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Techno-Economic Analysis of a Seaweed Extraction Process

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TECHNO-ECONOMIC ANALYSIS OF A SEAWEED EXTRACTION PROCESS

by

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ABSTRACT

The goal of this thesis was to perform a techno-economic analysis of a seaweed polysaccharide extraction process that could estimate how economically viable it would be to harvest and process seaweed in Maine to produce algal polysaccharides. I pursued two investigations to answer this question:

First, I continued the research I have been doing on an EPSCoR SEANET funded undergraduate research team working on the extraction and fractionation of sugar kelp (*Saccharina Latissima*) to produce three different separated polysaccharides: alginate, laminarin, and fucoidan. My contributions to this project were primarily to hydrolyze whole pieces of seaweed and extracted samples and quantify their saccharide composition by running the hydrolysates through HPLC. I also prepared samples for elemental analysis by ICP-MS and contributed to tasks associated with the extraction and fractionation work. The seaweed samples we used were harvested from various locations along the Maine coast and collected at different harvest times. Each of these samples were analyzed individually. In this way we could determine the relative amounts of each type of polysaccharide in the different samples.

Second, I constructed a process model of our extraction process in the modeling software program ASPEN Plus. A principle task in constructing the model was to translate our multi step batch processes used in the laboratory into a continuous unit operations-based model. I used this model to develop financial viability criteria for the economics of extracting polysaccharides from Maine seaweeds. The desired output of the model was to generate estimated values of the harvested seaweeds to a potential seaweed harvester in Maine.

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INTRODUCTION

The Big Picture

When one thinks of the seaweed industry, one would likely think of the vast seaweed farms in China and other East Asian countries. Japan is recorded as the first country to begin seaweed farming in 1670 (Borgese 1980). Today, China is the largest reported farmer of seaweed pulling in 10 tons per hectare per year. For reference, the U.S. produces 10 tons per hectare per year of corn (Seaweed Sustainability, 2015). However, they may not be in the lead forever, as need for sustainable agriculture increases, countries around the globe are beginning to try their hand at the task, including the United States.

The seaweed industry is expanding, and even farmers in Maine have started to grow their own seaweed. There aren't many right now, as most aquaculturists are focusing on those fish that have proven reliable and sustainable, such as oysters or salmon. But the number of seaweed farmers in Maine is increasing each year. Maine Sea Farms in Damariscotta, Maine opened in 2014 and has seen more and more business annually since then (Maine Sea Farms, 2015).

As the industry spreads, additional uses for the seaweed continue to be found. Seaweed has proven to be much more than a food source. There are many types of seaweed, and they contain different polysaccharides, which can be useful for multiple applications. As stated in the Advances in Food and Nutrition Research magazine in 2014, "seaweed polysaccharides, like agar, alginates, and carrageenans, are economically the most important products from macroalgae or seaweeds".

A polysaccharide is a long-linked chain carbohydrate molecule composed of many smaller sugars. There are many different polysaccharides, but there are only a few main ones that can be found in seaweed. Currently the most valuable polysaccharide is carrageenan. Carrageenan is used by the food industry as a preservative and a thickener. This particular polysaccharide comes from red seaweed, which is grown all over the world. However, there are three polysaccharides found in brown seaweed that aren't as commonly extracted; laminarin, fucoidan and alginate. All three can be found in brown algae. Laminarin is a polysaccharide of glucose and it is worth a lot of money, even in small amounts, due to how difficult it currently is to extract from the seaweed. Laminarin is being studied for its use as a pesticide to stimulate plant's natural disease defense mechanisms. (AGS, USDA).

Fucoidan is a polysaccharide of fucose and it is currently used as a dietary supplement. The polysaccharide is being studied for its uses as a potential antioxidant, and for its unique cognitive, anti-inflammatory, anti-angiogenic, anti-cancer, anti-viral, and anti-hyperglycemic properties (Collins). Alginate is the most commonly found polysaccharide of these three. It is used as an additive in dehydration and dehydrated products and useful in the manufacture of paper and textiles. Alginate is also used as sodium alginate to make impressions in the dentistry and other industries. Each of these polysaccharides is important for its own reasons, and so scientists have been trying to determine easier methods of extracting them.

The University of New England in Biddeford, Maine, is one of those communities that have taken a recent interest in seaweed farming. UNE tasked the van Walsum Lab at the University of Maine in Orono with determining if there were any problematic levels

of potentially toxic metals or arsenic present in the plant tissue, and thus if it were safe for them to grow large quantities of seaweed in the estuary of the Saco River for use as a food product or as a source for extracting these three polysaccharides. They gave us multiple seaweed samples grown in different locations near the UNE campus where they had transplanted individual algae from one cohort that had been grown in the UNE seaweed nursery. We worked to accomplish this task by using elemental composition analysis to look for potential toxins in the seaweed samples and we also extracted polysaccharides to determine if location and harvest time affected polysaccharide profiles.

In the Lab

The polysaccharide extraction process used by the van Walsum lab was created based on several different published methods. The process involves the extensive use of solvent extraction, repeated cycles of centrifugation, filtration, and freeze drying. This fractionation procedure has been completed (or mostly completed) on two sets of seaweed samples.

First, the seaweed samples are freeze dried to remove any moisture. Then 70% EtOH is used to extract pigments from the samples. Next 2% $CaCl_2$ is used to extract Fraction A from the seaweed, leaving behind residual solid to be used in the next extraction. Fraction A contains laminarin. 0.01 M HCl is used to extract Fraction B from the residual seaweed. This fraction contains fucoidan with trace amounts of alginate. Finally, 3% Na_2CO_3 is used to extract Fraction C, which comes out as sodium alginate. Fraction B and C are fine to freeze dry as they are, but the laminarin and fucoidan in Fraction A must be separated through the use of slurry packed column chromatography.

Much of my three years on the project was spent hydrolyzing the polysaccharide extracts and analyzing the hydrolysate with HPLC to determine the amounts present. I used an acid-based hydrolysis method adopted from standard methods used for terrestrial biomass, such as lignocellulose. This method worked well for two of the polysaccharides, but it turned out that alginate could not be easily hydrolyzed with acid. Instead of breaking the polysaccharide into its monosaccharides, the viscosity of the sample increased, and the color changed to black. It was determined that an enzymatic method would have to be used instead. This method allows for hydrolysis of targeted polysaccharides, instead of every polysaccharide. In this way, we were able to hydrolyze specifically only alginate with the alginate lyase enzyme.

Once the samples were hydrolyzed, via acid or enzyme, they were analyzed via use of an HPLC to determine the quantity of sugar extracted. This was done by determining the relative size of the peaks of each of the sugars after they were separated in the column. The HPLC column separates components such as the different polysaccharides based on their elution times. The components travel through the column at different speeds and either an infrared or an RI sensor shines a light on the sample and measures the refraction.

Enzymes could also be used to determine the amount of sugar by using them to hydrolyze a mass of sample, centrifuging the sample and then determining the change of mass of the solid. The enzyme hydrolyzes all the polysaccharide it targets, so comparing the mass of solid before and after and subtracting the mass of enzyme solution used will give you how much polysaccharide was hydrolyzed. **We had an alternative method via the use with a YSI Enzymatic Analyzer, but after three months of work it proved**

beyond repair. Glucose oxidase not hydrolysis of polymer. Automated assay, to monitor polysaccharides.

