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**BATH**

University of Bath  
Department of Chemical Engineering

## **Bioplastic Food Packaging from Waste Whey DP5(1)**

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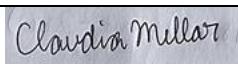
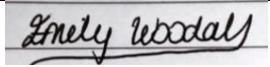
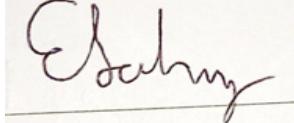
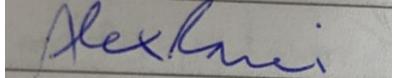
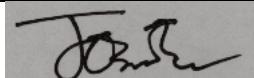
**2021-2022**



Authorship Declaration (see Attachment 2, to be signed by all members of the group)

#### AUTHORSHIP DECLARATION

I certify that I have read and understood the entry in the Programme Handbook for the Department of Chemical Engineering on Cheating and Plagiarism and that all material in this assignment is my own work, except where I have indicated with appropriate references or acknowledgements. I agree that, in line with Regulation 15.3(e) I will submit an electronic copy of this work for submission to a Plagiarism Detection Service for quality assurance purposes.

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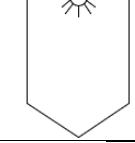
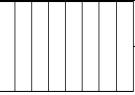
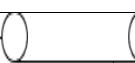
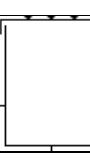
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## Nomenclature

Table 1: PFD and P&ID symbols

Symbol	Equipment	Symbol	Equipment
	Centrifugal pump		Gate Valve
	Spray dryer		Diaphragm valve
	Heat exchanger (HX1 representing the cooling heat exchanger in pasteurization)		Bursting disk
	Plate heat exchanger (Pasteurization) (Representing first heat exchanger in pasteurization process)		Pressure relief valve
	Fan		Temperature indicating control
	Sampling point		Flow indicating control
	Washing unit		Level indicating control
	Buffer Vessel (as part of the diafiltration module)		Temperature transmitter

	Stirred tank reactor with jacket (three reactors, with the methacrylation and polymerisation reactor having a cooling and heating jacket respectively)		Flow Transmitter
	Membrane Module (with additional UF/DF unit in parallel for membrane regeneration) UF DF HEPA filter		Level Transmitter
	Centrifuge		pH Transmitter
	Drum Dryer		Pressure indicator
	Process flows		Flow indicator
	Electrical signal		Temperature high alarm
	Process inflows and outflows		Level high alarm
	Pressure high alarm		Level low cut off
	Flow valve		Temperature valve
	Flow/Level valve		



Table 2: Nomenclature

<b>Symbol</b>	<b>Definition</b>	<b>Unit</b>
A	Area	m <sup>2</sup>
a,b,c,d	Coefficients for specific heat capacity	-
$c_p$	Specific heat capacity	J K <sup>-1</sup> kg <sup>-1</sup>
E	Energy	J
$\Delta E_K$	Kinetic energy change	kJ
$\Delta E_P$	Potential energy change	kJ
$F_i$	Flow rate of stream i	tonnes batch <sup>-1</sup>
G	Dry mass air flow rate	tonnes batch <sup>-1</sup>
H	Humidity	kg/kg
$\Delta H$	Enthalpy change	kJ
$\Delta H_v$	Latent heat of evaporation	kJ
$\Delta H_{rxn}$	Heat of reaction	kJ
$h_{fg}$	Specific enthalpy	kJ/kg
m	Mass	kg
$\dot{m}$	Mass flow	kg batch <sup>-1</sup>
n	Number of moles	mol
P	Pressure	Pa
Q	Heat transfer	kJ
$\dot{Q}$	Rate of heat transfer	kW
T	Temperature	K
$\Delta T_{lm}$	Log mean temperature difference	K
U	Heat transfer coefficient	W m <sup>-2</sup> K <sup>-1</sup>
$\Delta U$	Change in internal energy	kJ
V	Volume	m <sup>3</sup>
W	Air flow rate	tonnes batch <sup>-1</sup>
$W_s$	Shaft work	kJ
x	Mass fraction	-
$\lambda_0$	Latent heat at temperature T <sub>0</sub>	kJ/kg
$\eta$	Efficiency	-

<b>Subscript</b>	<b>Definition</b>
a	Air
c	Cold
f	Feed
g	Gas
h	Hot
i	In
l	Liquid
o	Out
p	Permeate
r	Retentate
s	Solid
TM	Transmembrane



## Executive Summary

### Objectives:

The primary objective of this project is to produce a waste-to-high value product which is relevant to at least three items on the environmental agenda at COP26. These include moving away from fossil fuel-based products, preventing the use of single-use plastics, and reducing waste. To achieve this primary goal, a number of daughter objectives were developed, considering things like economics, sustainability, and societal impact.

Economically, one objective was to create a profitable business idea which will break even in under 10 years, after which making a profit that will allow the research and design of future similar products.

In terms of sustainability objectives, the project aimed to reduce food waste by utilising unused whey to generate a bioplastic for food packaging applications. This will prevent the illegal disposal of waste whey into waterways, which can cause habitat damage due to its oxygen demands. Through aiming to provide a suitable bioplastic film for food packaging with a smaller environmental impact than fossil fuel-based plastics, the aim is to reduce the carbon footprint of the food industry and reduce the use of fossil fuels.

The societal objectives of the project are based on the local economy of the area and nationwide awareness. The project aims to boost the local economy in Somerset and provide skilled training and jobs, working to reduce poverty and increase the number of skilled workers in the area to increase the local average wage. An additional goal is to financially help struggling local farmers by removing their waste for free and providing them with packaging for their products at a reduced rate. The company aims to raise awareness for the need for bioplastic development through consumer use of this food packaging.

### Description of product and process:

In initial scoping studies, various methods were investigated to convert waste whey to bioplastic with four options evaluated in depth, including using fermentation processes with either *E.coli* or *H. mediterranei* to produce a polyhydroxy alkanoate (PHA) plastic or utilising either the liquid whey or whey powder to undergo a co-polymerisation process with the co-polymer with poly(ethylene glycol) methacrylate (PEGMA) to form a polyethylene-like plastic made up of rubbery PEGMA backbone and hard protein functional groups.

After evaluating the options, the chosen option was the co-polymerisation reaction with PEGMA, utilising the waste liquid whey due to consideration of the selection criteria: sustainability, cost, risk, process yield and product quality. Screening matrices and mock customer surveys were carried out.

For the co-polymerisation with PEGMA, literature was available describing the lab scale process (Chalermthai et al., 2019) for co-polymerisation and the industrial units for scale up of the process (Chalermthai et al., 2020) and were evaluated using a techno-economic analysis of the chosen process. The plastic produced in the polymerisation consists of protein (functionalised with methacrylate groups) and PEGMA at ratio of 30:70 respectively which was chosen for the superior mechanical properties including tensile strength at the selected ratio. The product made in the chosen process is a plastic in the form of shaved flakes. However, our desired product is plastic in the form of a film as that is what will be used as food packaging. Thus, further processing is then required for generating this plastic film. This processing is conducted by our partner company in order to maintain the scope of the project. Thus, the process designed is a streamlined method to convert liquid whey to a polyethylene-like plastic, which is later passed on to further processing.

To find the available feedstock, the market of cheese in the UK was evaluated and the quantity of waste whey generated was found, knowing that for every 1 kg of cheese produced, 9 kg of liquid whey are produced. This results in around 4,266,000 tonnes of waste whey generated per year. The determined feedstock chosen for the process was around 1% of the waste whey produced in the UK, relating to the quantity of cheese manufacturers in the area chosen for the plant in Somerset. However, this number is chosen as an initial estimate and would be refined in further design by contacting cheese producers

in the region to obtain an accurate figure. Thus, the feedstock for the process is 44,800 tonnes of waste whey, corresponding to 1.05% of the total waste whey produced in the UK.

In the process, consisting of: liquid whey processing, whey powder generation, chemical processing and plastic production, 100 tonnes of whey are processed per batch. Thus, 448 batches are to be processed each year, amounting to 3 batches run each day in series. This batch quantity amounts to producing 2.515 tonnes of plastic from each batch of 100 tonnes of liquid whey

Processing the 448,000 tonnes of waste whey feedstock yields 1126.7 tonnes of plastic product per year. This plastic has a water content of around 10%, as detailed by specifications, and some impurities due to incorporation of small quantities of carbohydrates, fats, and minerals from the raw feedstock protein along with unreacted species from the chemical processing. The mechanical properties of the plastic film produced at a lab scale are of  $3.8 \pm 0.2$  MPa tensile strength which would be unsuitable for applications such as rigid packaging or shrink wrap packaging, justifying why the chosen application is for those products which are packed with stiff film, form-fill-seal films and lid films replacing the current options which go directly to landfill.

In further research, the film should be tested for key properties such as oxygen permeability, resistance to heat and chemicals, transparency, and biodegradability. The required thickness (available range of 0.17 to 0.31 mm ((Wagh et al., 2013)) and any required additives would be agreed with each customer to provide the required plastic properties. Additionally, alternatives for less desirable components such as PEGMA should be devised, and research conducted on the mechanical properties of those novel polymers created. The plastic will be passed onto the partner company for further processing to plastic film and then sold onto the cheese manufacturers at a price of 70% of the conventional consumer price of £5.343/kg (or \$7/kg), as the cheese manufacturers provide the waste whey for free and provide whey storage when waiting for collection for processing. This was determined to be economically favourable for the company as it would allow for easy access of the feedstock without being responsible for any storage or refrigeration, and having a stable consumer to consistently utilise our product. Additionally, by using our packaging, cheese manufacturers will act as a form of advertisement for our product, widening the reach of the film packaging after few years of production and increasing customer base and reach for the product.

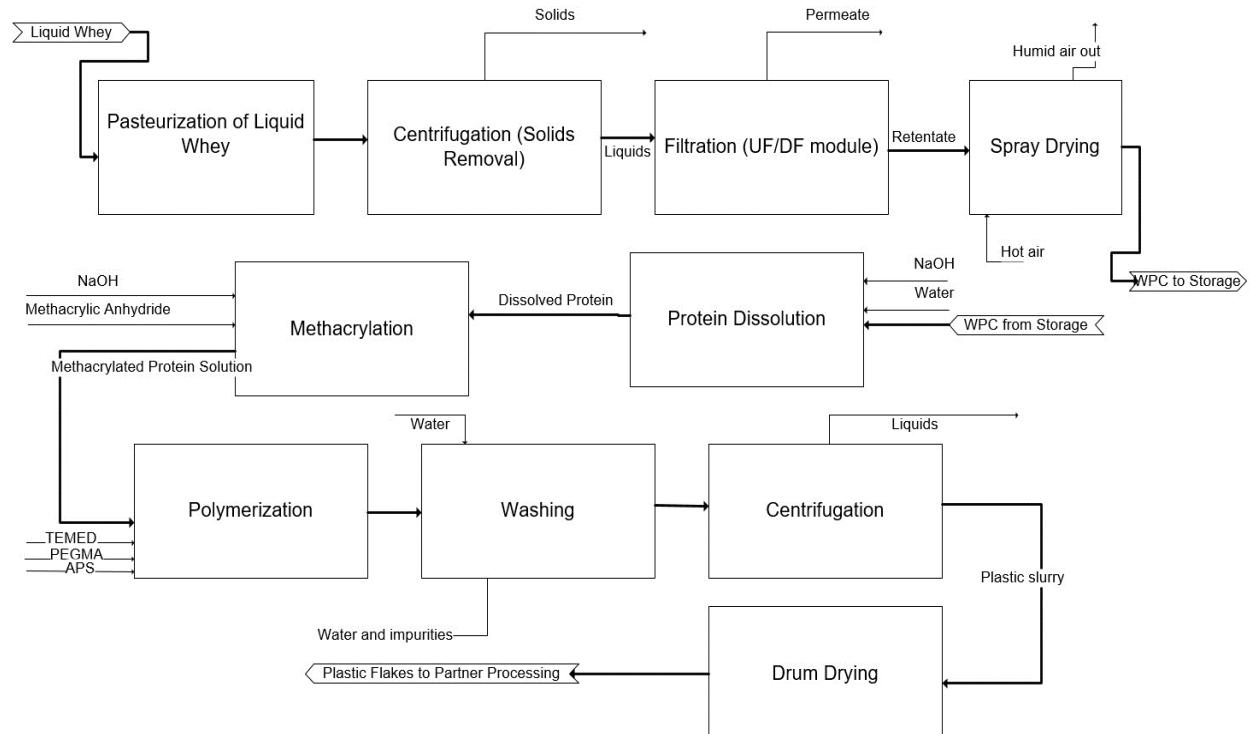


Figure 1: Simple flowsheet of the process



The process consists of 11 unit operations as shown in Figure 1. The initial step of pasteurisation removes any pathogens from the whey. This is followed by a centrifugation unit which removes the large solids such as fat. The outlet from the centrifuge feeds into an ultrafiltration unit which separates the whey protein from the lactose and other low molecular weight solutes by rejecting the whey protein. The retentate then goes through a diafiltration unit with a water buffer to further concentrate the protein and achieve a higher purity. Once the protein is sufficiently concentrated, the fluid goes through a spray dryer where it is dried to produce whey protein powder with a moisture content of around 10% - sufficient for plastic production. This powder is then dissolved in water in a protein dissolution unit to facilitate the next step of methacrylation. During methacrylation, the proteins are reacted to produce the methacrylated co-monomer before moving to the polymerisation step. Here, they are polymerised with PEGMA to form the final polymer. The plastic is then washed to remove any unreacted components or impurities, and centrifuged and drum dried to remove excess water.

### Safety considerations

Safety was considered within the process through safety evaluations at each stage of design with a hazard identification (HAZID) exercise first carried out on a simple process flow diagram (PFD) (Figure 4). In the HAZID, general safety considerations due to the location of the plant in Somerset, in proximity to livestock and agricultural land are mitigated throughout the design of the process by selecting units which will not pose a large threat to the surrounding areas. Factors such as an increase in vehicle traffic and proximity to residential areas are also identified as considerations. Additionally, staff safety was considered, choosing units operated at low temperatures and pressures and by utilising catalysts to facilitate reactions at atmospheric conditions. The only units occurring at high temperatures and pressures are the pasteurization, spray drying, and drum drying units where high temperature and pressure is attributed only to utility streams. Vessel sizing is also considered as a part of inherently safe design through appropriate mitigations for overfilling. Other guidewords such as the effect of natural disasters were also included within the HAZID, along with toxicity hazards due to the reagents used in the process. These include PEGMA, sodium hydroxide, Tetramethylethylenediamine (TEMED), and ammonium persulfate (APS), which are either combustible, flammable, skin irritants or oxidizers. Once the HAZID was conducted, some preliminary controls were added in a piping & instrumentation diagram (P&ID) consisting of each of the process units.

After the HAZID was conducted, the polymerisation reactor was taken to be the most hazardous in the process due to the presence of various reagents needed for the polymerisation. Thus, a hazard and operability analysis (HAZOP) was conducted on this unit P&ID, with the design team following a systematic approach with the aid of guidewords and deviations, evaluating the consequences, and needed safeguard of hazards present. The outcome of the HAZOP determined that control and alarm systems, both with level and temperature high alarms, should be applied to the reactor along with other mitigations such as a pressure relief valve and bursting disk to mitigate pressure increases which could be caused by a fire on site. The selected safeguards were applied to the individual P&ID node for the polymerisation reactor.

