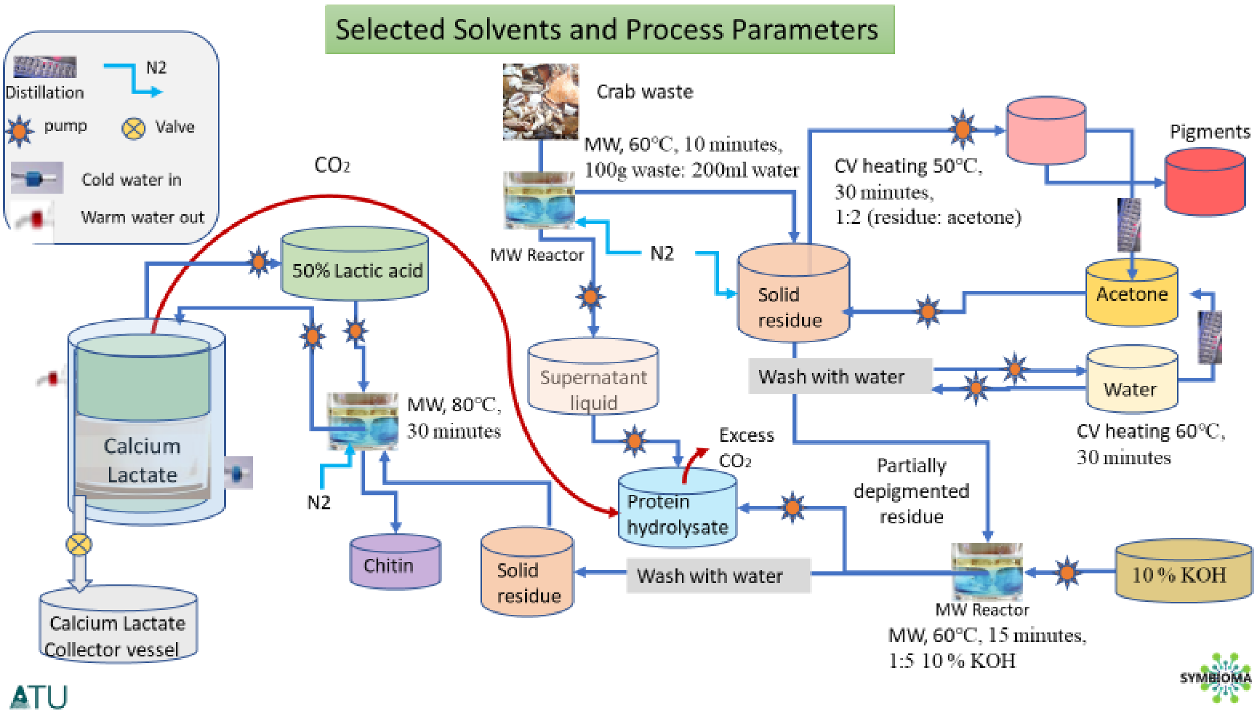

Figure 5 Integrated microwave-assisted biorefinery process of crab shell waste valorisation

Microwave (MW) reactor offers several advantages over the conventional heating reactor, as it is often more target-specific (reducing amount of secondary products), controllable[8 9], energy (non-contact energy transfer, volumetric energy absorption and dissipation)[10] as well as cost-efficient[11] (due to the shorter reaction time) and therefore in many cases may be a very promising tool for green technologies. During the last few decades, MW heating was successfully applied for biomass activation [12, 13], materials preparation[14, 15] and organic synthesis[16-18]. Furthermore, MW processing is effective at both pilot and industrial scales.[19] Application of lab-scale extraction of astaxanthin and chitin by applying microwave is already proven effective.[20, 21] In this proposed reactor design and chemical process, not only most of the obstacles of conventional batch processing and the environmental issue will be removed but will also be cost-effective while maintaining the high quality of the product.