One final analysis method we used to determine seaweed composition was elemental analysis in the form of ICP MS. The work for this method was done by the UMaine Soil Testing Lab. We requested the analysis of the carbon, nitrogen and phosphorus contents of the seaweed to determine if any seaweed location contained more nutrients of one kind or another. If a particular growth location did contain more nutrients, it would have been a better choice. However, there was very little difference in the C:N:P ratio of the different samples. This can be seen in Table 1 below where TC is total carbon and TN is total nitrogen. We also had them test the levels of the toxins and heavy metals in the seaweed, and as can be seen in the same figure, these levels were low or below detection levels. It should be noted though that if high levels of these heavy metals or arsenic were detected, that would not necessarily prove that these seaweed samples were toxic, since the bioavailability of these elements was not assessed. These numbers can also be seen in Table 1.

Table 1: Soils Lab Analysis of Seaweed Samples

Sample type: Seaweed																	
	ID	**TC**	**TN**	**Ca**	**K**	**Mg**	**P**	**Al**	**B**	**Cu**	**Fe**	**Mn**	**Zn**	total	total + S	**O + H**	total+OH
		%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm				
	1	32.2	1.60	2.56	5.65	0.576	0.303	99.2	144	0.873	119	8.08	15.8	42.9	44.0	48.315	91.2
	2	33.1	3.80	6.74	2.46	0.451	0.364	138	102	4.38	254	21.3	31.9	47.0		49.695	96.7
	3	26.9	1.83	1.10	10.2	0.580	0.356	91.8	142	1.83	86.9	5.86	15.2	41.0		40.41	81.4
	4	29.0	4.17	6.44	3.70	0.560	0.364	163	93.8	2.43	301	21.5	28.9	44.3		43.515	87.8
	5	32.6	1.76	2.82	4.00	0.541	0.274	51.8	117	1.58	137	9.05	15.8	42.0		48.84	90.8
	6	34.4	1.52	1.70	4.52	0.511	0.269	84.3	132	1.57	180	10.0	24.8	43.0		51.66	94.7
	7	33.4	1.22	1.50	5.23	0.488	0.198	47.3	126	2.45	149	7.36	20.4	42.0		50.04	92.1
	8	32.2	1.93	2.59	5.80	0.524	0.314	43.8	121	2.35	109	6.53	19.1	43.4		48.27	91.6
	9	32.1	1.71	2.52	5.19	0.522	0.292	42.8	126	2.18	75.7	4.98	14.2	42.3		48.105	90.4
	Element	**Units**	**Sample 1**		**Element**	**Units**	**Sample 9**										
	Cd	ppm	< 2.0		**As**	ppm	< 0.01										
	Cr	ppm	< 2.0		**Hg**	ppm	< 0.04										
	Pb	ppm	< 2.0														
	S	ppm	10337														

MATERIALS AND METHODS

Techno-economic Modeling

The purpose of techno-economic analysis is to determine the economic viability or feasibility of a project or technology. In the case of my thesis, I worked to determine the viability of our extraction process being utilized on an industrial scale. Since testing the process on an industrial scale was not possible, Dr. van Walsum and I decided to make use of a modeling software to determine if this process could be scaled up.

There were two choices of tool at my disposal; I could either use Aspen Plus, a standard process modeling software, or I could use Excel spreadsheets to calculate everything I needed. Both tools could be used to perform the calculations I required, but I ultimately decided to use Aspen for one main reason: some of the calculations included in my analysis required thermodynamic data and properties already present and accessible in Aspen's built in databases. If I were to use Excel, I would need to look up every required property myself and there could prove to be a lot required. Also, if the modeling exercise proved fruitful, it will be more easily expanded upon if more detailed insight or design work was desired.

Assumptions

While designing this model some initial assumptions were made regarding the process and the model. The first and likely most important assumption was that xylose, dextrose and ascorbic acid could be substituted for laminarin, fucoidan and alginate respectively in the model. This substitution was made because ASPEN does not have any information in any of its databanks about the polysaccharides. As stated previously, when initially generating the idea for the model, it was expected that some thermodynamic

calculations would be required, and so components chosen with similar chemical compositions were chosen. I initially attempted to make custom components for the polysaccharides, but ASPEN was stubborn and required more information about thermodynamic and chemical properties than I could find.

The second assumption is that in our initial extraction process, we got good, repeatable results. My model is based on the work we did in the Van Walsum lab over several years, and the input and output values used are similar to the results of this work. I chose to use the more recently generated results, since it is highly unlikely that we got completely accurate results in our initial extraction; there was likely some sample lost due to human error with this extraction being the first time we ever had done anything like this.

The third assumption I made is that by the end of the process approximately 99% of the polysaccharide is removed from the seaweed. It is currently not possible for us to know the final compositions of the extracted polysaccharides because some of them have yet to be freeze dried and thus still contain some mass fraction of water. Also, the method followed was intended to yield quantitative composition information and was presumably designed to err on the side of excess extraction steps to achieve high yield of the targeted compounds. The primary goal of my personal work on the project was to determine how much of each polysaccharide was in the samples via the use of HPLC, but this analysis requires dry samples. Therefore, I had to base my model on the best-case scenario for the extraction as a whole, while still keeping the values close to those in our experimental data. Once more data are collected in the lab, more accurate extraction percentages can be determined.

The fourth and final assumption I made was that the initial solid seaweed sample could be treated in ASPEN as a solution of liquified components at the expected ratio of components based on amassed literature data. ASPEN is not very good at dealing with solids, and so I decided that trying to make a solid out of the components that weren't even the polysaccharides would not provide an accurate result. Thus, I decided to treat everything as a liquid to remove this expected error.

Design

The goal at the outset of this thesis project was to design a model based on our extraction process and procedure and based on the results of our first extraction to decide if this extraction could be run on an industrial scale. The first step of this scaling up was to decide how much seaweed the process could run per day. I decided that a factory running this process could extract polysaccharides from 1000 kg of dry seaweed per day. I chose this number because I assumed that if any factory would be built to perform this extraction, it would not be a very large one at first due to this all being new to the processing community in Maine.

The next thing that I had to decide was how to model the process; that is, what unit operations I needed to include. First I tried using mixer and splitter blocks to combine and separate the streams based on experimental values. This worked fine except that this model didn't really prove anything. I was just presenting the data we had already collected in a visual form. ASPEN could not calculate any economic or thermodynamic data from this version of the model. This is because mixer and splitter blocks in ASPEN are not actual unit operations. These blocks manipulate flows as designed, but no calculation other than simple algebra are performed.

After realizing that no useful data could be gathered from this, I decided to try a different approach. To explain my next few design choices, I must note some of the things that Aspen has the ability to do that I required. Aspen can do mass and ideal energy balances by using mixer and splitter blocks, it can do non-ideal mixing thermodynamic calculations with separator blocks and can also do economics calculations, but as I'll explain, the economic calculations from the separator blocks didn't make sense, so I had to use a CSTR as a vessel with a residence time, size and pressure rating.