After both general HAZID and more specific HAZOP were carried out, a plant layout was generated considering the hazards in the process. Within the plant layout considerations for reagent toxicity and operational safety are considered, arranging units to minimise consequences of accidents and minimising the pipe crossings needed. Staff safety is again considered, placing offices outside of the range of hazardous reactor units

Finally, a start-up and shut-down procedure is devised to mitigate any hazards associated with the batch operations carried out in this process.

The safety aspects of this process should be re-evaluated for a more in-depth risk analysis in later stages of design, including in depth risk quantification and LOPA analysis.

### Environmental assessment outcome

The environmental impact of this process was assessed by consideration of the sourcing of the inputs into the system, the operations of the process and the waste created from the process.



Due to the location chosen for the plant and the form of feedstock chosen, the impact of sourcing the feedstock were minimised, with liquid whey provided directly from the dairy farms near the site. However, methacrylic anhydride, PEGMA, sodium hydroxide, APS and TEMED, all require transportation to the site. These inputs will be sourced from the closest producers available to reduce the carbon footprint of the transportation step. Producers will be assessed both on their emissions and their sustainable practices.

Utilities also have a significant effect on the environmental impact of the process. Water requirements of the process are high due to steam and water inputs throughout, which will influence the diminishing water resources. Steam is usually produced using the burning of fossil fuels, which contributes to many environmental issues (Chalermthai et al., 2021). Through further optimization, water usage will be minimised and electric boilers will be used, with the electricity coming from renewable suppliers.

The energy requirements in this LCA from whey powder to plastic were determined as 2.9 MJ/kg of plastic produced (Chalermthai et al., 2021). This was lower than for other plastic production methods, for example polylactic acid (PLA) production required 53 MJ/kg, polypropene 74 MJ/kg and PHB 42.9 MJ/kg (Chalermthai et al., 2021). However, this does not take into consideration the energy requirements upstream to purify and concentrate the liquid whey into the powder or the further processing requirements of converting our product into a film before it is to be of use. Since the overall process operates at relatively mild temperatures and pressures through most units, it will have low energy consumption requirements compared to many conventional processes. This energy consumption was estimated as 30.73 MJ/kg of liquid whey processed.

A full life cycle assessment (LCA) of the whole process would be performed in the detailed design stage, although a previous study identified that PEGMA and Methacrylic anhydride were the major contributors to environmental damage (Chalermthai et al., 2021). The process also produces a variety of waste streams. To reduce the impact of this waste it would be either further processed to produce valuable lactose or dried and used for animal feed. The waste from the washing must be sent off as aqueous waste to a treatment site as it contains potentially harmful chemicals. Even after treatment, some of this waste must be disposed of, which could cause water emissions associated with environmental issues such as eutrophication and terrestrial ecotoxicity.

Utilising whey, a second-generation biomass, is a sustainable method to prevent this non-edible biowaste, going to waste (Rosenboom et al., 2022). This overcomes ethical concerns of first-generation biomass use for bioplastics which can compete with the food industry, particularly in local settings (Rosenboom et al., 2022). If whey is not used for the manufacture of new products and is released directly into waterways without any treatment, its high polluting power can cause destruction of flora and fauna (Amaral and Silva, 2021). Hence, this project aligns with the COP26 agenda of a reduction of waste.

Furthermore, construction of this plant creates jobs for those in the surrounding areas and minimises the burden on smaller scale cheese producers to deal with the abundance of whey and can create a circular economy by using the waste and feeding it back into the cheese businesses for packaging purposes. This aligns with SDG8 to promote sustained, inclusive, and sustainable economic growth and with SDG12.

The use of whey protein as a co-polymer for the plastic produced also reduces the reliance on fossil fuels for plastic production, as conventional plastics are entirely fossil fuel based. This aligns with SDG13 of climate action and the agenda of COP26 of moving away from petroleum-based products. However, in comparison to other bioplastics such as polyhydroxyalkanoates (PHA) and PLA which are 100% bio-based, our product is less sustainable in terms of its composition, with 70% being made from PEGMA, which is derived from fossil fuels.

### **Economics outcomes**

The total capital cost was estimated to be £31.03 million. Contributions to this include: the plant and equipment cost of £19.33 million, the building cost of £5.087 million, and the land cost of £1.017 million.



The total operating costs were estimated to be £3.084 million. The cost of purchasing raw materials makes up the majority of this, as the annual cost of PEGMA is £2.478 million.

The selling price of the product is £5343 per tonne. A small portion of the product will be sold at a 70% discount to the cheese producers that provide us with the input liquid whey required. The total annual income from sales will be £5.646 million, and the annual gross profit will be £2.562 million. From this, 5% (£0.1281 million) of the profits will be given to the partner company, who will be producing plastic film from the final product. Therefore, the remaining annual income will be £5.518 million, and the remaining annual profit will be £2.434 million.

The lifetime of the plant was estimated to be 35 years. Using the above values for capital costs (CAPEX), annual operating costs (OPEX) and annual income, the net present value (NPV) of the project at end of the plant lifetime was calculated to be -£2.673 million. Therefore, with the current set operating conditions of the plant, the process is not economically viable. However, a sensitivity analysis was carried out on selected parameters, to investigate the effect on the final NPV. The parameters considered were the purchase price of the copolymer used, the annual number of batches, and the selling price of the product. Changes in these parameters could improve the project's economic feasibility.

## Conclusion

Overall, a process was designed as detailed above by evaluating existing process routes either in fermentation or co-polymerisation from literature and designing appropriate units for the conversion of liquid whey to bioplastic. The designed process can be taken as an initial short cut design, thus the level of detail in unit design is as such. Because of the nature of the project and the timeframe within which the design was completed, various assumptions were carried out in the design of the process. Assumptions mainly served to simplify balances and calculations, to eliminate the need for software-aided calculations.

For the liquid whey processing to powder whey the most significant assumptions made were:

- The composition of feedstock waste liquid whey is: 4% carbohydrates, 4.5% fat, 1% minerals, 1% protein and 89.5% water.
- In the pasteurisation unit, the whey is heated to 61°C to prevent denaturing protein content, and this temperature is assumed as sufficient for sterilization when the pasteurisation is run for 15 minutes.
- Liquid whey is assumed to have the heat capacity equivalent to water.
- Centrifugation is carried out at a sedimentation efficiency of 30%.
- Rejection coefficients are constant for each component passing through the ultrafiltration and diafiltration membrane, neglecting fouling.
- A transmembrane pressure for both the ultrafiltration and diafiltration unit was decided based on literature.
- The pump energy requirements were calculated from pressure differences.
- An amount of diafiltration buffer was calculated using a 20:1 ratio of permeate to retentate
- The required amount of water in the retentate of the diafiltration was found working backwards to reach a whey protein powder moisture content of 10%.
- Buffer tank was not a key unit and thus not sized.
- In the spray dryer, an air inlet humidity was assumed.
- The spray dryer inlet air temperature was assumed with the requirement for the product to not become denatured at high temperatures.
- Size of the whey particles required in the spray dryer outlet is assumed so a residence time can be defined.
- The inlet feed mass flow rate and inlet pressure of the spray dryer feed was set.
- Losses of product in the outlet air stream and from adherence to chamber walls are neglected.

For the chemical processing to final product stage the following assumptions were made:



- The conversion of the methacrylation reaction was taken to be 80%, with mole ratio of methacrylic anhydride/protein of 6.
- The cooling duty for the methacrylation reactor was assumed to be minimal so negligible cooling water is needed.
- In the polymerisation reactor, the polymerisation is assumed to occur at a 90% conversion by mass with a reacting ratio by mass of 30:70 methacrylated protein:PEGMA.
- The polymerisation reaction is assumed to be endothermic.
- The heating duty for the polymerisation reactor is calculated as minimal.
- APS and TEMED are taken as catalysts and initiator species that are consumed and then regenerated at 100% efficiency.
- The specific heat of the plastic and washing requirements were assumed to be equal to that of PHB
- In the drum dryer, dimensions were taken from an average of literature values.
- The steam temperature heating the drum dryer was set.
- Overall heat transfer coefficient for the drum dryer was assumed as  $600 \text{ W m}^{-2} \text{ K}^{-1}$ .
- Temperature increase due to friction between the blade and the plastic or drum were neglected.

These assumptions will be verified, rejected or validated in individual detailed design. However, these are not the full extent of assumptions made; further assumptions are detailed in the Unit Design section of the report. Each member in the group will be designing a key unit as part of detailed design and will verify the assumptions listed above through detailed design.

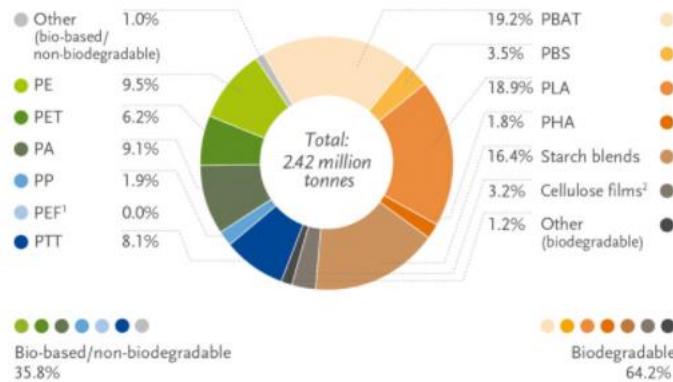
1. Fahim Ullah: Ultrafiltration module
2. Claudia Millar: Polymerisation reactor
3. Evan Johns: Methacrylation reactor
4. Alice Wilkening: Diafiltration module
5. Emily Woodall: Ultrafiltration module
6. Alex Raneri: Drum dryer
7. Jordan Osei-Tutu: Ultrafiltration module

To conclude, the project entailed designing a process to convert waste liquid whey to a high value plastic for food packaging applications. By assessing various process routes, carrying out market analysis and screening matrices, the chosen process was selected. Then, the required units were designed, and a model was established for a customer base and feedstock provider. Considerations for safety, environmental, societal, and economic impact were carried out. Finally, an analysis of assumptions applied and the required next steps for detailed design were devised.

## Introduction

Bioplastics currently represent less than one percent of the 367 million tonnes of plastic produced annually (European Bioplastics, 2022). Due to the environmental damage caused by conventional non-biodegradable, non-renewable fossil-fuel-based plastics, the market for bioplastics has increased significantly and is set to surpass 2% by 2025 (European Bioplastics, 2022). The most significant customers of the bioplastics market include packaging applications, making up 48% of the total share of bioplastics market. With new technological advancements, bioplastics are now approaching prices comparable to conventional plastics making them a more economical option for businesses to use (European Bioplastics, 2022). The definition of a bioplastic is a plastic partially or completely made from renewable sources. The industry of bioplastics consists of bio-based non-biodegradable plastics and bio-based biodegradable plastics; the difference being that biodegradable plastics can be decomposed by living organisms, meaning they take much less time to degrade.

*Global production capacities of bioplastics 2021  
(by material type)*



*Figure 2: Global production capacities of bioplastics 2021 (European Bioplastics, 2022)*

Asia is at the forefront of bioplastic production, contributing to almost 50% of global production. They are followed by Europe at 24.1%. The bioplastics currently available on the market include biodegradable and non-biodegradable polymers. Polybutylene adipate terephthalate (PBAT), polybutylene succinate (PBS) and bio-based polyamides (PAs) are key players in the market, this is demonstrated by Figure 2. Polylactic acid (PLA), polyethylene (PE) and polypropylene (PP) are also growing in capacity (European Bioplastics, 2022). The percentage of biodegradable plastics is expected to increase, above its current 64.2%, within the bioplastics market in the next few years due to advances in the development of PBAT, PBS and PAs (European Bioplastics, 2022).

### Plastic Pollution

Single-use plastics such as plastics bags and food packaging have been a significant cause of both marine plastic pollution and land contamination. Many market-based strategies and policies have been established to reduce the use of plastic bags, with little studies measuring the effectiveness of these reduction strategies. Future plans are in place to increase awareness of the problem and decrease plastic consumption (European Bioplastics, 2020).

Another key cause of plastic pollution is the degradation of plastics into microplastics. When plastics degrade or erode, they break down into small fragments referred to as microplastics. Researchers have been worried about the potential harms of microplastics for almost 20 years — although most studies have focused on the risks to marine life (Lim, 2021). Even if classed as biodegradable, many plastics require certain conditions to breakdown. This means even biodegradable plastics cause microplastic pollution if released into the environment, causing similar issues to traditional plastics.

Plastic spills occurring during transportation and handling have also caused plastic to enter the environment. Although there is current framework built to control this, companies are not held accountable. In the production of these bioplastics, safety mechanisms will be put in place to minimise any plastic loss in the transfer from the plant to the partner film-producing company (Karlsson et al., 2018).

### Fossil fuels

Over 99% of plastics in use today are derived from hydrocarbons from crude oil, natural gas and coal (Center for International Environmental Law, 2017). These resources are quickly disappearing, and it is estimated that these will be completely depleted this century if things don't change. If trends in oil consumption and plastic production continue as expected, by 2050 the plastic sector will account for 20% of the total consumption of oil (Center for International Environmental Law, 2017). Minimising plastic production can therefore reduce the consumption of and reliance on fossil fuels.

### Issues Regarding Recycling Complications



With no legal rules to ensure consistency, each council has their own recycling system, resulting in confusion over what and where we can recycle. Confusion over which bin and which plastics has had a negative effect on the efficiency of our recycling centres. Uncertainty between compostable, biodegradable and bioplastic terms on packaging has increased this. There is concern that by adding new plastics, which will need to be sent to industrial composting centres, this will cause added confusion and therefore contamination of current recycling streams. Some believe the system is already confusing enough for the population, with more than 55% of people in the UK are still confused by what can and cannot be recycled (Cardboard: Beyond the Box, n.d.). Some biodegradable plastics are collected by local supermarkets; however, the majority of people are unaware of this. It is likely that further education and campaigns on how to recycle/dispose of plastics is needed to reduce this confusion and concern.

The availability of industrial composting facilities to dispose of the bioplastics needs to be considered and awareness is needed in the proper disposal methods for consumers. Although not fossil-fuel-based, because of the relative immaturity of the process, in some cases the footprint is high due to the amount of processing required throughout the life cycle.

### **Market Value of Bioplastics**

The cost of bioplastics ranges from \$2 - \$7 per kilogram (Chang, 2022), but as the market is growing and developing prices are closing in on the cost of oil-based plastics (Coren, 2016). This will make it a more realistic option for smaller companies.

### **Concerns Around Bioplastics in the Food Industry**

The possible effect of chemicals and nanoparticles used in plastic food contact materials (FCM) on human health has been a concern over recent years. This concern has equally been raised about bioplastics, even more so due to insufficient research on long term effects and health risks. The often food-based sources of the materials raise worries over possible conflicts with allergies or specific diets, for example chitosan-based materials triggering shellfish allergies or vegan diets disagreeing with animal-based products (Renton, 2020). There are also risks of contamination from the growing conditions of the agriculture-based components, possibly resulting in bacterial issues (Renton, 2020). This links with the concern about the lack of specific regulations or labelling requirements and limited guidance for testing for bio-based FCMs (Renton, 2020).