A techno-economic evaluation of the process is developed, as shown in Figure 6. The cost breakdown the process is shown in the calculation section. The true techno-economic viability of the process could be evaluated once the gained high-end products market is secured.

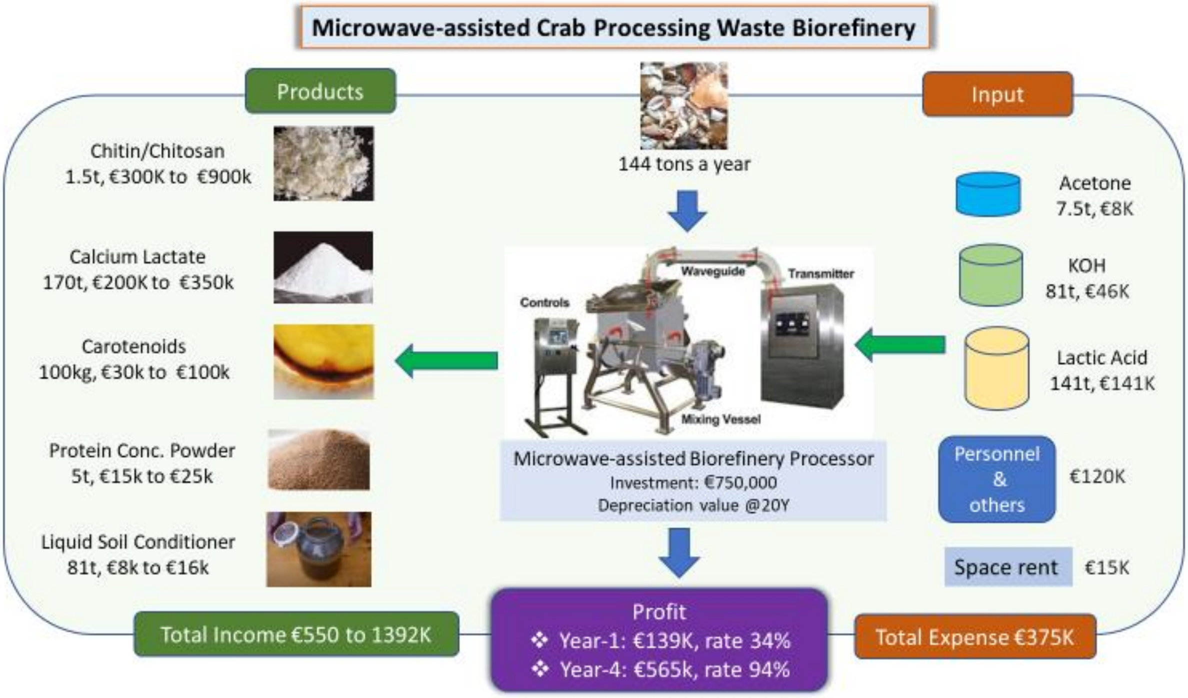

Figure 6 Techno-economic analysis of crab processing side-streams biorefinery development.

Calculation

Processing plant setup and operation cost

Processing plant setup and operation cost	Euro
MW processor installation (6KW, 120L capacity, 60L sample volume per operation per hour), 640L per day processing	750,000

All costs, excluding setup

Material	**Cost/year (Euro)**
Chemical	240,366
Personnel	60,000
Electricity	15,000
Other Maintenance/breakdown cost	21,000
Routine testing Cost	24,000
Space rental	15,000
Total	**375,366**
Plant depreciation cost (twenty-year terms)	37,500
Grand total/year	**412,866**

Product Values

Product	**Amount**	**Unit Price/kg**	**Yearly revenue (Euro)**	**Ref**
Calcium Lactate	170t	1.17 to 2.07	198,900 to 351,900	[26]
Crude Chitin/Chitosan	1.5t	200 to 600	300,000 to 900,000	[2]
Crude Carotenoid	100kg	300 to 1000	30,000 to 100,000	[27]