First I replaced each mixer and splitter combination with a separator block. This simplified the process a lot, and I was able to get the inputs and outputs that I desired. Once I got the overall inputs and outputs sorted, I decided to expand my model. In the extraction process we run three extractions on the seaweed with each solvent to remove all of each of the polysaccharides. Initially I designed my model such that all extractions were done in one separator block but in order to make the model more accurate I split up each of the extractions to be represented by individual separator blocks. In order to keep 99% of the polysaccharide extracted, I had to determine the percentage to be used for each of the three extractions. I calculated that if 78% of the polysaccharide was removed each time, after the third extraction we would have a total of 99% extracted. The restructuring of the model based on separator blocks was useful in so far as I was now able to determine the heat duty of each block. The heat lost in each separator was very small, at approximately 0 kJ/hr. This makes sense because most of the process is run at around room temperature.

There was still one major flaw in my model; I could not use Aspen to calculate any capital costs for the equipment. I attempted to do so, but the programmed capital cost calculations made it so that every separator was the same size and so cost the same amount of money no matter how much I changed the flow rates. This made no sense as the size should change based on mass flow changes. Thus, I had to find another way to model these interactions that allowed me to use Aspen's built in capital cost software. I wanted to use the built-in software to minimize the error associated with using two different programs to find the cost of the blocks. I was initially planning to use the Capcost macro sheet in Excel to find these costs but decided to use Aspen's built in Process Economic Analyzer instead.

Since I couldn't find the capital cost of the separator blocks, I had to find another way to get any capital cost for equipment. There was no reaction in this extraction process that I could easily model based on my previously made assumptions and design simplifications. Thus, I needed a way to model the size of the theoretical separator blocks using a different block. I decided that I wanted to use some sort of storage block to model this block so I could calculate its size and the cost.

There was a serious problem with this plan because Aspen cannot easily model storage tanks. The program is intended for continuous flow reactions and processes and thus doesn't include simple ways to represent batch processes. When we were taught Aspen, we were instructed to use pipes to model storage tanks. However, I wanted to include the cost and energy consumption of a mixing device in my separator, and so found an alternative way to represent the tanks as a continuously stirred tank-reactor (CSTR) . I used a CSTR to estimate the cost of the theoretical separator. There was

another problem though; in Aspen, in order to use a CSTR you need to include a reaction, but our process didn't include any reactions. I was able to circumvent this requirement by including additional components with the same chemical composition as each of the polysaccharides. This allowed me to program a reaction that turned one component into the same component with a different name, therefore not actually reacting anything and so not changing the model in any way.

Next, I decided not to manually replace each of my separator blocks with these reaction-less CSTRs. Instead I took the inlet flow of the initial separators for each stage of the extraction process and created a parallel model intended solely to generate economic numbers. Thus, I duplicated these flows outside the main process and connected them to CSTRs. Then I included the name-changing reaction of whichever polysaccharide was being extracted. Once I ran the program again I was able to determine the capital cost of the CSTRs for each extraction. I assumed that in an industrial process these tanks would be bought in bulk, and the initial tank would be the largest one, so in my overall cost calculations I multiplied the capital cost of each tank by three to represent the three extractions.

I knew that the next step in determining the financial viability of the process was to determine the raw materials costs for the process. None of the initial components included in this process are highly expensive, but this process does require a lot of each and so the price does seem to add up. This is especially true considering how little of each polysaccharide is extracted once the extracts are dried. My economic calculations and comparisons in the next section will show you if this process was viable or not.

RESULTS

Economic Analysis

Aspen can be used as a powerful economic tool, but it does have some limitations, as I found out during my thesis work. Aspen has built in economic parameters that can't easily be changed and to find them one must explore deep in Aspen's files. Thus, I didn't change them in any of my economic calculations using Aspen. Some other problems arose from not being able to change these variables, the biggest one being that no matter the size of a separator block, it always cost the same. This meant I could not use separator blocks in my calculations, so I used CSTRs instead.

Economic Analysis – Base Case

The base case for this project is the closest to representing the extraction as performed in the lab on an industrial scale. There have been no modifications to the process, other than increasing the flow rates to scale up the model. I decided that a reasonable estimate for the amount of seaweed a plant could process was one ton per day. Based on lab data and research I decided to define my base case composition of seaweed on a dry mass basis as 25% laminarin, 15% fucoidan, 30% alginate and 30% ash, protein and pigments. The lab process uses a 7:1 mass ratio of solvent to seaweed for the pigment extraction, a 9:1 mass ratio for the next two extractions and a 10:1 ratio for the last extraction.

I simulated the base case in Aspen and got some economic results. I realized from the capital cost results something was wrong. Aspen can mass separators, but it doesn't change the cost based on flow. All separators cost the same. This isn't reasonable for my

model. So, I chose to separately model the CSTRs as tanks. Once I did this, my results made more sense.

The price of dry seaweed in Maine is currently $25/lb. according to maineseaweedfarms.com. In the simulation, 1 metric ton of seaweed is processed per day. This means that the seaweed feed will cost $55,115/day. The process also uses solutions of different chemicals for the extraction. These solutions include 28 tons of 70% ethanol solution, 27 tons of 2% calcium chloride solution, 27 tons of 0.01 M hydrochloric acid solution, and 30 tons of 3% sodium carbonate solution per day. Based on current market prices from eMolecules.com, the use of these solvents would prove expensive. Costs can be seen in Table 2 below.

Table 2: Costs of Raw Materials

Process Component	Daily Cost/Revenue	
Seaweed ($/day)	$	55,115
Ethanol ($/day)	$	183,750
CaCl2 ($/day)	$	31,126
HCl ($/day)	$	157
Na2CO3 ($/day)	$	5,886
Total raw materials ($/day)	$	281,096

The capital cost of the plant is also very high, as are the other associated costs of running this plant. These costs can be seen in Table 3 below.

Table 3: Equipment, Operating, Utilities and Capital Cost

	Cost	
4 x EtOH Separator	$	50,627,200
3 x CaCL2 Separator	$	27,723,840
3 x HCl Separator	$	27,792,690
3 x Na2CO3 Separator	$	29,606,100
Total Capital Cost	$	135,749,830
Utilities Cost	$	5,437,722
Operating Cost	$	27,316,120

These costs all seem very high for a brand-new industrial process, but based on current market price, the profit for the process has the potential to far outweigh its costs. The best price I could find for pure laminarin was $34/100mg (Sigma Aldrich). The process produces 148.5 kg of Fraction A per day. This means that the potential profit from Fraction A sales, if it were possible to sell all this laminarin at this price, is $50,490,000 per day. This number already shows that the process is profitable, but the sale of the other fractions produces even more money. Fucoidan can currently be purchased at a price of $208/500mg (Sigma Aldrich). 247.5 kg of fucoidan is produced per day. So, the revenue from fucoidan should be around $102,960,000 per day, again if all this material could be sold at the current chemical price. Alginate, unlike the other two polymers, is currently being mass produced in the form of sodium alginate, and so will make a smaller profit. Sodium alginate can be purchased for $137/kg (Sigma Aldrich). The extraction process would produce 2,673 kg/day. Therefore, the process should make $4,976 per day on alginate. A summary of this analysis can be seen in Table 4 below.