On the commercial side, there are concerns about the effect on the shelf life of the products contained. Any effect could cause an increase in food waste and possible risks to health if the best-before dates are not adjusted. New testing protocols need to be made to check for any interactions between any substances the packaging could encounter. Strength is also a potential issue, as bioplastics generally do not have the strength and other properties of a traditional plastic, meaning they are more susceptible to damage and less effective at protecting the food product (Robbins, 2020). Biodegradable plastics especially are structurally dissimilar to conventional plastics and can be easily breakable. For this reason, often co-polymers are added to strengthen the product. Coca-Cola for example have created a recyclable plastic with 30% bioplastic made from sugar cane and 70% traditional plastic (Robbins, 2020).

Economically, there is concern about the manufacturing and disposal costs as well as the effect on the cost of plastic packaged goods. The effect of the plastic packaging tax is yet to be seen, with the tax to be introduced 1 April 2022 in the UK at a value of £200 per tonne. The tax only targets plastics which have been produced containing less than 30% recycled plastic (GOV.UK, 2021)

### **Applications of Bioplastics**

Bioplastics can be applied in various industries despite packaging being the prominent use, taking up 48% of the bioplastic market (European Bioplastics, 2022). These other applications include catering, electronics, agricultural, automotive and consumer goods.

In the food packaging industry, some companies have already taken the leap to use bioplastics. Brands such as Vittel, Volvic and Heinz already use bio-PET while companies such as CocaCola have signed agreements to test PEF bottles (European Bioplastics, 2020). Microbial coatings are often added to improve the barrier properties of the plastics. The lack of recyclable films and flexible plastics available



leaves a gap in the market for biobased products to fill. The properties of bioplastics, which are often weaker than traditional plastics makes this a suitable purpose. In catering, uses include cutlery and cups, both reusable and single-use (European Bioplastics, 2022)

Applications in the agriculture industry include use for mulching films and reduction of pesticide use. Companies like SABIC have developed biodegradable polymer-coated fertilizers to replace the current polymers used to control the release of the nutrients to the soil and reduce the pollution to the soil and water supply (SABIC, 2022).

### **Whey characteristics**

Whey is the major by-product of the cheese or casein manufacture. Whey composition varies according to several factors: the type of whey (sweet (obtained from addition of rennet) or acidic (from lactic fermentation)), the source of the milk, the feed of the animal used for milk production, the type of cheese processing, the time of year and the stage of lactation (Panesar et al., 2007). Acid whey has higher salt and lower protein and lactose content than sweet whey, and it is more difficult to process with higher disposal costs than sweet whey (Pescuma et al., 2015).

### **Environmental Effect of Waste Whey**

Approximately 120 million tons of whey are produced annually, of which only 50% are used for products used in feed for humans and animals (Nikodinovic-Runic et al., 2013). Whey has always been an issue for cheese producers: for every pound of cheese produced, 9 pounds of whey is left. Although there are many commercial uses for whey, an industrial processor would need around 30,000 gallons per pick up to make the trip worthwhile. This would require additional storage and processing facilities, an expense which is not possible for many cheese producers (Danovich, 2018)

Due to this overload of whey, producers often end up paying farmers to remove and use it for fertilizer or livestock feed. Much of this whey ends up in waterways after running off the fields. Excess whey is removed by waste handlers or even by some, poured down the drain (Danovich, 2018).

The average values of chemical oxygen demand (COD) and Biological oxygen demand (BOD) are around 1280 and 703 mgO<sub>2</sub>/L (Nacera, 2016). This contributed to categorising whey as waste, as it causes large growth concentrations of algae in waterways because of the high protein and lactose levels.

### **Finding a solution to Waste Whey**

To overcome these problems, technologies have been implemented for CW valorisation. Valuable whey compounds such as individual proteins or whey protein concentrates (WPC) and lactose can be recovered, or powdered CW can be produced. Furthermore, bioconversion can be applied to obtain value-added products, such as bioplastics (Mollea et al., 2013). Whey protein has already been explored in packaging applications due to its excellent oxygen barrier properties and abundant availability (Sharma and Luzinov, 2013).

### **Available Feedstock**

There are two feedstocks considered: dry whey protein concentrate (WPC) and liquid whey. The feedstock of WPC could either be bought from large cheese producers who can afford onsite treatment or expired WPC from the protein powder industry (Chalermthai et al., 2020). A total of 95375 tonnes of powdered whey was produced in 2019, giving an estimate for the available feedstock (Shabandeh, 2022). The other option would be to invest into onsite treatment for smaller producers.

To find the available feedstock of waste liquid whey, a calculation was carried out with statistics stating that 474,000 metric tonnes of cheese were produced in the UK in 2020 (Shabandeh, 2022) and 1 kg of cheese creates 9 kg of whey (EIP-AGRI, 2022), thus 4,266,000 tonnes of whey were produced in 2020. The process to create bioplastic aims to use around 1% of the whey produced, so around 42660 tonnes in a year.



Sweet whey has many commercial uses, though industrial-scale buyers need to buy in bulk to make the effort worth it. Uplands, a small American cheese producer, says that while his operation produces 1,000 gallons of whey a day, an industrial processor would likely need closer to 30,000 gallons per pick up to make the trip worth its while. Uplands would have to invest in additional storage and processing facilities to store that kind of volume, an expense that is not in budget (Danovich, 2018). For cheese producers, whey disposal has proved to be a major obstacle due to the quantity produced.

Currently, small-scale producers dispose of the whey in the following ways:

- Use on fields as fertilizer
- Feeding to local farm animals, such as pigs. To make it worthwhile for the farmers, companies pay the farmers to take the waste whey, making it expensive.

This can cause issues as using too much as fertilizer can pollute waterways, killing aquatic creatures.

### Market Value of Whey

The price of liquid whey directly from the farms is lower than the price of dry whey powder, as it requires reduced processing costs for the cheese producer. Waste whey is already bought by large fast moving consumer goods (FMCG) companies, but only from producers with a high enough capacity to make collection economically beneficial. When sourced from smaller-scale cheese makers, who are often forced to pay for its removal, the price will be much lower – if not non-existent. This source also prevents any conflict with the food industry and the UN zero hunger goal.

The average cost of whey globally ranges from 1.154€ to 1.350€ per ton for dry whey powder, with separated whey protein coming at around 2.958€ per ton. Purified lactose is priced at around 779€ per ton. These prices together demonstrate the net market value of liquid whey (CLAL, 2009).

### Plant Location

The UK produces 474,000 metric tons of cheese a year, giving it a ranking of 12<sup>th</sup> globally. When choosing a location for the plant, other options were considered, including the USA, Germany, and France and Italy who produce 5.95, 2.27, 1.92 and 1.31 million metric tons respectively. Multiple factors were considered, including total unused whey available, transportation and societal impacts. Despite the volume of cheese produced in the US providing a large feedstock of whey, the size of each cheese producer means onsite processing is common and the whey is sold to the food industry. Although not all producers have sufficient whey for this, the distance between farms would cause logistical problems such as the whey spoiling and economic and environmental issues in terms of transport. For these reasonsm the USA was excluded from the options. The UK was chosen over the others as the density of cheesemaking in certain areas is high, meaning transportation of sufficient whey will be more economical. The production capability means most farms produce insufficient whey for large scale collections, meaning most goes to local farms or waste. Another key factor in the choice is the social impact caused by the plant. Somerset is widely recognised as a low wage economy with a significant number of jobs in lower wage sectors, the average wage at 8% lower than the rest of Great Britain (Office for National Statistics (ONS), 2016)

This is an increasing issue and as a result 14.1% of children are living in poverty (Somerset Intelligence, 2016). The bioplastic plant would bring skilled jobs to the area, helping to increase the average wage. Training would be provided to provide jobs to allow flexibility to lower skilled applicants, adding the personal and vocational skills required for sectors with the highest growth potential, such as engineering (Somerset County City Council, 2016)

Since BREXIT, UK farmers have been struggling due to the loss of EU subsidies, with all EU-style subsidies being phased out in 2024-25. The use of agricultural/food production waste will provide a new income source for UK farmers, giving them more financial stability.

To decrease transportation costs, the possible plant location must consider proximity to local cheese producers. Due to the large amount of cheese produced in Somerset, this area was investigated. The village of Ditchet is chosen for this product; there is available land next to a cheese manufacturer, "Barber's 1833" which produces up to 80 tonnes of cheese per day, making 720 tonnes of whey (White, 2019). They currently process this whey to produce baby formula ingredients and lactose. The local area has many other cheesemakers, including Somerset Cheese Company and Batch Farm Cheesemakers who produce cheese on a smaller scale. Thus, the whey waste stream from these smaller producers would be used and directed to the bioplastic processing plant. In case a larger feed

is required, whey could also be bought from Barber's at a low price as they may be interested in investing in bioplastics for their products. Ditcheat has close access to both the A37 and A371, each within 2 km (Historic England, 2022). The area is rich with nearby farms, making it the ideal location for the plant. It is a small village of population 694 (CityPopulation, 2022); constructing the plant there would help develop the local economy by providing jobs to a low-economy area and draw attention to the town. Using the waste whey would prevent its use as fertilizer, avoiding the polluting side-effects.

This means the waste whey may need to be transported in liquid form, unless drying facilities are installed on site which can be economically unfavorable due to the transport costs and emissions caused. The cost and environmental effect of water-use later in the process must also be considered.

If the whey were to be sourced as a powder, the location in the UK would be less important although to reduce transportation costs it would be placed near a large whey powder producer. My Supplement Brand is a possible source in Somerset for whey powder, providing various protein concentrations (My Supplement Brand, 2015)

## Competitors

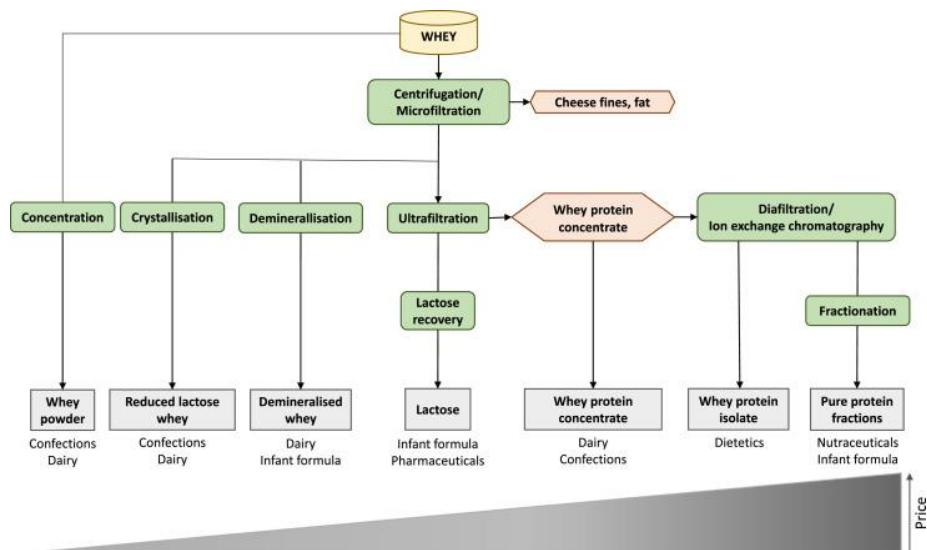


Figure 3: Applications of sweet whey (Ramos et al., 2016)

Competitors who use waste whey are either within the food industry or the energy industry. Waste whey in the food industry can be sold for protein supplements, producing ricotta and other cheeses, and creating alternative alcohols. Biogas can be generated using biodigesters which can contribute to energy integration of cheesemaking plants if sufficient biogas is produced to justify capital costs. There are also companies, Wheypack and Ypack for example, who have begun to use the lactose from whey in fermentation to produce bioplastics and will be our direct competitors.

Large producers use on-site processing facilities which convert the whey into value-added products such as whey protein powder. As indicated in Figure 3, sweet whey is valuable to the food industry and can also be used in the pharmaceutical industry. A greater purity in product relates to a greater price, with protein costing more than lactose. Sweet whey is often turned into protein powders for use in sports drinks, nutrition bars, and other foods including probiotic dairy-based beverages (ScienceDirect.com, 2022)

The largest plants generate enough to justify a biodigester, which breaks down the waste whey into biogas, which can be used for electricity for the plant. However, this comes with a huge expense. Wyke Farms use their whey by-products as well as local farmyard waste in Somerset to produce biogas (Into Somerset, 2022). Oregon State's Lisbeth Goddick is working on research that may help small manufacturers find ways to turn whey into vodka, something that companies like Vermont Spirits have already tried (Danovich, 2018). This could be more desirable for producers as the profits will be higher and the shelf-life of products longer. Since many dairy farmers are struggling, they may simply choose the higher profit option. However, this option does require more time, effort and investment than simply



selling off the whey, and only 2.5% of the whey is converted to alcohol, so the waste stream is still large (Danovich, 2018).

Traditional ricotta cheese is made from waste whey from cheesemaking. These days, it is often combined with milk due to the increase in popularity of the product (Lucey, 2020). Ricotta producers could be another competitor for our business, for example, Westcombe dairy in Somerset uses their waste whey to produce a Ricotta cheese (Westcombe Dairy, 2021). Brunost (a norwegian cheese) is also produced using waste whey (Skeie and Abrahamsen, 2017).

Whey butter can also be produced and is considered healthier than normal butter. This is mainly associated with the West of England. Producers of whey butter are rare due to production methods being time consuming, labour intensive and requiring specific skills that are only known by a limited number of dairymen. Therefore, it is not easy to find commercially (Slow Food in the UK, n.d.). Ethanol can be produced by fermentation of lactose in whey. Ireland started producing fuel ethanol from whey in 1985, and New Zealand started using fuel ethanol produced from whey in August 2007 (ScienceDirect.com, 2022). Research into using whey permeate to grow edible mushrooms is also in progress (Song et al., 2007).

### **UN sustainability goals**

There are three main UN sustainability goals that this project relates to:

- Responsible consumption and production – To ensure sustainable consumption and production patterns. By producing a biodegradable plastic from a waste product, we reduce the use of oil-based plastics, create a more sustainable process and a new use for waste whey (United Nations, 2015).
- Zero hunger – End hunger, achieve food security and improved nutrition and promote sustainable agriculture. The feedstock will be a waste stream from food production, this will provide economic assistance to the farmers and reduce the use of land in growing primary feedstock for bioplastics (United Nations, 2015).
- Climate action – Take urgent action to combat climate change and its impact. The reduction of use of traditional plastics will prevent ground pollution caused by landfill and littering. The use of a second-generation feedstock also reduces the pollution caused by the waste whey (United Nations, 2015).

Another concern in the production of bioplastics is the land use. The land used to grow renewable feedstock for bioplastic production is estimated to be 0.7 million hectares in 2021, accounting for 0.01% of global agricultural area with bioplastic production growth estimated to increase the share to below 0.06%. This percentage almost appears negligible; however, efforts should still be made to ensure second-generation feedstocks are used in place of primary feedstock to save the available land for the food industry (European Bioplastics, 2022).

## **Market Survey and Project Scoping**

### **Customer Analysis**

The targeted customers for this bioplastic are local cheesemakers, supermarkets and food companies who want to produce bio-based biodegradable packaging to increase the sustainability of their brand and appeal to the conscious consumer.

Other interested parties include cheese producers looking for sustainable methods to use their waste, as whey is considered one of the major issues in the dairy industry due to the quantity produced. As well as this, environmental agencies and local governments will be interested in the project to reduce waste in the local area and reduce the environmental impact. Waste management companies will also be interested as they will need to be aware of how to manage this new plastic waste to prevent contamination of recyclables. Competitors and investors will be interested to see how effective this bioplastic is, both at its function and the following life cycle of the packaging.