Protein Concentrate Powder (type C)	5t	3 to 5	15,000 to 25,000	
Residual Liquid	81t	0.1 to 0.2	8,100 to 16,000	
Total Revenue per Year			552,000 to 1,392,900	
Average price after three years of product development in collaboration with potential partners			972,450	

Annual Profit/loss prediction

Year	fixed asset depreciation	Expense	Total expense	Return	Profit/loss	Rate of profit/loss (pre-tax)
Year-1	37,500	375,366	412,866	552,000	139,134	33.69%
Year-4 (with 5% flat inflation)	150,000	450,438	600,438	1,162,940	562,502	93.68%

Comparison of composting with proposed biorefinery process

The comparison of the two techno-economic analyses would depend on the situation and case by case basis. The composting process requires low investment and low technology. While the investment in composting requires only €150K, the proposed microwave-assisted process would be needed an annual expense of €375K in addition to a one-off process installation cost of €750K. But when it comes to the return of the profit, the composting process returns no profit in the first year of the starting of the process. In composting from the second year, a steady profit return of €25K will be gained with a profit rate of 17% if all of the low-value products could be sold in the competitive market. It should have to remember that, in the composting, crab organ is mixed with crab shell as one of the rest raw materials of the process. And in the compositional analysis of Table 5 demonstrates that the heavy metal contamination in the final composting product comes from crab offal. To reduce the cadmium contamination and comply with the regulation, more bulking agents, such as sand, are added to compost. The compost on sale, in return, becomes less attractive to a buyer as the nutritional composition is reduced per mass. Although it is described in the literature that chitin on the shell has some strong selling point, the bargaining price of a various composting product in the market make it a difficult sale. If the product cannot be sold in season, the storage space of the unsold product becomes an issue. It is needed to mention here that the composting process occupies a huge industrial space and any unsaleable products mean further pressure on the valuable space.

On the other hand, setting up a microwave-assisted processing plant would require only compact space if the raw material storage is nearly identical. The products that will be generated in the microwave process are highly demandable with strong financial returns. In this process, the first-year profit will €139K, with a profit margin of 34%. As the business will mature in terms of product development into more high quality, the market demand will only increase and secure more profit as time goes by. It is projected that in year four, the profit will almost be doubled with a figure of €565K.

Yet, which model would a business is likely to follow will depend on the present operational situation of composting business or a new entrant into the business models from the waste disposal scenario. Suppose the business has an existing infrastructure for compositing space and has a good connection to the composting market and little access to the investment cost of a high-tech industrial plant. In that case, composting may still be the first step into waste valorisation. But suppose it is possible to secure a research collaboration of continuous product development in the first few years and a secure source of finance for a microwave processing facility, such as through a grant or partial loan. In that case, the proposed microwave processing facility may sound lucrative.

Pilot cases business models

The SYMBIOMA project partner Atlantic technological University collaboratively started working with De Brun Iasc Teo at the early stage of this project. The company is interested in further collaborative work with ATU for pilot scale product valorisation on this proposed microwave-assisted biorefinery process.

It is worth noting that, There are five Shellfish processors in the Co. Kerry area. Those are Spa Seafoods, Kerry Coast Shellfish (T/A/ Kush Seafarms), Kenmare Bay Seafoods, Glenbeigh Shellfish, and De Brun Iasc Teo. All those are located within a 45-minutes driving radius. The plant will be based at De Brun's premises if the De Brun area is able to secure contributing funds to run the project. Another option is to set up the plant in an independent area within the Centre of the 45 minutes driving distance of all other crab meat processing in the Co. Kerry area.

It is aimed that the project outcome would not only help waste management to cash generation but would show the way to the other four crab processors in the Co. Kerry region is located within a 45-minute driving radius. There are 28 shellfish processors in Ireland, most of which are clustered in a few regions only. A significant of those crab processing facilities are located in the NPA region Cork, Donegal, Galway, Mayo and Clare. The success of this project would impressively be shown by turning the waste issues into the value of Irelands NPA regions crab processors as a whole.

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