Table 4: Base Case Summary

Process Component	Daily Cost/Revenue	
Seaweed ($/day)	$	55,115
Ethanol ($/day)	$	183,750
CaCl2 ($/day)	$	31,126
HCl ($/day)	$	157
Na2CO3 ($/day)	$	5,886
Total raw materials ($/day)	$	281,096
Capital cost ($)	$	135,749,830
Utilities cost ($/year)	$	5,437,722
Operating cost ($/year)	$	6,829,030
Laminarin sales ($/day)	$	50,490,000
Fucoidan sales ($/day)	$	102,960,000
Alginate Sales ($/day)	$	40,689
Total sales ($/day)	$	153,490,689
Profit ($/day)	$	153,166,401

These profits seem highly unreasonable, and they are. There aren't many good mass extraction processes for these polysaccharides. This is part of the reason why they are so expensive. The other part is that there is a specialized market for them right now, and so prices are artificially high to meet the demand with few buyers. Once these polysaccharides can be mass produced, and once people recognize the uses for these polymers that I discussed earlier in this paper, these numbers will go way down.

Economic Analysis – Alginate Only

It is not safe to assume that this process could sell any fucoidan or laminarin, and so I had to determine how a profit could be made if only alginate could be sold. I performed the calculations seen in Figure 9 to find the minimum sale price for the alginate that would be required to break even if the other polymers were still extracted. This sale price was approximately $1092/kg. This is very high price for alginate since it can currently be purchased for $137/kg. Next I calculated how much alginate could be sold for if only pigments and alginate were extracted. This allowed the required sale price for alginate to go down a lot. The sale price was now $369/kg.

These calculations prove that this process could only be profitable if the minimum prices that the alginate was sold for were way above the prices currently offered for the polymer. The plant would be no competition at all and would never be able to make money. However, I still wanted to find a way for this extraction to make money, so I tried something else.

Economic Analysis – All Together

As proven earlier, this proposed production line would flood the market with laminarin and fucoidan. As such, there is no way that these polysaccharides could be sold for as much as they are currently listed for. It is also likely that there is little demand for these two polymers because not much research has been done on how to extract them and the general public doesn't realize their uses. Therefore, I wanted to see if it would instead be profitable if all the polysaccharides were sold together, in one package.

I treated the product as a combination of the three extracted polysaccharides. I used the same feed concentrations as before, but I added all the products and their sale prices together. This resulted in a sale price required to break even of $468/kg of polymer blend. This is a much lower price than selling the alginate alone. It is also only around 19 times the price of the raw dry seaweed. The Aspen simulation predicts a 20% ROI, so it would take 5 years to pay back the cost of building the plant. It turns out this wouldn't be a reasonable sale price either and the whole system is unprofitable in this way as well.

Economic Analysis – Combined Approach

I had the idea to use the calculations from this analysis to see how much laminarin and fucoidan would need to be sold together to make a profit if all the alginate was sold at its normal price of $7.6/lb. It turns out that at ten percent of the market prices for fucoidan and alginate, only 4.03kg of those two polysaccharides would need to be sold per day. It is unlikely that selling this relatively small an amount of the two polysaccharides would flood the market, and there would be tons of produced

polysaccharide left over that could be stored. This also means that the process wouldn't have to be run every day, saving on operating and raw materials costs over time.

A summary of all the modified case results can be seen in Table 5 below.

Table 5: Modified Cases Summary

Alginate Only	
Alginate Sale Price ($/kg)	$ 929
Alginate Sale Price (no pigments) ($/kg)	$ 369
Profit ($/day)	$ -
All Together	
Mixed Product Sale Price ($/kg)	$ 468
Profit ($/day)	$ -
Combined Approach	
Alginate Revenue	$ 20,345
Amount of Laminarin and Fucoidan per day	4.03kg
Profit ($/day)	$ -

In order to drive down prices even more, I decided to see if it would be possible to reduce the number of extractions down to one for each different solvent. This mean that we would only extract around 78% of each product, but it would also reduce the capital costs by around 2/3. Thus, I calculated these new capital costs and the new possible revenue and used each of the modified cases once more to see if it was possible to make the industrial process more feasible.

Table 6: 1/3 Capital Reduction

Alginate Only		
Alginate Sale Price ($/kg)	$	468
Alginate Sale Price (no pigments) ($/kg)	$	423
Profit ($/day)	$	-
All Together		
Mixed Product Sale Price ($/kg)	$	537
Profit ($/day)	$	-
Combined Approach		
Alginate Revenue	$	16,029
Amount of Laminarin and Fucoidan per day	1.85kg	
Profit ($/day)	$	-

From Table 6 it can be seen that the required alginate sale price to break even is reduced by a about ½. However, the minimum sale price for the mixed product increases by $69. Finally, the amount of laminarin and fucoidan required to be sold per day is reduced by around ½ as well. Therefore, it would not improve the process any to reduce extractions in the mixed product method but it would appear that money could be saved in the other modified methods.

One last method I wanted to try was to take the 1/3 capital reduction modified methods and implement an ethanol recycle. I noticed that the daily cost of ethanol was very high and the process itself wasted a majority of it. If a recycle stream for the ethanol was added, a lot of money could be saved. The results from implementing this recycle stream can be seen in Table 7 below. The method of recycle used was a distillation column with 90% recovery of ethanol.

Table 7: Additional Distillation of Ethanol

Alginate Only		
Alginate Sale Price ($/kg)	$	488
Alginate Sale Price (no pigments) ($/kg)	$	443
Profit ($/day)	$	-
All Together		
Mixed Product Sale Price ($/kg)	$	234
Profit ($/day)	$	-
Combined Approach		
Alginate Revenue	$	16,029
Amount of Laminarin and Fucoidan per day	1.3kg	
Profit ($/day)	$	-

DISCUSSION

From my analyses, it has become apparent that this process has the potential to be economically viable on an industrial scale, but more must be researched about the current markets for fucoidan and laminarin in order to reach a definite conclusion. In the initial base case, it is easily possible to make a profit, but only theoretically. It is impossible for all the product to be sold at one time because there is not nearly enough demand. The capital costs are far too high and the required price to break even in both modified cases is also very high. It might still be possible to make these versions of the process economical, but my Aspen simulation is limited in its ability to determine what must be done to do so. One modification to the process could be to reduce the number of extractions to one for each of the polysaccharides. This would reduce the equipment costs but would also reduce the product output and thus the possible profits. From the fourth analytical case, it is clear that if even a just a fraction of the laminarin and fucoidan produced could be sold at one tenth the current asking price, the process could make money and pay back all initial costs quickly.

If someone wanted to continue my research and analysis there are a few things they could look at. It would be possible to implement a counter current extraction method in the third and fourth ethanol extraction steps due to the low concentrations of pigment. In addition to the discussed ethanol recycle, this could save on ethanol costs.

Another component of the overall extraction discussed briefly previously that was not implemented into my model is drying of the products. The products would not be sold in liquid extract form; they would be sold as a powder. In the lab, we dry the extract via

freeze drying, but as discussed this method would not be viable on an industrial scale. Thus, another method of drying the product, such as evaporation, would need to be investigated and implemented into the final plant.