Results of a consumer study showed awareness of the benefit of reducing fossil fuel use, however, some of the environmental professionals and plastic experts mentioned concerns on biomass feedstock and the associated food security and agricultural land management. The recyclability of bio-based



plastics was also considered (Mehta et al., 2021). Some vegetarians and vegans in the sample group were opposed to the idea of animal-based waste as feedstocks, which could be a similar concern with whey-based bioplastics, as vegans may be concerned about the involvement of the dairy industry. Other concerns were expressed about the energy consumption and the production process. 90% of European customers want to buy products with minimal impact on the environment (European Bioplastics, 2022) but the most they would be willing to pay is 20p extra. (Mehta et al., 2021). Our primary customers would be food processing companies which outsource feedstock for their plastics with large players such as Unilever looking to move towards biodegradable plastics and small food producers with sustainable focus such as the cheese manufacturers which provide the whey feedstock.

## Discussion of MOCK Survey

The survey was taken over a large range of ages and professions to give a proportional view of the attitudes towards bioplastics, biodegradability and the requirements of our customers and future users. The full survey is given in Appendix A. Awareness of alternative packaging is high after high-profile media coverage on plastic pollution and the negatives impact of using fossil fuels. Therefore, the survey reflects this with high values given for the importance of biodegradable/compostable/recycle and bio-based packaging. Concerns were also raised about the quality, functionality and price of the product in comparison to traditional plastics, as current methods of production mean the price is usually higher. In general, customers are not willing to pay more than 20p extra for bio-based packaging due to having other financial priorities and responsibilities. Due to the variation in disposal methods of bioplastics, there is often confusion as to whether they can be recycled and where to dispose of them.

For consumer requirements, industry professionals were surveyed to research possible supply quantities and desired product properties. Depending on the size of the company, the quantity required ranged from 100 tonnes for small companies to 100,000 tonnes per year for largest companies companies. The importance of transparency, durability, flexibility, low oxygen permeability, heat resistance and water-resistant properties was shown in the results. The preference between compostable, bio-degradable and recyclable plastics was mixed, due to extra costs involved in collection of compostable and bio-degradable plastics and transport to the industrial processing plants.

Environmental stakeholders were also surveyed. This highlighted the problem of recycling contamination, given that 525,000 tonnes of household recycling collected was rejected in 2019/2020 due to contamination (Moore, 2021). Although the use of bio-degradable bioplastics reduces the use of fossil fuels and plastic pollution, they can cause more recycling contamination due to confusion as to whether they can be recycled with other plastics. Concern was also expressed on green-washing, as it leads to more confusion and misleads customers into believing companies are sustainable. A separation technique as well as an informative campaign will need to be development to ensure they are disposed of to the right place.

Some stakeholders were reasonably concerned about the land competition between food and bio-plastic feedstocks, mentioning that the UN zero hunger goal should be considered. They mentioned the use of waste streams to avoid using primary feedstocks.

However, evidence suggests that plastics should not be labelled as 'Bioplastics' as the term is ambiguous and offers little value to the public. Labelling should make clear appropriate information on how to dispose of products alongside whether they are biobased and/or biodegradable.

## Plastics in food packaging

Thermoplastics are the primary plastics materials used in packaging, as they can be easily fabricated into a variety of shapes by heating to fulfil the package function (Raj, 2005). Principal families of thermoplastics in food packaging include polyolefins (such as low-density or high-density polyethylene (PE), polypropylene (PP), polystyrene, polyester etc) (Raj, 2005). Based on a thickness of 25 m resin films, PP has a tensile modulus of around 300 MPa, which is significantly higher than for PE (particularly low-density PE). However, PE has a higher elongation to break which is anywhere between 200-800%, in comparison to 200-350% for PP. For high density PE and PP the O<sub>2</sub> permeability is similar at around 2000 cm<sup>3</sup>/m<sup>2</sup>/day.atm25°C, whereas this is higher for low-density PE at 7000-8000 cm<sup>3</sup>/m<sup>2</sup>/day.atm25°C.



PE can function over a greater temperature range than PP, with the lowest temperature operation for PP being 5°C. (Raj, 2005)

Many properties of plastics make them ideally suited for food packaging. Plastics are lightweight, which is important for consumer convenience and a way for processors to reduce shipping costs, they can seal at low temperatures (100-250°C), and all types of common plastics can be readily converted into thin, strong and clear films (Raj, 2005). Plastic packaging is also tear and puncture resistance, and films remain flexible at low temperatures (Raj, 2005). These features indicate the abundance of plastics used in the food packaging industry in preference to other packaging materials.

## Product Specification

The product chosen is a flexible film that can be used as shrink wrap, form-fill-seal films and lid films to replace the current options which go directly to landfill without decomposing for decades. The target customer is the cheese producers and the farms the whey originated from, as well as supermarket own branded products. The required thickness (available range of 0.17 to 0.31 mm (Wagh et al., 2013) and any required additives would be agreed with each customer to provide the required plastic properties. This was determined as an important product for investment, as there are a multitude of products in the food industry which incorporate these films, from fresh produce packaging to films on ready meal packages, and almost all these films are non-biodegradable oil-based plastics that can seldom be recycled.

Key specifications of the product include:

- The plastic needs to be chemically resistant against possible chemicals and food items it will be in contact with (NaturePlast, 2022).
- The product needs to be recyclable or at least partially biodegradable, to have a smaller impact on the environment than conventional plastic.
- The plastic needs to be transparent to properly display the product to customers.
- The packaging needs to be durable and maintain structure for the duration of the shelf life of the product.
- The films should add little weight to the product and fit closely to the shape of the food/package, wasting little space during storage and distribution (Allahvaiisi, 2012).
- Plastic should be easy to handle and convenient for the manufacturer, retailer and consumer (Allahvaiisi, 2012).
- The plastic must be flexible and not brittle to allow for handling and transport.
- Any labelling of products sold in the packaging must be accurate to avoid greenwashing, with disposal methods clear for consumers.
- The polymer should be able to be processed using current technology to avoid extra costs.
- The product will require a level of thermal resistance to ensure the plastic doesn't melt when heated, as this heat will be required when sealing (NaturePlast, 2022).
- The plastic will need to correspond with UK standards for bioplastics, in order to be referred to with the correct word. Labelling needs to be based on standards given by International Organization for Standardization (ISO) with clear ways to identify the different types of plastics and their environmental impact. In Europe, there is no common agreed percentage of bio-based material to be considered a bioplastic. However, Japan consider it to be 25% and the US and Austria use defined ranges (European Bioplastics e.V., 2016).

## Process Routes

### Microbial fermentation of whey

One of the methods for bioconversion is microbial fermentation utilising lactose in whey. Lactose is responsible for most of the biochemical oxygen demand of whey; therefore, it is essential to find a biotechnological use for this (Prazeres et al., 2012). One of the main disadvantages with this is that this carbon source is that it cannot be fermented by certain industrially relevant microorganisms (Pescuma et al., 2015). Whey is also a complex, unsterile and often variable by-product, thus direct application in fermentations comes with complications (Zikmanis et al., 2020). Biodegradable and biobased plastics that can be produced by fermentation means include PHAs and PLAs.



Some of the best-described PHA-producing microbial species are unable to directly produce PHAs from whey (Fernandez-Castillo et al., 1986). *H. mediterranei*, despite being capable of consuming lactose, does not efficiently grow and produce PHA from lactose (Koller et al., 2007). *A. latus* can convert whey lactose, however, the yield is not comparable to yields in other carbon sources (Berwig et al., 2016). The low capacity of microorganisms such as *H. mediterranei* to produce PHAs could be improved through chemical or enzymatic conversion of whey lactose to glucose and galactase prior to fermentation (Marangoni et al., 2002). Genetic engineering has also been utilised, for example, *E. coli* cells capable of consuming lactose were modified to express PHA biosynthesis genes from high PHA-producing microorganisms (Ahn et al., 2000). There is also the option to utilise mixed microbial cultures (MMCs) instead of single microbial strains. They have been associated with lower yields of PHA production but are advantageous as they do not require sterile conditions (Colombo et al., 2016). However, despite flexibility and cost advantages, using unknown microbial community to produce PHAs results in uncertainty in efficiency and consistency of polymer characteristics (Janarthanan et al., 2016). The production of PHAs by this means has also not yet been attempted.

PLA is another biodegradable bioplastic that can be produced by wild-type strains such as *S. laevolacticus*, *L. plantarum*, *S. ilulins*, *L. bulgaricus*. PLA is a good substitution for hydrocarbon-based polymers, but due to the high cost of D-LA (D-lactic acid) fermentation, its production is not a competitive solution (Awasthi et al., 2018). However, utilisation of waste whey infers reduced costs. Non-GMO *Lactobacillus* have been used to transform lactose from deproteinised lactose whey into D-LA suitable for conversion to bioplastics (Cellulac, 2014).

### Polymerisation of whey

Bioplastics can also be produced through polymerisation of whey protein. Cow and goat milk generally consists of 80% casein proteins and 20% whey proteins, and in cheese production the casein is coagulated, whereas the residual whey is normally discarded (Ceballos et al., 2009). The major components among whey proteins are  $\beta$ -lactoglobulin,  $\alpha$ -lactalbumin, bovine serum albumin, and immunoglobulin, representing 50, 20, 10, and 10% (w/v) of the whey fraction, respectively. These are the major monomers in the polymerisation of whey protein (Domínguez-Niño et al., 2018).

Although in terms of sustainability it is preferred to use a purely bio-based plastic, proteins themselves do not have sufficient plasticity to be handled and show brittle properties, and utilisation of a different monomer combined with the whey protein decreases the intrinsic stiffness/brittleness of whey bioplastics (Felix et al., 2017). Blending polymers can overcome issues associated with protein-based bioplastics such as thermal and water stability, reliability and consistency of mechanical performance and cost competitiveness (Sharma and Luzinov, 2013)

Free-radical polymerisation is a method to co-polymerise proteins with other monomers to produce plastic sheets or films. For this, following modification of the protein structure through functionalizing it with a reactive group (for example, by methacrylation with methacrylic anhydride) the side chains and N-termini in the protein molecules conjugate with other compounds to form a polymer (Nichol et al., 2010). Co-polymerisation then occurs to form the bioplastic. The properties of the protein used for co-polymerisation, the mass ratio between the monomers, reaction conditions, downstream processing and plasticisers used all impact the properties of the bioplastic produced. (Khawaldia et al., 2004). PEGMA has effectively been used as a co-polymer with methacrylated whey protein (Chan et al., 2017). Chalermthai et al investigated the effect of different ratios of PEGMA:methacrylated whey protein on the properties of the final product. The optimum ratio in terms of tensile strength in this study was determined as 30:70, as a higher proportion of protein created more brittle polymer sheets that couldn't be used for tensile strength testing, and below this the sheets were too fragile to handle (Chalermthai et al., 2019). WPC can be purchased from the market for use of this method and can also be produced from conversion of waste liquid whey directly from cheese farms.

### Options for comparison

Based on the methods discussed above, the options to be carried forward for screening are:



1. Enzymatic hydrolysis of lactose from liquid whey followed by fermentation using *H. Mediterranei*.
2. Fermentation of lactose from liquid whey with mixed microbial cultures (genetically engineered-recombinant culture) and using *E. Coli* with genes synthesising PHB introduced to produce PHB (Ahn et al., 2000).
3. Methacrylation and co-polymerisation of whey powder with PEGMA with whey powder as the process input (30:70 ratio of methacrylated protein:PEGMA).
4. Methacrylation and co-polymerisation of whey powder with PEGMA with liquid whey as the process input (30:70 ratio of methacrylated protein:PEGMA).

Although a variety of organisms were able to produce PHAs directly/indirectly through fermentation, many of these organisms, such as *A. Lactus* were associated with low yields, which would make the production of this unfeasible on a large scale. Many organisms were also able to produce PLAs, however, this product is much less desirable than PHAs, as although it closely resembles polystyrene (PS) and polypropylene (PP) in most of its properties, compared to PHA its brittleness and low crystallinity leaves it with low thermal stability and limited applications (Bioplastics Guide, 2016), it has a high degradation time of around 2 years (Naser et al., 2021) and there is a lack of composting infrastructure within the markets, which is required for the commercial use of PLA (Lamba and Singh, 2021)

## Selection criteria

The selection criteria considered for the process are as follows:

1. Sustainability: This considers the source of the feed streams, alongside the emissions and waste streams of the process and the degradability of the products.
2. Cost: Includes the CAPEX and OPEX, as well as costs related to acquiring feedstocks of the process and selling of the products.
3. Risk: Incorporates business risks relating to the client and process safety risks
4. Process Yield: The yield of plastic with the specified process.
5. Quality: The quality of the product relates to the similarity in properties to the conventional plastics used for packaging in the food industry.

Table 3: Screening matrix

Selection Criteria	Weighting Factor	Option 1	Option 2	Option 3	Option 4
Sustainability	0.35	5	4	3.5	4.5
Process Cost	0.25	5	2.5	8	7
Risks	0.1	5	4	4.5	5.5
Process Yield	0.1	5	6.5	8	8
Quality	0.2	5	4	3.5	3.5
Total	1	5	3.875	5.175	5.375

Option 1 was used as the benchmark case, and the other options compared to this.

As the client's priority is sustainability, which will be considered throughout the entire lifetime of the product, this criterion is weighted as the highest. This also factors in consumer interest in buying sustainably.

Process costs were weighted highly as it is important that a process is economically viable, and the client makes profit otherwise for a project to run. However, this is weighted lower than sustainability, as although this is an important factor, consumers are willing to pay more for sustainability due to growing for more environmentally friendly alternatives, and hence many clients are prepared to make this



investment. To gauge the cost of each of the options, preliminary calculations are carried out based on chemical engineering plant costs index (CEPCI) values and the Lang factor for a solid-liquid processing plant.

The risk criterion is weighted low, as although risk is an important aspect in all processes, the processes considered to produce the required product are not associated with many risks, both business and safety related.

Process yield is also weighted low, as despite a process requiring sufficient yield for it to be economical, there are enough local cheese farms to ensure the required demand is produced with the raw material which is low cost (or free for the case of options 1, 2 and 4), even if yields are relatively low.

The quality of the product is weighted higher, as it is important to create a product which reliably imitates conventional plastics and carries out the required function for it to become a competitive product.

For all options considered, further steps are to be taken to convert from the powder to films, however, this is not in our scope as it will be of the responsibility of our partner company.

## Option 1

### General Process Description

Enzymatic hydrolysis is required for this method as *H. mediterranei* cannot directly utilise lactose. To obtain lactose from the liquid whey for this process, the liquid whey must undergo centrifugation to remove suspended particulate matter, and ultrafiltration to remove the fat and proteins. Following this, ion exchange and reverse osmosis are used to purify and concentrate the lactose (De Souza et al., 2010). The conversion of lactose to dry PHA powder is then as follows: hydrolysis of lactose to produce glucose and galactose with a lactase enzyme, exiting streams mixed with salts and other nutrients, fermentation with *H. Meditarranei* to produce PHA polymers, transfer of broth to storage tank, centrifugation to separate cells from spent medium, extraction of cells through osmotic shock to release PHA polymers, centrifugation and wash to improve purity, spray drying to produce a powder (Wang et al., 2022)

### Selection criteria

This option utilises the liquid whey. The site for the processing plant is to be local to the dairy farms, therefore transport emissions are not of concern for this option. This also results in the direct use of waste that the dairy farmers may have difficulty in storing/ disposing of. This method is an environmentally friendly approach which does not require as much mass and energy inputs as acid-catalysed hydrolysis (El-Zawawy et al., 2011). However, there are multiple sources of waste throughout the process. If the protein and fats removed are not utilised through other means, these products will be wasted. The fermentation and poly(3-hydroxybutyrate) (PHBV) extraction, purification and drying also results in wastes of: residual biomass, glucose, galactose, lactose, ammonium chloride, enzyme, and water. Furthermore, separating the cell mass through centrifugation results in spent minimum saline medium (MSM) waste (Wang et al., 2022). These wastes will need to be dealt with and treated. However, there is the option to recover some of these wastes based on the facilities (for example, re-using enzymes and recycling spent brine required to create the saline conditions for the organism) (Wang et al., 2022). MSM and ammonium chloride are of particular environmental concern. MSM entering the environment results in salt release to environment, which can damage vegetation and effect aquatic conditions, and ammonium chloride release is damaging due to it being biocidal and hence destroys living things (DeLeo et al., 2020).

PHAs such as PHBV produced for this process show biodegradable behaviour in all aerobic and anaerobic environments defined by ATM standards, and can be used to make completely compostable, and soil and marine biodegradable products (Meereboer et al., 2020). PHAs have a degree of biodegradation of around 80% (Weng et al., 2010).

*H. mediterranei* has high robustness and stability. The risk of contamination during cultivation is restricted to a minimum and therefore reducing energy demand due to lower sterility requirements compared to for other strains. However, the high salinity requirements for the growth of this organism requires special material demands for the bioreactor equipment (Koller et al., 2012). The CAPEX and OPEX for the processes for converting the lactose to the PHA in December 2021 was determined as \$40 million and \$5773 per tonne of plastic produced respectively ((CEPCI, 2021), (Wang et al., 2022)). However, the conversion of the liquid whey to the lactose will incur greater CAPEX and OPEX. PHBV product selling price was assumed as \$10/kg (Wang et al., 2022). It is assumed that the liquid whey obtained is free, as small industries are not able to utilise this, and although some farms in Italy store



liquid whey and sell them at a rate of \$21.21/tonne, some yoghurt producers pay farmers to pick up this liquid whey at \$300 per 6000 gallons (Chalermthai et al., 2020).

The total land requirement for the process units may be larger than the land area available, particularly due to the large number of process units involved, as there are 13 process units in total. *H. Mediterranei* can only effectively produce PHBV in saline environments as it requires around 18% of salts to maintain a suitable growth environment (Wang et al., 2022). The fermentation process will also be sensitive to reaction conditions such as nutrient content, pH and temperature, and hence this option poses production risks as it is volatile and if conditions are not suitable there may be insufficient PHBV product produced. The use of ammonium chloride also poses a safety risk to workers, as it is extremely poisonous and toxic and causes damage to organs by long-term exposure (National Institute for Occupational Safety & Health, 2021).

The conversion yield for whey sugars to PHA was calculated with 0.33 g/g. After further optimising the production conditions (yielding P(3HB-co-6%-3HV)) productivity on hydrolysed whey permeate was increased to 0.09 g/L h (Koller et al., 2012).

## Option 2

### General Process Description

The steps required for this process is based on the work by García et al (Lopez García et al., 2011). Whey is initially treated via ultrafiltration to remove the protein content, and the lactose concentration is increased through evaporation. This is then heat sterilised before being used as a fermentation medium. The recombinant *E. coli* CGSC 4401 strain then uses the lactose as a carbon source to produce PHB in the fermenter. For downstream processing, the bacterial cells are collected through centrifugation, a surfactant solution is added to the microbial biomass followed by hypochlorite digestion, which results in the microbial lysis (breaking down the cell membrane) and separation of PHB from the residual cell material. Aqueous solution which contains this is then separated by centrifugation, and PHB granules are washed with water and dried with a spray dryer (Lopez García et al., 2011).

### Selection criteria

Similarly to option 1, this method utilises the liquid whey produced from the cheese farmers directly, hence preventing waste and reducing the environmental impact if the farmers were to dispose of it into the environment, and transport emissions are again not of concern. This method also incurs protein and fat wastes from the initial whey processing, as well as wastes of: water, hypochlorite, surfactant, residual biomass (Lopez García et al., 2011). After use, residual surfactants are discharged into sewage systems or directly into surface waters, and most end up in environmental compartments e.g., soil, water or sediment. They are toxic to aquatic organisms, and if not treated properly could have series consequences on ecosystems (Ivanković and Hrenović, 2010). Hypochlorites are moderately toxic, and when acidified liberates chlorine, which is toxic and could have environmental impacts (Public Health England, 2015). This option has 5 more process units than option 1, due to the greater complexity of extraction and purification. This incurs greater energy consumption hence greater emissions during production. Biodegradability of the product is considered the same as for option 1, as both products are PHAs. From this, sustainability was given a score of 4, as sustainability in terms of raw material, wastes and biodegradation are similar, but emissions in the production process are likely greater for option 2.

The equipment cost for option 2 was determined as \$9.484 m in 2011 (Lopez García et al., 2011). Multiplying by the Lang factor for a solid-liquid processing plant (3.63) (Wolf, 2022), the total plant cost in 2011 was \$40.78 million. Using the CEPCI's from February 2011 (574.6) and September 2021 (754.0) (CEPCI, 2011) the present CAPEX is \$45.18 million. The OPEX in 2011 was \$3.420 million per tonne of plastic produced, therefore the present OPEX is \$4.488 million per tonne. The purchase price of the liquid whey, similarly to option 1, as it is the main waste stream of the dairy industry. As PHB is also a type of PHA, it can be assumed that the selling price is the same as for PHBV in option 1. Hence, as the CAPEX is greater than for option 1 and the OPEX is significantly larger, option 2 was given a score of 2.5 in relation to costs.

One of the main risks associated with this method is the application of genetic engineering. Firstly, public perception of genetic engineering techniques is often negative, and hence this may make the



product less desirable to consumers. Furthermore, the use of genetically engineered strains requires more controlled production plants, as the wide application of genetically modified microorganisms raises concern of accidental release of genetically modified species into the environment, and subsequent gene transfer to microorganisms/non-micro-organism's host (Ahn et al., 2000). Use of hypochlorites also poses a risk to workers, as the chlorine gas may be inhaled which is toxic, and it is corrosive and may irritate the skin (Public Health England, 2015). Therefore, this process entails greater risks than for option 1 and so scores 4 for risk.

A PHB productivity of 2.57 g/L.h under optimal operating conditions was achieved by Ahn et al with this method (Ahn et al., 2000). This is a larger productivity than for option 1, hence for a given volume and time option 2 will produce a greater quantity of bioplastic than for option 1. Therefore, this option scores 6.5 in terms of yield.

PHB possesses several properties similar to that of PP, which is commonly used in food packaging. Both plastics have melting points of around 175 and tensile strengths of around 40 MPa. However, PHB has a much lower extension to break of around 6% in comparison to around 400% for PP, and poor solver resistance (Markl, 2018). Nevertheless, it has been found that PP can be replaced by PHB for packaging of fatty products, such as cheese, which is appropriate for this project. (Markl, 2018). The PHBV copolymer produced in option 1 has better physical properties such as impact resistance, flexibility and other properties involved in the manufacturing process (Wang et al., 2013). Furthermore, the degradation of temperature of PHB produced in option 2 is just a few degrees above its melting temperature, whereas PHBV has a larger processing window (Wang et al., 2013). Therefore, this option scores a 4 in terms of quality of product.

### Option 3

#### General description

This process is based on the work by Chalermthai et al (Chalermthai et al., 2020). The chemical processing steps for this involves the following: protein dissolution, where the powder was dissolved in water and NaOH was added to ensure protein precipitation does not occur, methacrylation, where methacrylic anhydride is added to the pH-adjusted protein solution, and polymerisation, where the copolymer PEGMA was added, alongside ammonium persulfate (which acts as an initiator) and TEMED (the catalyst to the process). The ratio of methacrylated protein:PEGMA in the bioplastic is 30:70, as this was determined as the optimum ratio. Following this, plastic making is carried out through the following processes: the unreacted monomer and chemicals are washed off, water from the polymerised content was then removed through centrifugation, and more water was evaporated in a drum dryer to produce a dry polymer (Chalermthai et al., 2020)

#### Selection criteria

Using WPC as the initial input is a less sustainable option, as unless WPC powder that had expired and was unfit for human consumption was sourced, this method would not be directly utilising waste, and would leave smaller dairy farmers with this waste that they may have difficulty in disposing of. Using WPC powder will also have increased emissions associated with transport. Sources of waste for this process include water and aqueous wastes, which is composed of unreacted PEGMA and protein, and chemicals such as ammonium persulfate and sodium hydroxide (Chalermthai et al., 2020). This aqueous waste is to be treated, which will result in use of fossil fuels in the waste treatment facilities. Furthermore, the final product of these facilities, although less of an environmental impact, is still to create some level of waste and harm on the environment. Nevertheless, this method uses only 6 process units (Chalermthai et al., 2020), hence the energy consumption and land requirements are likely much lower than for option 1. A life cycle assessment carried out by Chalermthai et al for this process determined that the copolymer PEGMA is the biggest contributor to most of the environment impacts; one of the reasons for this is that it consists of ethylene oxides that are derived from fossil-based sources (Chalermthai et al., 2021). The biodegradability of this bioplastic is not yet known, as creation of whey plastic through this co-polymerisation method is novel (Chalermthai et al., 2021). Due to the use of WPC powder as opposed to liquid whey, and the lack of knowledge on the biodegradability of the product, option 3 scores 3.5 in terms of sustainability.



The CAPEX for this process in February 2020 was \$19.13 million (Chalermthai et al., 2021). Using the CEPCI value from September 2021 (754.0)(CEPCI, 2021) and for February 2020 (637.8)(CEPCI, 2020), the CAPEX is determined as \$22.62 million. The OPEX is given as \$3680 per tonne of plastic produced (Chalermthai et al., 2020), so the present OPEX is \$4350 per tonne. The WPC must be bought in comparison to the waste liquid whey for option 1 which was assumed to be free. The sales price for WPC lies between \$25/kg to \$40/kg (Amazon, 2022), and the unit selling price was set at \$7000/t, which is the same as for algae-derived plastics using the same methods of methacrylation and polymerisation (Bochenksi et al., 2018). Therefore, profits will be lower for this method per tonne of plastic produced, however, the CAPEX and OPEX is significantly lower than for option 1, mainly attributing to fewer process units. Therefore, this is given a score of 8 for costs.

Using WPC as the input poses a business risk, as it is a desired product for a variety of markets, but as mentioned previously, this risk would be eliminated if expired WPC powder was utilised. This option also poses a risk as there is less research done for this method than for option 1, with the properties of the product not fully understood. However, his method poses a lower risk in reliable production of the product, as it does not utilise sensitive microorganisms as used for the fermentation method in option 1. The reagents used for this option are associated with safety risks. PEGMA is an irritant, and it is a combustible liquid (Merck, 2022d) ammonium persulfate is an oxidiser, irritant and may cause allergic reactions (NCBI, 2022a) and sodium hydroxide is caustic and can cause harm to workers who contact it, as it can burn the eyes, skin and inner membranes (National Institute for Occupational Safety & Health, 2021). This method has greater business risks; however, the process has less risk in production reliability. Therefore, this option scores 4.5 for risks.

Due to extraction complexity and sensitive cultures associated with fermentation and this option having fewer process units, it is likely that a greater quantity of product can be extracted for this option than for option 1. Hence, it is given a score of 8 for process yield.

Whey protein-based films have lower oxygen permeability than conventional plastics such as PE under similar conditions, however, this makes them potentially useful for oxygen sensitive products (Schmid and Müller, 2018). The bioplastic produced by this method produces a polyethylene-like plastic (Chalermthai et al., 2019). The tensile strength of bioplastics produced with a 30:70 ratio of WPC methacrylated protein:PEGMA had a tensile strength of around 2.2 MPa, which is similar to the tensile strength of milk protein films used for cheese packaging of around 0.7-4 MPa and indicates the effective application for this purpose which will be for some of our customers, however, compared to synthetic polyethylene films such as LDPE and HDPE, this plastic has a much lower tensile strength and modulus, which indicates that improvements may be required for other uses of these films (Chalermthai et al., 2019). The plastic has a thermal stability of around 275°C, which is similar to conventional plastics and indicates the processability properties for this plastic (Chalermthai et al., 2019). Given that the quality of the plastic produced is not as similar to conventional plastics used for food packaging as for option 1, this option scores 3.5 in terms of quality.

## Option 4

### General description

This option is also based on the work by Chalermthai et al. Pre-treatment of the liquid whey includes pasteurisation to remove bacterial impurities, and centrifugation to separate large molecules such as fats from the waste whey (Chalermthai et al., 2020). The whey is then converted to WPC through the following process steps: ultrafiltration, where proteins are retained and lower molecular weight solutes permeate through the membrane, diafiltration to remove more permeating components or fats, carbohydrates and minerals, spray drying to remove the water content, and storage of the WPC powder (Chalermthai et al., 2020). The chemical processing and plastic making steps are the same as discussed in option 3.

### Selection criteria

The sustainability associated with the raw material is the same as for option 1, as both options use waste liquid whey. The waste produced in this option includes the wastes discussed in option 3, as well as fat, carbohydrates and minerals (Chalermthai et al., 2021). If these substances are not used in other applications, they will be lost as waste. The energy requirements associated with this process are likely similar to that of option 1, as this option has 12 units in comparison to 13 for option 1 (Chalermthai et al., 2021), hence process emissions are likely similar. The biodegradability of the product is the same



as discussed for option 3. The raw material and process emissions are similar to option 1, however, as the biodegradability of the bioplastic is not known, this option scores 4.5 for sustainability.

The CAPEX for this option in February 2020 was \$33.56 million (Chalermthai et al., 2021). Using the most recent CEPCI from September 2021 of 754.0 (CEPCI, 2021) and the value for February 2020 of 637.8 (CEPCI, 2020), the estimated present CAPEX is \$39.68 million. The OPEX in February 2020 was \$3850 per tonne of plastic produced (Chalermthai et al., 2021) and the present operating cost is \$4551 per tonne. Similarly to option 1, the liquid whey is assumed to be free of charge, and the selling price for this plastic is the same for option 3, therefore, this option will result in less profit per tonne than for option 1, however, both CAPEX and OPEX values are lower than for option 1, therefore, this option scores a 7 for cost.

This novel process poses a risk and the risks of the reagents for this option are the same as discussed in option 3, and this process is associated with lower production risks than for option 1 as fermentation is a much more volatile process than polymerisation. Therefore, this option is given 5.5 for risk.

Similarly to option 3, option 4 is expected to have a greater yield than for option 1 as a result of greater extraction complexity and less reliable production in option 1. Therefore, it scores an 8 for yield.

The product is the same as for option 3, hence the product quality is the same. Therefore, option 4 scores 3.5 for product quality.