In terms of research it is likely the polysaccharide composition of the seaweed is different to what has been reported, and if more fucoidan or laminarin could actually be produced, that would benefit the process. It could also be that fucoidan and laminarin are or can potentially be in high demand, and so making a large amount of these two polymers would be beneficial in the short and the long term for the market.

I believe it is still possible to make this process economically viable on an industrial scale, but my model lacks the ability to prove this definitively. Further research done in the van Walsum lab should be done to confirm how much polysaccharide could be produced on the small scale and economic research should be done in the market to see how much demand there is for these polymers. For now, I have created an accurate model of the process as it would be used on an industrial scale and shown that it could be possible to make a profit.

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APPENDIX A:

Figures

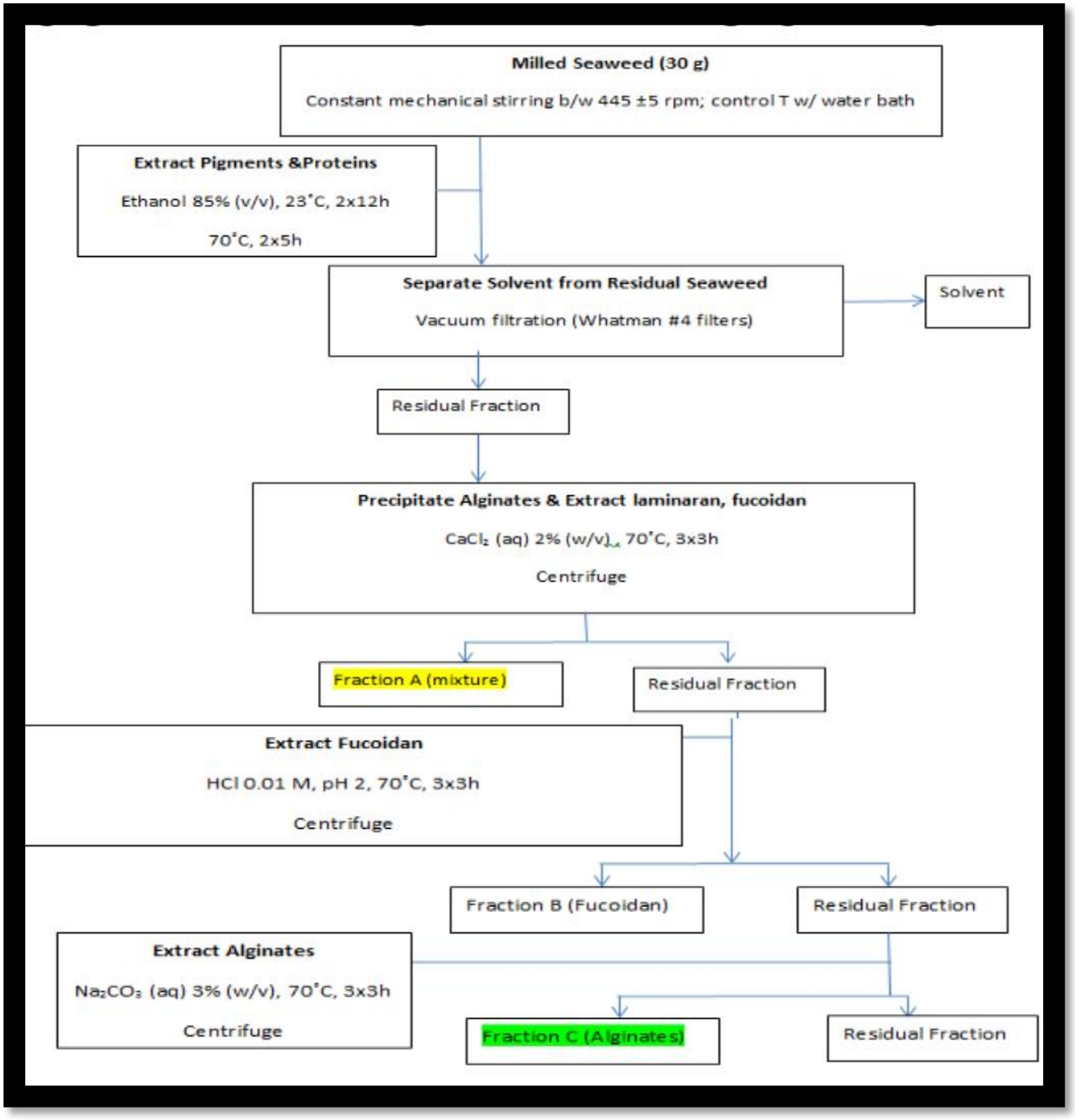

Figure 1: Extraction Process Diagram

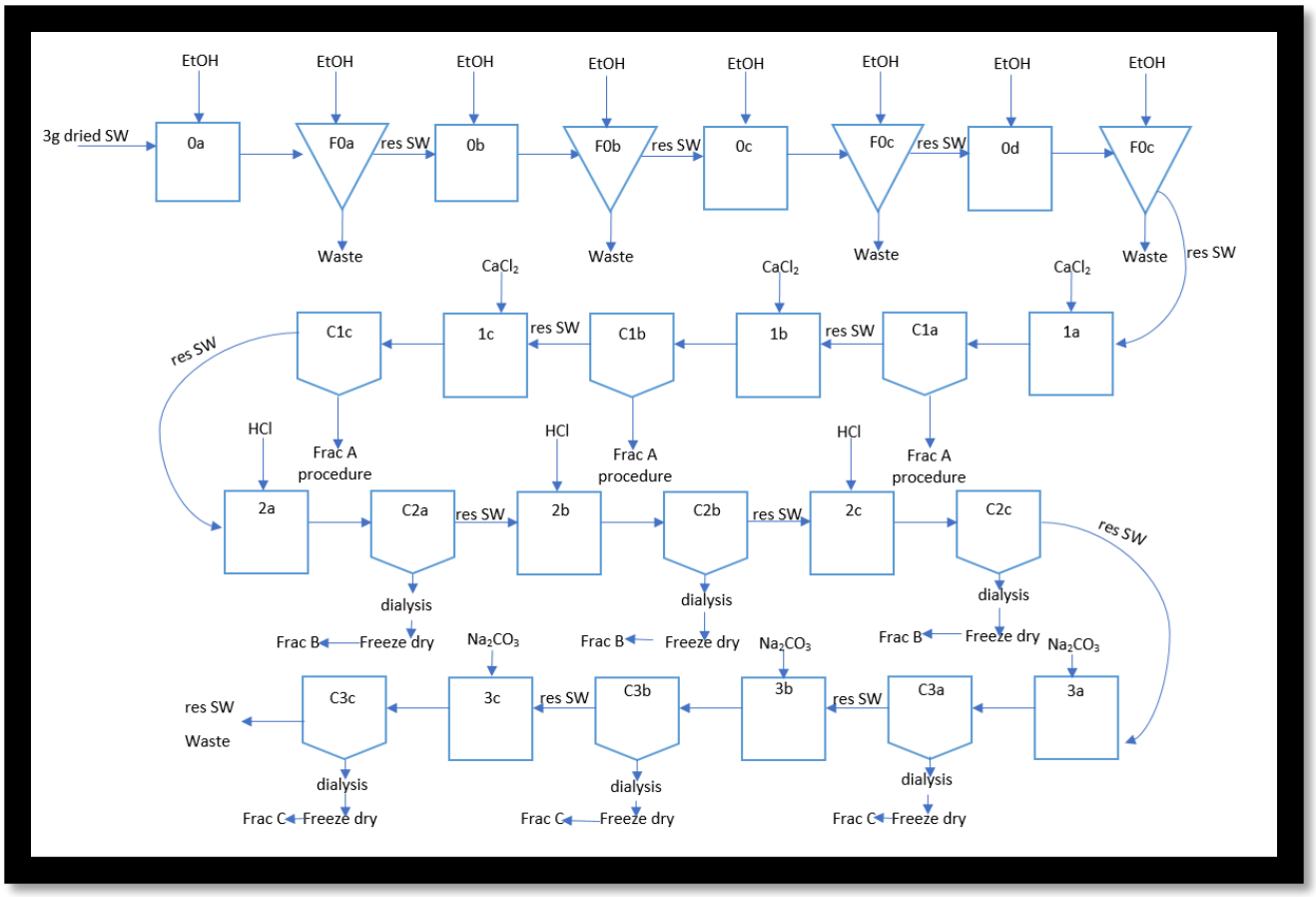

Figure 2: Extraction Flow Diagram

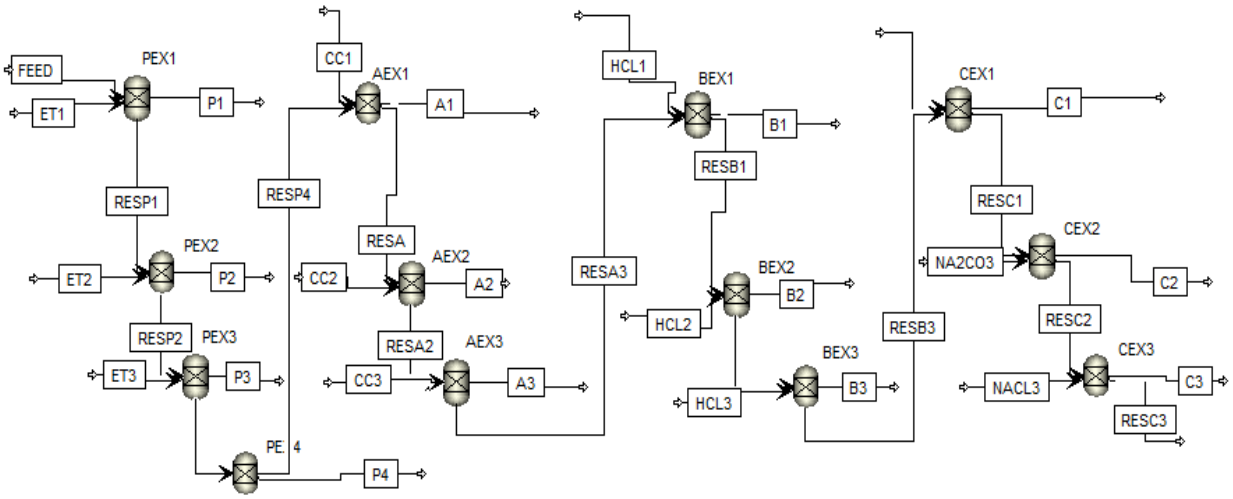

Figure 3: Base Case Aspen Design

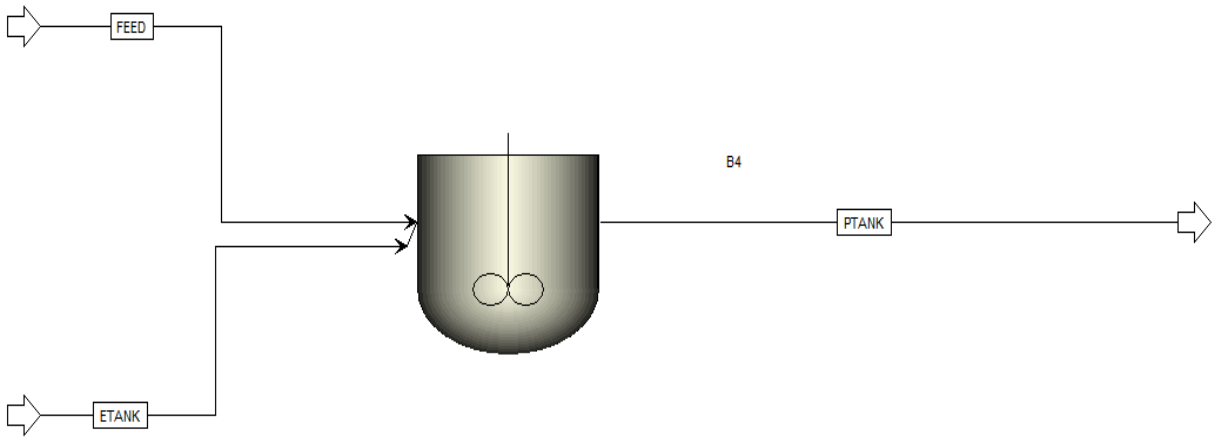

Figure 4: General CSTR for Economic Calculations

Seaweed

$P_{SW} := 25 \ \frac{¤}{lb}$ — Price of seaweed

$F_{SW} := 1000 \ \frac{kg}{day}$ — Flow rate of seaweed feed

$Cost_{SW} := P_{SW} \cdot F_{SW} = 55115.566 \ \frac{¤}{day}$ — Daily cost of seaweed

Ethanol

$P_{Et} := \frac{1500 \ ¤}{160 \ kg}$ — Price of ethanol

$Et := 0.7 \cdot (7 \cdot F_{SW}) = 4900 \ \frac{kg}{day}$ — Amount of ethanol used

$Cost_{Et} := 4 \cdot P_{Et} \cdot Et = 183750 \ \frac{¤}{day}$ — Daily cost of ethanol

Figure 5: Calculations for Daily Cost of Seaweed and Daily Cost of Ethanol

CaCl2

$P_{CaCl2} := \frac{1441\ ¤}{25\ kg}$ Price of calcium chloride

$Et := 0.02 \cdot (9 \cdot F_{SW}) = 180\ \frac{kg}{day}$ Amount of ethanol used

$Cost_{CC2} := 3 \cdot P_{CaCl2} \cdot Et = 31125.6\ \frac{¤}{day}$ Daily cost of calcium chloride

HCl

$P_{HCl} := \frac{96.65\ ¤}{5\ kg} = 19.33\ \frac{¤}{kg}$ Price of hydrochloric acid

$HCl := 0.01 \cdot (9 \cdot F_{SW}) = 90\ \frac{kg}{day}$ Amount of HCl used

$Cost_{HCl} := 3 \cdot P_{HCl} \cdot HCl = 5219.1\ \frac{¤}{day}$ Daily cost of HCl