## Selected option and considerations

Option 4 scores 5.375 from the screening matrices, which is the highest score. Therefore, this option is recommended to be carried forward onto the design phase. This option will help support the smaller local businesses which cannot process their liquid whey surrounding the process site. Although this is a relatively novel process which will require further investment for research and development into the properties and extent of biodegradability, this option is still to provide a more environmentally friendly and sustainable plastic than conventional plastics for food packaging. The fermentation methods and the product characteristics for options 1 and 2 are better known, however, these options are much more expensive and with further research into the option chosen, this could be a more viable alternative.

## Design Basis

The selection of this process option has been discussed and agreed with the client, with a feed of 100 tonnes per batch, with 3 batches running at once. Based on the work of Chalermthai et al., (Chalermthai et al., 2020) the batch time is 53 hours, the plant will operate for 330 days in a year and there will be 47 working weeks.

It was aimed to process around 1% of the total amount of whey produced in the United Kingdom. However, to ensure consistency in batch times and number of batches, it was determined that 44800 tonnes of whey per year was to be used as the input to the process – around 1.05% of the total whey produced in the U.K. This would require 448 batches per year. Based on mass balance calculations, this produces 1126.7 tonnes of plastic product per year.

The composition of the whey waste input is taken as an average from literature values: 4% carbohydrates, 4.5% fats, 1% minerals, 1% proteins and 89.5% water (Chalermthai et al., 2020). Assuming the whey protein powder that undergoes chemical processing has a moisture content of 10% (Chalermthai et al., 2020), from mass balance calculations 89.98% of the whey powder is protein, with the remaining composition made up of carbohydrates, fats and minerals. The final product is 91% protein-PEGMA polymer, 9% water.

It is to be assumed that the cheese producers will store the liquid and pay for the refrigeration of this, in return for purchase of the product at 70% of the original price. Our partner company Biome Bioplastics will shape our product into a flexible film (Biome Bioplastics, 2022) and in return will receive 5% of our profit. Hence, the system boundary for the process considers the liquid whey as the input, to the production of the bioplastic in chunks from the drum dryer.



It is to be ensured that the cheese producers will have enough packaging for all their cheese, and the remaining packaging produced will be sold to supermarkets and other interested buyers.

## Process Description

The process, based on the work of Chalermthai et al., 2019, is divided up into pre-treatment of liquid-whey, production of whey powder, chemical processing and the plastic making.

Pre-treatment (step A):

1. Pasteurization: this step is carried out to eliminate pathogens from waste whey (e.g. bacteria) with the pasteurization happening at 61°C for 15 seconds to prevent the denaturing of proteins in the whey.
2. Centrifugation (1): The pasteurized liquid whey is cooled and passed to a centrifuge where large solids such as fat are separated from the soluble proteins and other components of the process such as lactose and minerals.

Whey powder production (step B):

3. Ultrafiltration and Diafiltration: The centrifuged liquid outlet is filtered via consecutive ultrafiltration unit and diafiltration units where the whey protein is separated from the lactose and low molecular weight solutes. The retentate from the ultrafiltration unit is then diluted with water and passed through another ultrafiltration membrane to further concentrate the whey liquid to achieve a protein concentration of nearly 80%.
4. Spray dryer: The retentate of the diafiltration unit is dried in a spray dryer to evaporate 93% of the water content to yield a whey protein powder with a moisture content of about 10%, which is acceptable for plastic making applications.
5. Storage: To facilitate batch processing, the whey protein powder ready for plasticization is stored in a vessel.

Chemical processing (step C):

6. Protein dissolution unit: The whey protein powder is dissolved in water and sodium hydroxide (NaOH) is added to facilitate protein dissolution by increasing the pH from around 6-6.7, which is the typical pH of whey protein powder (American Dairy Products Institute, 2022) to 8-9, past the isoelectric point at a pH of the proteins of 4-5 where proteins would precipitate. Protein dissolution occurs in a stirred tank in batches to facilitate the reactions in the following steps occurring in solution.
7. Methacrylation: The pH adjusted solution is transferred to another stirred batch reactor where the methacrylation of the proteins occur, acting on amine functional groups on the proteins to produce a methacrylated co-monomer which is later reacted to produce the polymer. During this methacrylation reaction the pH is also adjusted by NaOH to prevent protein precipitation due to the by-product of methacrylic acid.
8. Polymerisation: The methacrylated content is passed to a polymerisation reactor where the methacrylated proteins bond with PEGMA, which provides a rubbery backbone for the plastic. The reaction occurs with an initiator and a catalyst of the polymerisation, ammonium persulfate (APS) and tetramethyl ethylenediamine (TEMED) respectively.

Plastic making (step D):

9. Washing: The plastic is washed with water to remove unreacted monomer and other chemicals to prepare for centrifugation and drying.
10. Centrifugation (2): The plastic is centrifuged to remove water from the polymerised content
11. Drum dryer: where the plastic is further dried and scraped into flakes by a knife. The solid plastic is then transferred for further processing at a partner plastic packaging manufacturer.

Sterilization UHT is an alternative option for removal of pathogens from the liquid whey. Sterilization UHT uses temperatures of over 100°C, whereas pasteurization is based on the minimum heat requirement to deactivate specific microorganisms, thus typically operating at a temperature below 100°C (Santonja et al., 2019). Sterilization allows for complete disinfection (Santonja et al., 2019); however, this is not required for this product. Temperatures higher than the denaturing temperature of the protein would damage the protein, which is one of the monomers of the final product, hence would result in loss of yield. Therefore, pasteurization is a better method for bacterial impurity removal for this process.

A centrifuge was utilised as these are commonly used for the rapid separation of curd from whey (Berk, 2009) and play a fundamental role in whey treatment processing to make it suitable for concentration.



Ultrafiltration (UF) was chosen as it is an attractive method for whey protein concentration, as it does not involve phase change hence does not use heat, which reduces costs when compared to other processes such as evaporation and prevents protein damage (Baldasso et al., 2022). UF retains the protein and allows selective permeation of lactose, minerals, water and lower molecular mass substances (Baldasso et al., 2022).

Diafiltration (DF) is then used following the ultrafiltration module, which also incorporates a membrane to concentrate and purify the protein whilst using wash-water and is used in protein purification to promote a more efficient removal of lactose and mineral salts (Baldasso et al., 2022). The combination of UF/DF is an effective technique for the concentration and desalting of protein solutions (Baldasso et al., 2022). Carrying out centrifugation prior to these steps is important to remove the fats as much as possible to retain a higher concentration of proteins with minimal fat content and to reduce fouling effects.

Spray drying is the most used industrial process for particle formation and drying and is suitable for whey applications due to the thermal sensitivity associated with it (Tetra Pak, 1995). This can ensure the whey protein powder complies with set requirements, for example, moisture content and bulk density (Tetra Pak, 1995). During the spray drying process, the liquid feed is atomized and contacts hot air; evaporation of the water then takes place to obtain dried particles, which are subsequently separated (Domínguez-Niño et al., 2018). These powders can be stored at ambient temperature for prolonged periods without the stability being affected and are easy to handle in manufacturing plants (Domínguez-Niño et al., 2018). The rapidity of drying and relatively low temperature experienced by the solids during drying make it appropriate for heat-sensitive products, such as the proteins (Harrison et al., 2015)

All three chemical processing units are chosen as stirred reactors as the reactions occur in liquid phase in a batch configuration thus making stirred reactors the only reasonable choice for the process.

The drum dryer was selected as it is the most universal unit procedure for this step of the process (Chalermthai et al., 2020), hence it is applicable for this use to make flakes of bioplastic.

Table 4: Properties used for calculations

Property	Value	Unit	Reference
Specific heat capacity of water, $C_{p,l}$	$75.4 \times 10^{-3}$	$\text{kJ mol}^{-1}\text{K}^{-1}$	(Felder et al., 2016)
Heat transfer coefficient of steam, $U$	1500	$\text{W m}^{-2}\text{K}^{-1}$	(Sinnott Ray K., 2009)
Heat exchange surface area for pasteurization, $A$	500	$\text{m}^2$	(HISAKA, 2022)
Heat exchanger 1 surface area, $A$	1600	$\text{m}^2$	(HISAKA, 2022)
Steam heat capacity constants	$a = 33.46 \times 10^{-3}$ $b = 0.6880 \times 10^{-5}$ $c = 0.7604 \times 10^{-8}$ $d = -3.593 \times 10^{-12}$		(Felder et al., 2016)
Inlet air humidity, $H_1$	0.02	$\frac{\text{kg water}}{\text{kg dry air}}$	(Masilungan-Manuel et al., 2015)
Latent heat of water, $\lambda_0$	597	kcal/kg	(Harrison et al., 2015)
Specific heat of the protein, $C_{p,s}$	1.26	$\text{J K}^{-1}\text{g}^{-1}$	(Yang and Rupley, 1979)
Density of whey protein isolate, $\rho_{solids}$	380	$\text{m}^{-3}$	(Bruno De Carvalho-Silva et al., 2013)
Transmembrane pressure	2	bar	(Baldasso et al., 2022)
Density of water, $\rho_{water}$	997.05	$\text{kg m}^{-3}$	(Beaton et al., 1989)
Pump efficiency, $\eta$	80%		(Exxon Mobil, 2018)
Pressure inlet to spray dryer nozzle	50	bar	(Park and Haenlein, 2013)
Molecular mass of PEGMA, $M_w$	500	g/mol	(Merck, 2022d)
Molar mass of beta-lactoglobulin	18363	g/mol	(Merck, 2022a)
Density of wet air	1.00	$\text{kg m}^{-3}$	(Harrison et al., 2015)
Viscosity of reactor contents	2.63	$\text{mPa s}$	(González-Tello et al., 2009)
C-N	305	kJ/mol	(Song and Le, 2019)
O-H	467	kJ/mol	
C-O	358	kJ/mol	
N-H	391	kJ/mol	
C=C	614	kJ/mol	
C-C	347	kJ/mol	

## PFD

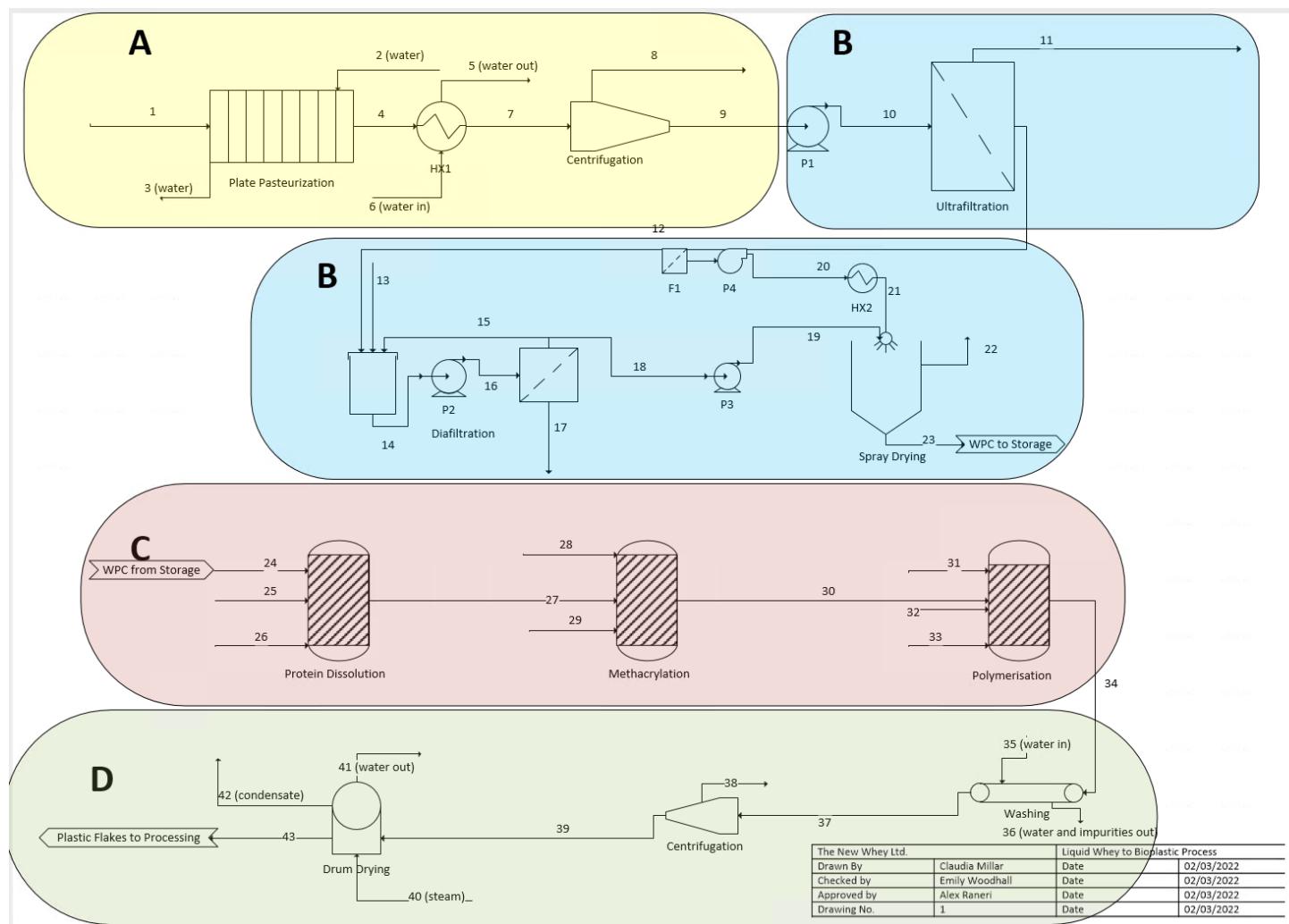


Figure 4: PFD for the process, where section A is the pre-treatment, B is the production of whey powder, C is the chemical processing and D is the plastic production



## Stream Table

Table 5: Stream Table

<b>Process Step</b>	A	A	A	A	A	A	A	A	A
Line No.	1	2	3	4	5	6	7	8	9
Stream	Waste Whey inlet	Steam In	Steam out	Pasteurized Whey	Cooling water outlet	Cooling Water inlet	Cooled Whey	Centrifuge Waste	Fat Reduced whey
Batch Mass Flow (tonnes)	100	12.62	12.62	100	124.82	124.82	100	30	70
Pressure (bar)	1.013	0.496	0.496	1.013	1.013	1.013	1.013	1.013	1.013
Temperature (celsius)	25	81.3	56.75	25	21	49.84	25	25	25
pH	-	-	-	-	-	-	-	-	-
<b>Components Mass Fraction</b>	-	-	-	-	-	-	-	-	-
Protein	0.01	-	-	0.01	-	-	0.01	0	0.04
Carbohydrates	0.04	-	-	0.04	-	-	0.04	0.04	0.0386
Fats	0.045	-	-	0.045	-	-	0.045	0.06	0.01
Minerals	0.01	-	-	0.010	-	-	0.010	0.01	0.0143
Water	0.895	1	1	0.895	1	1	0.895	0.89	0.897
NaOH	-	-	-	-	-	-	-	-	-
Methacrylic Anhydride	-	-	-	-	-	-	-	-	-
Methacrylated Protein	-	-	-	-	-	-	-	-	-
Methacrylic Acid	-	-	-	-	-	-	-	-	-
PEGMA	-	-	-	-	-	-	-	-	-
APS	-	-	-	-	-	-	-	-	-
TEMED	-	-	-	-	-	-	-	-	-
Polymer	-	-	-	-	-	-	-	-	-
Air (not including water vapour)	-	-	-	-	-	-	-	-	-
Total	1	1	1	1	1	1	1	1	1



<b>Process Step</b>	B	B	B	B	B	B	B	B	B	B
Line No.	10	11	12	13	14	15	16	17	18	19
Stream	UF inlet	UF Permeate	UF Retentate	Buffer Solution	Pump inlet	Recycle	DF inlet	DF permeate	DF retentate	Spray Dryer Inlet
Batch Mass Flow (tonnes)	70	66.5	3.5	45.06	NB	NB	3.5	46.13	2.428	2.428
Pressure (bar)	4.94	1.013	1.013	1.013	1.013	1.013	4.94	1.013	1.013	50
Temperature (celsius)	25	25	25	25	25	25	25	25	25	25
pH	-	-	-	-	-	-	-	-	-	-
<b>Components Mass Fraction</b>	-	-	-							
Protein	0.04	0.00075	0.271	-	NB	NB	0.271	0.000206	0.387	0.387
Carbohydrates	0.0386	0.0417	0.008	-	NB	NB	0.008	0.000600	0.000115	0.000115
Fats	0.01	0.0402	0.00771	-	NB	NB	0.00771	0.000579	0.000111	0.000111
Minerals	0.0143	0.0104	0.002	-	NB	NB	0.002	0.000150	2.88E-05	2.883E-05
Water	0.897	0.907	0.711	1	NB	NB	0.711	0.998	0.612	0.612
NaOH	-	-	-	-	-	-	-	-	-	-
Methacrylic Anhydride	-	-	-	-	-	-	-	-	-	-
Methacrylated Protein	-	-	-	-	-	-	-	-	-	-
Methacrylic Acid	-	-	-	-	-	-	-	-	-	-
PEGMA	-	-	-	-	-	-	-	-	-	-
APS	-	-	-	-	-	-	-	-	-	-
TEMED	-	-	-	-	-	-	-	-	-	-
Polymer	-	-	-	-	-	-	-	-	-	-
Air (not including water vapour)	-	-	-	-	-	-	-	-	-	-
Total	1	1	1	1	1	1	1	1	1	1



<b>Process Step</b>	B	B	B	B	C	C	C	C	C
Line No.	20	21	22	23	24	25	26	27	28
Stream	Air inlet	Hot Air	Air outlet	Whey Powder to storage	Process whey powder	Water	NaOH	Dissolved whey powder	Methacrylic Anhydride
Batch Mass Flow (tonnes)	43.7	43.7	45.1	1.045	1.045	9.971	0.133	11.15	0.05175
Pressure (bar)	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013
Temperature (celsius)	25	150	70	70	25	25	25	25	25
pH	-	-	-	-	-	-	-	10	-
<b>Components Mass Fraction</b>									
Protein	-	-	-	0.8998	0.8998	-	-	0.0844	-
Carbohydrates	-	-	-	0.00027	0.00027	-	-	2.512E-05	-
Fats	-	-	-	0.000258	0.000258	-	-	2.422E-05	-
Minerals	-	-	-	6.697E-05	6.697E-05	1	-	6.279E-06	-
Water	0.01962	0.04962	0.0728	0.0996	0.0996	-	-	0.904	-
NaOH	-	-	-	-	-	-	1	0.0119	-
Methacrylic Anhydride	-	-	-	-	-	-	-	-	1
Methacrylated Protein	-	-	-	-	-	-	-	-	-
Methacrylic Acid	-	-	-	-	-	-	-	-	-
PEGMA	-	-	-	-	-	-	-	-	-
APS	-	-	-	-	-	-	-	-	-
TEMED	-	-	-	-	-	-	-	-	-
Polymer	-	-	-	-	-	-	-	-	-
Air (not including water vapour)	0.9804	0.9504	0.927	-	-	-	-	-	-



Total	1	1	1	1	1	1	1	1	1
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Process Step	C	C	C	C	C	C	C	D
Line No.	29	30	31	32	33	34	35	
Stream	NaOH	Methacrylated content	PEGMA	Ammonium Persulphate	TEMED	Polymerised Content	Water	
Batch Mass Flow (tonnes)	0.166	11.37	2.415	0.1748	0.003565	13.96	22.82	
Pressure (bar)	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013
Temperature (celsius)	25	25	25	25	25	26	25	
pH	-	9	-	-	-	-	-	
Components Mass Fraction								
Protein	-	0.0165	-			0.0135		-
Carbohydrates	-	2.463E-05	-	-	-	2.006E-05		-
Fats	-	2.375E-05	-	-	-	1.934E-05		-
Minerals	-	6.158E-06	-	-	-	5.014E-06		-
Water	-	0.886	-	-	-	0.722		1
NaOH	1	0.0263	-	-	-	0.0214		-
Methacrylic Anhydride	-	0.00122	-	-	-	0.000992		-
Methacrylated Protein	-	0.0677	-	-	-	0.00551		-
Methacrylic Acid	-	0.00186	-	-	-	0.00152		-
PEGMA	-	-	1	-	-	0.0573		-
APS	-	-	-	1	-	0.0125		-
TEMED	-	-	-	-	1	0.000255		-
Polymer	-	-	-	-	-	0.165		-
Air (not including water vapour)	-	-	-	-	-	-	-	-
Total	1	1	1	1	1	1	1	1



<b>Process Step</b>	D	D	D	D	D	D	D	D
Line No.	36	37	38	39	40	41	42	43
Stream	Waste from Washing	Cleaned Polymer	Centrifuge Waste (Liquids)	Centrifuged content (Solids)	(Heat Exchanger) Steam Inlet	(Heat Exchanger) Condensate Outlet	Evaporated Water	Bioplastic Product
Batch Mass Flow (tonnes)	24.08	12.7	8.89	3.81	4.230	4.230	1.295	2.515
Pressure (bar)	1.013	1.013	1.013	1.013	4.765	1.013	1.013	1.013
Temperature (celsius)	25	25	25	25	150	96.43	N/A	72°C
pH	-	-	-	-	-	-	-	-
<b>Components Mass Fraction</b>								
Protein	NB	NB	*	*	-	-	-	*
Carbohydrates	NB	NB	*	*	-	-	-	*
Fats	NB	NB	*	*	-	-	-	*
Minerals	NB	NB	*	*	-	-	-	*
Water	0.9476	0.8121	0.9623	0.4	1	1	1	0.09
NaOH	NB	NB	*	*	-	-	-	*
Methacrylic Anhydride	NB	NB	*	*	-	-	-	*
Methacrylated Protein	NB	NB	*	*	-	-	-	*
Methacrylic Acid	NB	NB	*	*	-	-	-	*
PEGMA	NB	NB	*	*	-	-	-	*
APS	NB	NB	*	*	-	-	-	*
TEMED	NB	NB	*	*	-	-	-	*
Polymer	-	0.1653	*	*	-	-	-	*
Polymer and impurities	-	-	0.0377	0.6	-	-	-	0.91
Air (not including water vapour)	-	-	-	-	-	-	-	-
Total	1	1	1	1	1	1	1	1



For streams 36 and 37, the impurity components are indicated by NB, as although the quantity of impurities washed off can be estimated, the composition of these impurities cannot be determined. Hence, the total composition for these streams do not add to 1, however, the sum of the component mass fractions labelled NB and the defined mass fractions would result in the total mass fraction being equivalent to 1.

A \* is put in the table for individual components in the impurities for streams 38, 39 and 43, as although these are present, they are accounted for in the polymer and impurities row of the table.

Calculated values in the stream table are given to 4SF.

## Material and Energy Balances

### A: Pre-treatment of Whey

*Mass balances:*

#### Pasteuriser

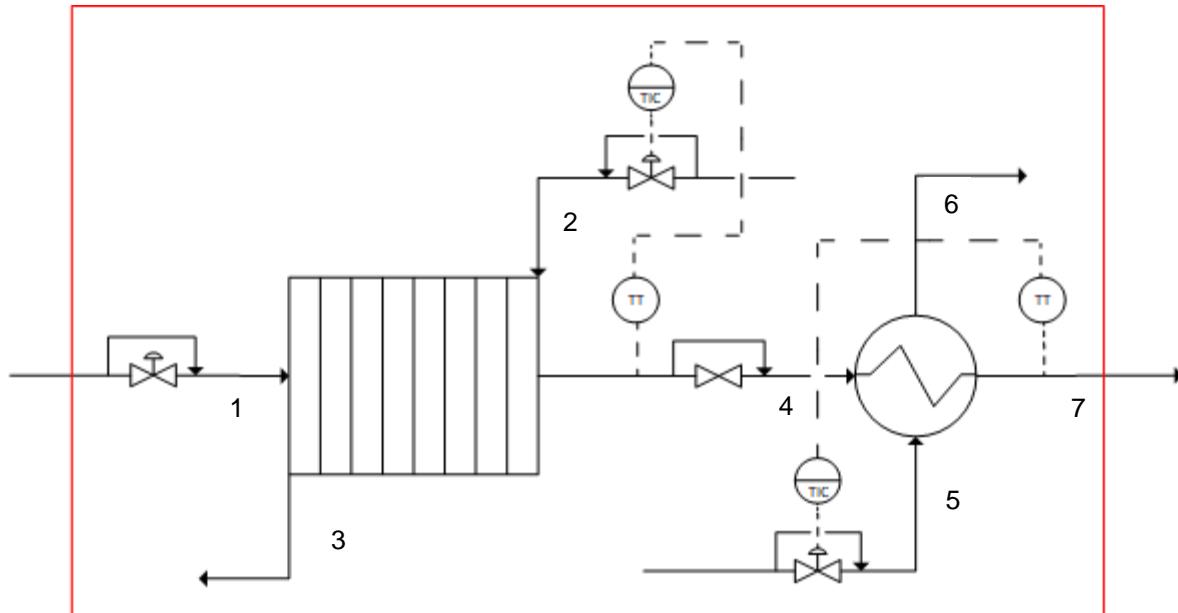


Figure 5: System boundary of Pasteuriser

The chosen feedstock of 44800 tonnes of whey per annum is considered. 100 tonnes of waste liquid whey will be processed in 448 batches per year to achieve this. The mass balance for the inlet of the pasteuriser per batch is as follows.

$$F_1 = \frac{44800}{448} = 100 \text{ tonnes batch}^{-1}$$

It is assumed that the pasteuriser operates at steady state with no accumulation or fouling within the plate pasteuriser and the plate cooler. Therefore, the batch mass flow of stream leaving the pasteuriser is determined.

$$F_1 = F_4 = 100 \text{ tonnes batch}^{-1}$$

#### Centrifuge

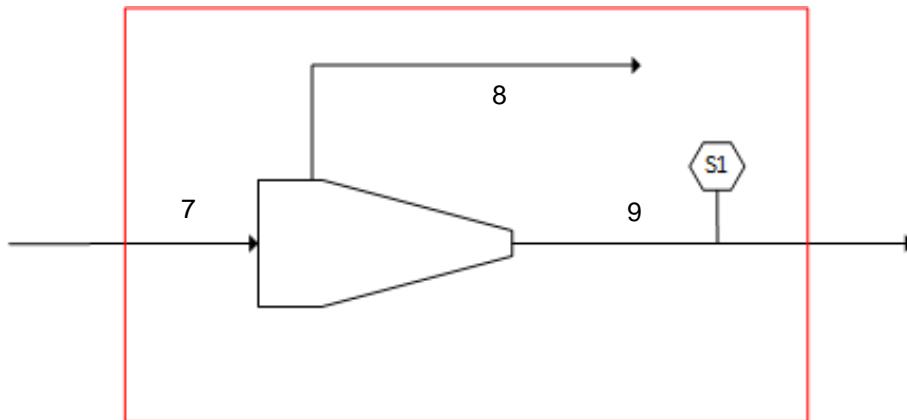


Figure 6: System boundary of Centrifuge



The pasteurised whey is then centrifuged to remove any large solids, including denatured microorganisms, in suspension. It is assumed that the centrifuge in use will have a sedimentation efficiency of 30% (Chalermthai et al., 2020). Therefore, the waste left in the centrifuge and fat reduced whey leaving the unit is calculated.

$$F_8 = 100 \cdot 0.3 = 30 \text{ tonnes batch}^{-1}$$

$$F_9 = F_4 - F_8 = 100 - 30 = 70 \text{ tonnes batch}^{-1}$$

As only microorganisms are denatured in the pasteurisation unit, the inlet composition to the centrifugation unit is the same as the composition of the waste liquid whey: 4% carbohydrates, 4.5% fat, 1% minerals, 1% protein and 89.5% water (Chalermthai et al., 2020).

The centrifuge has a solids removal of: 70% carbohydrates, 60% fats, 70% minerals and 100% proteins (Chalermthai et al., 2020), implying that 30% of the carbohydrates, 40% of the fats and 30% of the minerals by mass are removed in the centrifuge waste. From this, it is determined that 1.2 tonnes of carbohydrates, 1.8 tonnes of fat and 0.3 tonnes of minerals are removed in the centrifuge waste stream,  $F_8$ , and hence the mass of water is 26.7 tonnes to make up the remaining centrifuge waste stream of 30 tonnes. The fat reduced whey stream,  $F_9$ , is composed of 1 tonne protein, 0.7 tonnes minerals, 2.8 tonnes carbs, and 2.7 tonnes fat. Therefore, the mass of water in this stream is 62.8 tonnes to make up the remaining whey stream of 70 tonnes.

### *Energy balances*

It is assumed that the liquid whey is transported to the plant at ambient temperatures and pressures (298.15 K, 1.013 bar). It is assumed that the pre-treatment step operates at isobaric conditions.

The unit has been simplified to ease the overall design of the pasteurisation process. Usually, the pasteurisation process is operated at 71.7°C to 77.8°C for around 15.4 to 16.4 seconds (Doyle et al., 1987). However, the temperature cannot be raised to the standard 77.8°C because certain proteins within the liquid whey, that are required for the methacrylation and polymerisation, denature at different temperatures.  $\beta$ -lactoglobulin at 78°C,  $\alpha$ -lactalbumin at 62°C, and bovine serum albumin at 64°C (Chalermthai et al., 2020). Hence, the liquid whey is heated to 61°C to prevent denaturing.

The unit only consists of a plate pasteuriser and a plate heat exchanger that have been overdesigned to heat and cool the liquid whey respectively. This negates the requirement for a holding tub and redundant pumps. It is assumed that the heating and cooling of the whey both take 15 minutes to ensure that the liquid whey is heated to 61°C and stays in the heat exchanger for sufficient time for sterilisation. The pasteuriser carries out this heating, and the second heat exchanger is utilised to cool down the stream leaving the pasteuriser to 25°C, as this is the temperature required for downstream units.