Figure 6: Calculations for Daily Cost of Calcium Chloride and Hydrochloric Acid

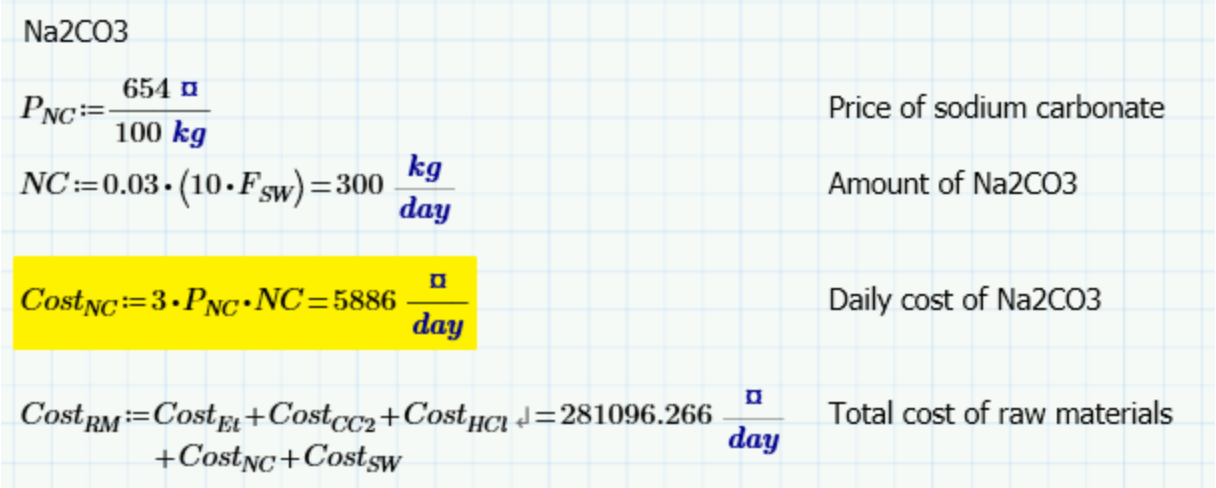

Figure 7: Calculations for Daily Cost of Sodium Carbonate and Total Raw Materials

EQUIPMENT

$Cap_{Et} := 4 \cdot 12656800$ ¤ $= 50627200$ ¤ Ethanol extractor capital cost

$Ut_{Et} := 4 \cdot 669052 \frac{¤}{yr}$ Ethanol utility cost

$Cap_{CC2} := 3 \cdot 9241280$ ¤ $= 27723840$ ¤ CaCl2 extractor capital cost

$Ut_{CC2} := 3 \cdot 440989 \frac{¤}{yr}$ Calcium chloride utility cost

$Cap_{HCl} := 3 \cdot 9264230$ ¤ $= 27792690$ ¤ HCl extractor capital cost

$Ut_{HCl} := 3 \cdot 440989 \frac{¤}{yr}$ HCl utility cost

$Cap_{NC} := 3 \cdot 9868700$ ¤ $= 29606100$ ¤ Na2CO3 extractor capital cost

$Ut_{NC} := 3 \cdot 491670 \frac{¤}{yr}$ Sodium carbonate utility cost

$Cap_{tot} := Cap_{Et} + Cap_{CC2} + Cap_{HCl} + Cap_{NC} = 135749830$ ¤ Total capital cost

$Ut_{tot} := 0.8 \cdot 1\ yr \cdot \left(Ut_{Et} + Ut_{CC2} + Ut_{HCl} + Ut_{NC}\right) = 5437721.6$ ¤ Total utility cost

Figure 8: Calculations for Capital Costs and Utilities Costs using Values from Simulation

$PBP := 5\ yr$

$Cost_{CAP} := \frac{135749830\ ¤}{PBP} = 27149966\ \frac{¤}{yr}$

$Cost_{UT} := 5437721.6\ \frac{¤}{yr}$

$Cost_{OP} := 6829030\ \frac{¤}{yr}$

$F_P := 0.99 \cdot (0.3 \cdot F_{SW}) = 297\ \frac{kg}{day}$ Amount of pigments and ash

$F_L := 0.99 \cdot (0.15 \cdot F_{SW}) = 148.5\ \frac{kg}{day}$ Amount of laminarin

$F_F := 0.99 \cdot (0.25 \cdot F_{SW}) = 247.5\ \frac{kg}{day}$ Amount of fucoidan

$F_A := 0.99 \cdot (0.3 \cdot F_{SW}) = 297\ \frac{kg}{day}$ Amount of alginate

$F_{All} := F_L + F_F + F_A = 693\ \frac{kg}{day}$ Total amount of product

Figure 9: Calculations for Capital, Utility and Operating Costs and Amounts of Products

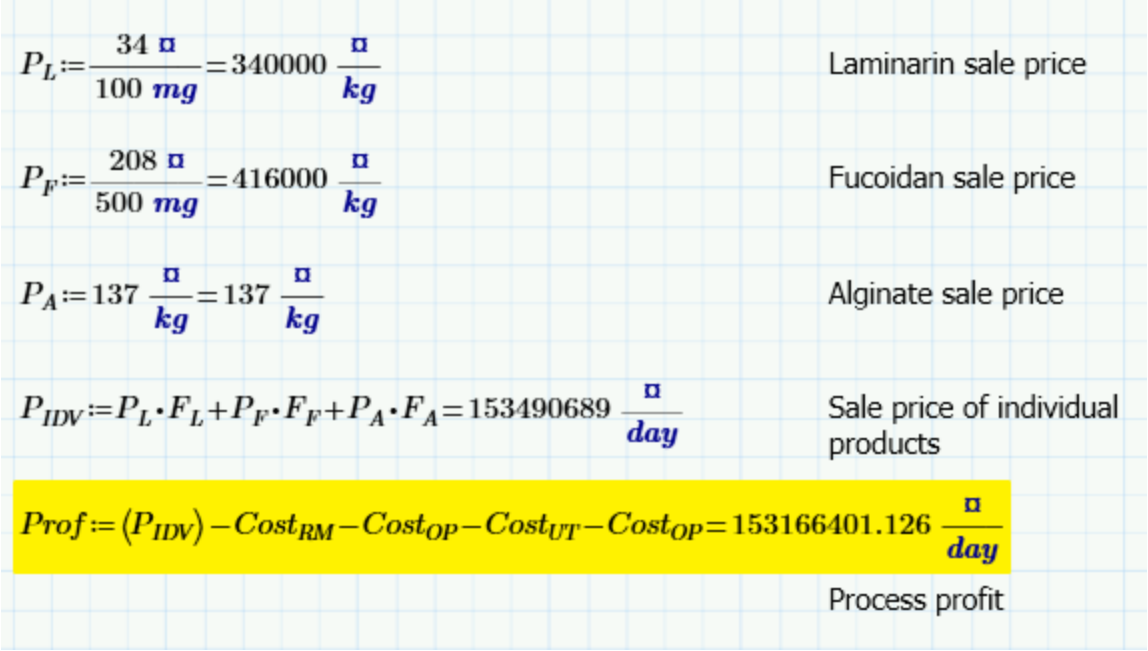

Figure 10: Individual Product Profit Calculations

$P_A := 1092 \frac{¤}{kg}$ Alginate sale price

$P_{AO} := P_A \cdot F_A = 118456810.878 \frac{¤}{yr}$ Alginate revenue

$Prof := \langle P_{AO} \rangle - Cost_{RM} - Cost_{OP} - Cost_{UT} - Cost_{OP} = 36.126 \frac{¤}{day}$ Process profit

Figure 11: Alginate Only Profit Calculations

$P_{All} := 468 \ \frac{¤}{kg}$ Sale price of mixture of products

$F_{All} = 693 \ \frac{kg}{day}$ Total amount of product

$Prof := (P_{All} \cdot F_{All}) - Cost_{RM} - Cost_{OP} - Cost_{UT} - Cost_{OP} = 36.126 \ \frac{¤}{day}$ Process profit

Figure 12: All Products Combined Profit Calculations

$P_L := 0.1 \cdot \frac{34\ ¤}{100\ mg} = 34000\ \frac{¤}{kg}$ Laminarin sale price

$P_F := 0.1 \cdot \frac{208\ ¤}{500\ mg} = 41600\ \frac{¤}{kg}$ Fucoidan sale price

$P_A := 0.5 \cdot 137\ \frac{¤}{kg} = 68.5\ \frac{¤}{kg}$ Alginate sale price

$P_{AO} := P_A \cdot F_A = 20344.5\ \frac{¤}{day}$ Profit of alginate only

$P_{LF} := P_L + P_F = 75600\ \frac{¤}{kg}$ Profit of laminarin and fucoidan

$M_{LF} := 4.03\ \frac{kg}{day}$

$Prof := \left(M_{LF} \cdot P_{LF} + P_{AO}\right) - Cost_{RM} - Cost_{OP} - Cost_{UT} - Cost_{OP} = 724.626\ \frac{¤}{day}$

Process profit

Figure 13: Combined Approach Profit Calculations

APPENDIX B:

Tables

Table 1: Soils Lab Analysis of Seaweed Samples

Sample type: Seaweed

ID	TC	TN	Ca	K	Mg	P	Al	B	Cu	Fe	Mn	Zn	total	total + S	O + H	total+OH
	%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm				
1	32.2	1.60	2.56	5.65	0.576	0.303	99.2	144	0.873	119	8.08	15.8	42.9	44.0	48.315	91.2
2	33.1	3.80	6.74	2.46	0.451	0.364	138	102	4.38	254	21.3	31.9	47.0		49.695	96.7
3	26.9	1.83	1.10	10.2	0.580	0.356	91.8	142	1.83	86.9	5.86	15.2	41.0		40.41	81.4
4	29.0	4.17	6.44	3.70	0.560	0.364	163	93.8	2.43	301	21.5	28.9	44.3		43.515	87.8
5	32.6	1.76	2.82	4.00	0.541	0.274	51.8	117	1.58	137	9.05	15.8	42.0		48.84	90.8
6	34.4	1.52	1.70	4.52	0.511	0.269	84.3	132	1.57	180	10.0	24.8	43.0		51.66	94.7
7	33.4	1.22	1.50	5.23	0.488	0.198	47.3	126	2.45	149	7.36	20.4	42.0		50.04	92.1
8	32.2	1.93	2.59	5.80	0.524	0.314	43.8	121	2.35	109	6.53	19.1	43.4		48.27	91.6
9	32.1	1.71	2.52	5.19	0.522	0.292	42.8	126	2.18	75.7	4.98	14.2	42.3		48.105	90.4

Element	Units	Sample 1	Element	Units	Sample 9
Cd	ppm	< 2.0	**As**	ppm	< 0.01
Cr	ppm	< 2.0	**Hg**	ppm	< 0.04
Pb	ppm	< 2.0			
S	ppm	10337			

Table 2: Costs of Raw Materials

Process Component	**Daily Cost/Revenue**
Seaweed ($/day)	$ 55,115
Ethanol ($/day)	$ 183,750
CaCl2 ($/day)	$ 31,126
HCl ($/day)	$ 157
Na2CO3 ($/day)	$ 5,886
Total raw materials ($/day)	$ 281,096

Table 3: Equipment, Operating, Utilities and Capital Cost

	Cost	
4 x EtOH Separator	$	50,627,200
3 x CaCL2 Separator	$	27,723,840
3 x HCl Separator	$	27,792,690
3 x Na2CO3 Separator	$	29,606,100
Total Capital Cost	$	135,749,830
Utilities Cost	$	5,437,722
Operating Cost	$	27,316,120

Table 4: Base Case Summary

Process Component	Daily Cost/Revenue	
Seaweed ($/day)	$	55,115
Ethanol ($/day)	$	183,750
CaCl2 ($/day)	$	31,126
HCl ($/day)	$	157
Na2CO3 ($/day)	$	5,886
Total raw materials ($/day)	$	281,096
Capital cost ($)	$	135,749,830
Utilities cost ($/year)	$	5,437,722
Operating cost ($/year)	$	6,829,030
Laminarin sales ($/day)	$	50,490,000
Fucoidan sales ($/day)	$	102,960,000
Alginate Sales ($/day)	$	40,689
Total sales ($/day)	$	153,490,689
Profit ($/day)	$	153,166,401

Table 5: Modified Cases Summary

Alginate Only	
Alginate Sale Price ($/kg)	$ 929
Alginate Sale Price (no pigments) ($/kg)	$ 369
Profit ($/day)	$ -
All Together	
Mixed Product Sale Price ($/kg)	$ 468
Profit ($/day)	$ -
Combined Approach	
Alginate Revenue	$ 20,345
Amount of Laminarin and Fucoidan per day	4.03kg
Profit ($/day)	$ -

Table 6: 1/3 Capital Reduction

Alginate Only		
Alginate Sale Price ($/kg)	$	468
Alginate Sale Price (no pigments) ($/kg)	$	423
Profit ($/day)	$	-
All Together		
Mixed Product Sale Price ($/kg)	$	537
Profit ($/day)	$	-
Combined Approach		
Alginate Revenue	$	16,029
Amount of Laminarin and Fucoidan per day	1.85kg	
Profit ($/day)	$	-

Table 7: Additional Distillation of Ethanol

Alginate Only		
Alginate Sale Price ($/kg)	$	488
Alginate Sale Price (no pigments) ($/kg)	$	443
Profit ($/day)	$	-
All Together		
Mixed Product Sale Price ($/kg)	$	234
Profit ($/day)	$	-
Combined Approach		
Alginate Revenue	$	16,029
Amount of Laminarin and Fucoidan per day	1.3kg	
Profit ($/day)	$	-

AUTHOR BIOGRAPHY

Zachary Applebee was born in Bangor, Maine on December 4th, 1996. He was raised by his mother Allison Applebee and his Father Vinal Applebee. He has lived in Orono, Maine his entire life. After graduating from Orono High School in 2015, he went on to pursue a bachelor's degree in Chemical Engineering at the University of Maine in Orono.

He worked in several different labs on campus over the course of his High School and University careers, but he spent the longest working under Dr. van Walsum where he studied polysaccharides in seaweed. He worked in the van Walsum lab for four years and his Honors Thesis is based on this work. After graduation he plans to find a job in the Chemical Engineering field or in research. He can't wait to leave his hometown and see what experiences his time spent at UMaine will offer him.