### **Plate Pasteuriser**

Heating liquid whey from 25°C to 61°C in the first heat exchanger:

$$Q = m C_p (T_2 - T_1) \quad (1)$$

It is assumed that there is only a change in temperature and no change in enthalpy due to a constant pressure. No chemical reaction occurs. Eq.(1) is used to calculate the thermal duty of the heat exchanger. As the liquid whey is mainly composed of water, it is assumed that the liquid whey has thermal properties similar to water (Felder et al., 2016).

$$C_{p,l} = a + bT + cT^2 + dT^3$$

*Table 6: Thermal properties of water* (Felder et al., 2016)

	$a \times 10^{-3}$	$b \times 10^{-5}$	$c \times 10^{-8}$	$d \times 10^{-12}$
Water	75.4	-	-	-

$$C_{p,l} = 75.4 \times 10^{-3} \text{ kJ mol}^{-1} \text{K}^{-1} = 4.189 \text{ kJ kg}^{-1} \text{ }^{\circ}\text{C}^{-1}$$



$$Q_1 = 100 \times 10^3 \cdot 4.189 \cdot (334.15 - 298.15) = 15.08 \times 10^6 \text{ kJ batch}^{-1}$$

The pasteurisation process takes 15 minutes. Therefore:

$$\dot{Q}_1 = \frac{15.08 \times 10^6}{15 \cdot 60} = 16720 \text{ kW}$$

The log mean temperature difference of the heat transfer area can be calculated from equation 2:

$$\Delta T_{lm} = \frac{(T_{h,i} - T_{c,o}) - (T_{h,o} - T_{c,i})}{\ln \frac{(T_{h,i} - T_{c,o})}{(T_{h,o} - T_{c,i})}} \rightarrow \Delta T_{lm} = \frac{\dot{Q}}{UA} \quad (2)$$

It is assumed that the heat transfer coefficient,  $U$ , for the steam is  $1500 \text{ W m}^{-2} \text{ K}^{-1}$  (Sinnott Ray K., 2009). The heat exchange surface area,  $A$ , is based off HISAK RX-50 (HISAKA, 2022), with maximum  $500 \text{ m}^2$ .

$$\Delta T_{lm} = \frac{16720}{1.5 \cdot 500} = 22.29 \text{ }^\circ\text{C}$$

The temperature and pressure of the inlet steam is  $81.3^\circ\text{C}$  and  $50 \text{ kPa}$ . The properties of the steam chosen are suitable for operation in a heat exchanger design similar to HISAKA RX-50. A saturated steam temperature of  $81.3^\circ\text{C}$  is selected to optimise the cost of the pasteuriser, as a steam temperature is used with  $15-20^\circ\text{C}$  above the required temperature of the fluid being heated (Bell & Gossett, 2016). Hence, the temperature of the hot liquid whey stream leaving the pasteuriser can be determined:

$$22.29 = \frac{(354.45 - 334.15) - (T_{h,o} - 298.15)}{\ln \frac{(354.45 - 334.15)}{(T_{h,o} - 298.15)}}, T_{h,o} = 49.75 \text{ }^\circ\text{C}$$

Using goal seek, the outlet temperature of the steam is  $49.75^\circ\text{C}$ .

### Heat Exchanger 1

This is utilised to cool the liquid whey from  $61^\circ\text{C}$  to  $25^\circ\text{C}$ .

Similarly to the pasteuriser, Equation 1 can be used to calculate the thermal duty of the heat exchanger, with the same value of specific heat capacity (Felder et al., 2016). Hence:

$$Q_2 = 100 \times 10^3 \cdot 4.189 \cdot (298.15 - 334.15) = -15.08 \times 10^6 \text{ kJ batch}^{-1}$$

The cooling process will also take 15 minutes. Therefore:

$$\dot{Q}_2 = \frac{-15.08 \times 10^6}{15 \cdot 60} = -16756 \text{ kW}$$

It is assumed that the heat transfer coefficient,  $U$ , for the steam is  $1500 \text{ W m}^{-2} \text{ K}^{-1}$ . The heat exchange surface area,  $A$ , is based off HISAK RX-90 (HISAKA, 2022) with maximum  $1600 \text{ m}^2$ . Using equation 2, the log mean temperature difference of the heat transfer area can be calculated:

$$\Delta T_{lm} = \frac{-16756}{1.5 \cdot 1600} = (-)6.980 \text{ }^\circ\text{C}$$

The cooling agent will be supplied by Wessex Water and it the calculation is based in the temperatures of water reservoirs during the summer (Environment Data, 2018). The temperature and pressure of the inlet cooling water is assumed as  $294.15 \text{ K}$  and  $1 \text{ atm}$ . Using Equation 2, the outlet temperature of the cooling water stream can be determined:

$$-47.99 = \frac{(334.15 - T_{c,o}) - (298.15 - 294.15)}{\ln \frac{(334.15 - T_{c,o})}{(298.15 - 294.15)}}, T_{c,o} = 323.0 \text{ K (4sf)}$$



Using goal seek, the outlet temperature of the cooling water is 49.85°C (4sf).

### Heating & Cooling Capacity

#### *Heating the liquid whey*

Steam is used as a heating agent for the plate pasteuriser. The heat duty calculated for the pasteuriser is 16720 kW, therefore, the mass batch flow rate of steam can be calculated using equation 3.

$$\dot{m} = \frac{\dot{Q}}{C_p(T_2 - T_1)} \quad (3)$$

$$C_{p,l} = a + bT + cT^2 + dT^3 \quad (4)$$

Table 7: Heat capacity constants of steam

	$a \times 10^{-3}$	$b \times 10^{-5}$	$c \times 10^{-8}$	$d \times 10^{-12}$
Steam	33.46	0.6880	0.7604	-3.593

The heat capacity of the steam at the inlet stream temperature, 81.3°C, is calculated using Equation 4.

$$C_{p,l} = 33.46 \times 10^{-3} + (0.6880 \times 10^{-5} \cdot 81.3) + (0.7604 \times 10^{-8} \cdot 81.3^2) - (3.593 \times 10^{-12} \cdot 81.3^3)$$

$$C_{p,l} = 0.034 \text{ kJ mol}^{-1} \text{ K}^{-1} = 1.892 \text{ kJ kg}^{-1} \text{ }^{\circ}\text{C}^{-1}$$

The mass flow rate of steam is determined using the temperature difference between the steams inlet and outlet temperature, 354.45 K and 322.90 K, respectively. Hence using Equation 3:

$$\dot{m} = \frac{16720}{1.892(322.99 - 354.45)}$$

$$F_2 = F_3 = 12.62 \text{ tonnes batch}^{-1}$$

#### *Cooling the pasteurised whey*

Cool water is used as a cooling agent for the heat exchanger. The heat duty calculated for the heat exchanger is -16756 kJ therefore, the mass batch flow rate of steam can also be calculated using equation 3.

The mass flow rate of water is determined using the temperature difference between the cooling agent's inlet and outlet temperature, 21°C and 39.85°C respectively.

$$\dot{m} = \frac{16756}{4.189(322.99 - 294.15)}$$

$$F_5 = F_6 = 124.8 \text{ tonnes batch}^{-1}$$

## B: Whey to whey powder

### Mass balances

#### Ultrafiltration, streams 9 - 12:

Assumptions:

- Steady state permeate flux and diafiltration input flow rate.
- No effect of fouling considered.
- Constant composition of feed.

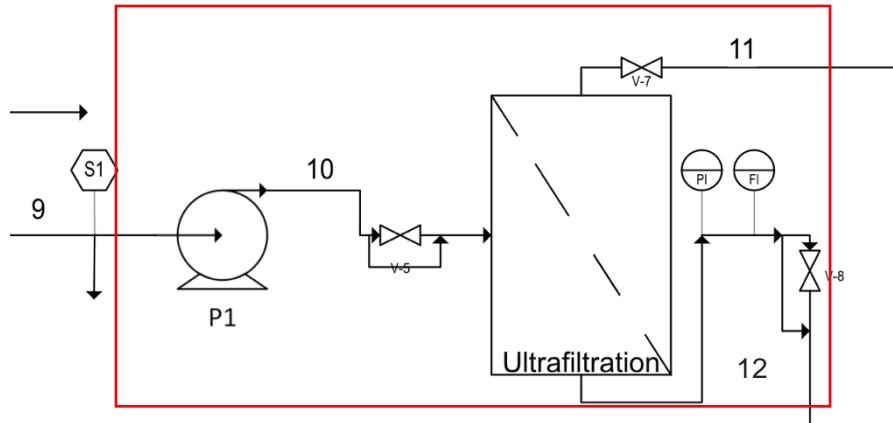


Figure 7: System boundary of ultrafiltration mass balance

The membrane is designed to remove large molecules and particulate components that are in suspension of the liquid to maximise the concentration of whey protein. This will ensure that the whey protein powder produced is of the greatest quality for methacrylation and polymerisation. The membrane will aim to have a rejection coefficient,  $R_C$ , of 0.95 for proteins (Chalermthai et al., 2020). It is assumed that this rejection coefficient remains constant over time. The feed to retentate mass ratio is 20:1 (Chalermthai et al., 2020).

$$F_9 = F_{11} + F_{12}$$

The mass balance was performed using the system boundary shown in Figure 7. The value of  $F_9 = 70 \text{ t batch}^{-1}$  is used as calculated in the previous unit mass balances and the ratio of feed to retentate of 20:1 is used. The flowrates of streams 11 and 12 can be calculated with these values.

Ultrafiltration membrane separation permeate:

$$F_{11} = \frac{19}{20} F_9 = 66.5 \text{ tonnes batch}^{-1}$$

Ultrafiltration membrane separation retentate:

$$F_{12} = \frac{1}{20} F_9 = 3.50 \text{ tonnes batch}^{-1}$$

Using membrane rejection coefficients of 0.01 for carbohydrates, 0.01 for fats, 0.01 minerals, 0.95 for proteins (Chalermthai et al., 2020), the composition of the permeate and retentate streams can be determined.

F11 (permeate stream) consists of: 2.772 tonnes of carbohydrates, 2.673 tonnes of fats, 0.693 tonnes minerals, 0.05 tonnes protein. Using the total permeate mass of 66.5 tonnes (total F11), the mass of water in F11 is determined as 60.31 tonnes. F12 (retentate stream) consists of: 0.028 tonnes carbs, 0.027 tonnes fats, 0.95 tonnes proteins, 0.007 tonnes minerals. Using the total retentate mass of 3.5 tonnes (total F12), the mass of water in F12 is determined as 2.488 tonnes.

Example calculation of component using rejection coefficient:

$$F_{12,\text{protein}} = 0.95 F_{11,\text{protein}} = 1 \times 0.95 = 0.95 \text{ tonnes batch}^{-1}$$

$$F_{13,\text{protein}} = 0.05 F_{11,\text{protein}} = 1 \times 0.05 = 0.05 \text{ tonnes batch}^{-1}$$

Full composition breakdown of each stream can be found in the stream table (Table 5).

#### Diafiltration, streams 12 - 18:

Assumptions:

- Steady state permeate flux and spray dryer input flowrate.

- No effect of fouling considered.
  - Constant density of feed.
  - Perfect mixing of buffer and recycle in diafiltration.

The diafiltration unit is designed to remove more of the large molecules and particulate components that are in suspension of the liquid to maximise the concentration of the whey protein. This will ensure that the whey protein powder produced is of the greatest quality possible. The membrane will aim to have a rejection coefficient,  $R_C$ , of 0.95 for proteins (Chalermthai et al., 2020). It is assumed that this rejection coefficient remains constant over time. The feed to retentate mass ratio is also assumed to be 20:1 (Chalermthai et al., 2020).

It is assumed that the membrane rejection coefficients are the same as for ultrafiltration of 0.01 for carbohydrates, 0.01 for fats, 0.01 minerals, 0.95 for proteins (Chalermthai et al., 2020).

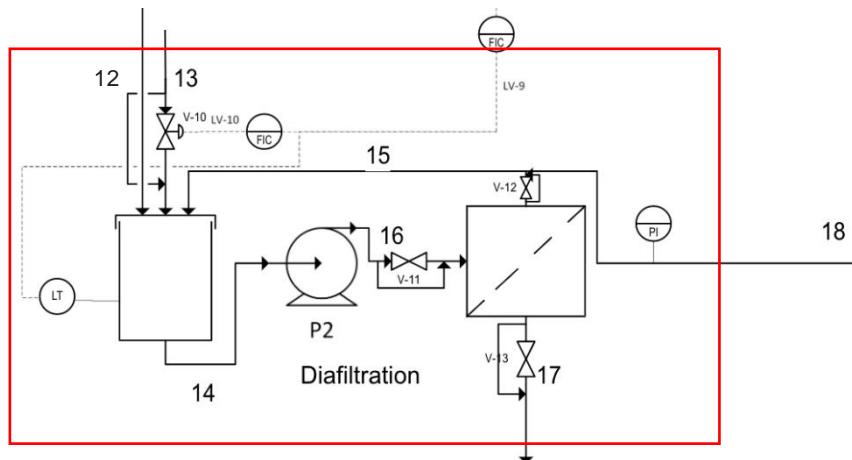


Figure 8: System boundary of diafiltration mass balance on section of P&ID

The system boundary used for this mass balance is shown in Figure 8. The mass of stream 12 is known from the retentate stream of the ultrafiltration unit. Since the target composition of the powder after the spray dryer is known to contain 10% water, a value sourced from a techno-economic analysis (Chalermtchai et al., 2020), goal seek in Microsoft Excel was used to find the composition of stream 18. This composition, with the rejection coefficients of the membrane, allowed the mass of stream 18 to be calculated.

$$\begin{aligned}
 F_{18} &= F_{protein,18} + F_{carbs,18} + F_{fats,18} + F_{minerals,18} + F_{water,18} \\
 &= 0.95F_{protein,12} + 0.01F_{carbs,12} + 0.01F_{fats,12} + 0.01F_{minerals,12} + 0.01F_{water,12} \\
 &\quad = 2.43 \text{ tonnes batch}^{-1}
 \end{aligned}$$

The discarded protein, carbohydrates, fats and minerals are in the permeate. The rest of the mass comes from the water added in the initial feed and the buffer.

The ratio of feed to retentate was again assumed to be 20:1 as in ultrafiltration (Chalermtai et al., 2020) and the total buffer was calculated from this to ensure the filtrate volume was constant. The change in density of the stream was assumed to be negligible so the mass was assumed to be constant. The buffer and recycle stream are dependent on the volume and composition of the retentate which will vary throughout the diafiltration, however this would be detailed in further design. The mass balance of the system boundary given in Figure 8 is as follows:

$$F_{12} + F_{13} = F_{17} + F_{18}$$

Using the 20:1 ratio:

$$\frac{F_{12} + F_{13}}{20} = F_{18}$$

The mass of buffer can be determined:

$$\therefore F_{13} = (F_{18} \times 20) - F_{12} = (2.43 \times 20) - 3.50 = 45.06 \text{ tonnes batch}^{-1}$$

From the overall mass balance of the system, the permeate stream can be determined:

$$\begin{aligned}\therefore F_{17} &= F_{12} + F_{13} - F_{18} = F_{12} + F_{13} - \frac{F_{12} + F_{13}}{20} = \frac{19(F_{12} + F_{13})}{20} = \frac{19(3.50 + 45.06)}{20} \\ &= 46.13 \text{ tonnes batch}^{-1}\end{aligned}$$

To check the mass balances:

$$3.50 \text{ tonnes batch}^{-1} + 45.06 \text{ tonnes batch}^{-1} - 46.13 \text{ tonnes batch}^{-1} - 2.43 \text{ tonnes batch}^{-1} = 0$$

Specific composition for each stream can be seen in the full stream table (Table 5).

### Spray drying, streams 18 - 23:

Assumptions:

- Constant composition and temperature of feed.
- Constant temperature of drying chamber.
- Constant air flowrate.
- Effect of particle interaction on kinetic energy negligible .
- All product entering the spray dryer leaves in the outlet product stream (no product is lost in the chamber / in the outlet air stream).
- Constant humidity between stream 20 and stream 21.

The spray dryer is assumed to remove 93% of the water in the feed (Chalermthai et al., 2019). This allows a composition to be calculated in the outlet, stream 23. This is shown in the full stream table (Table 5).

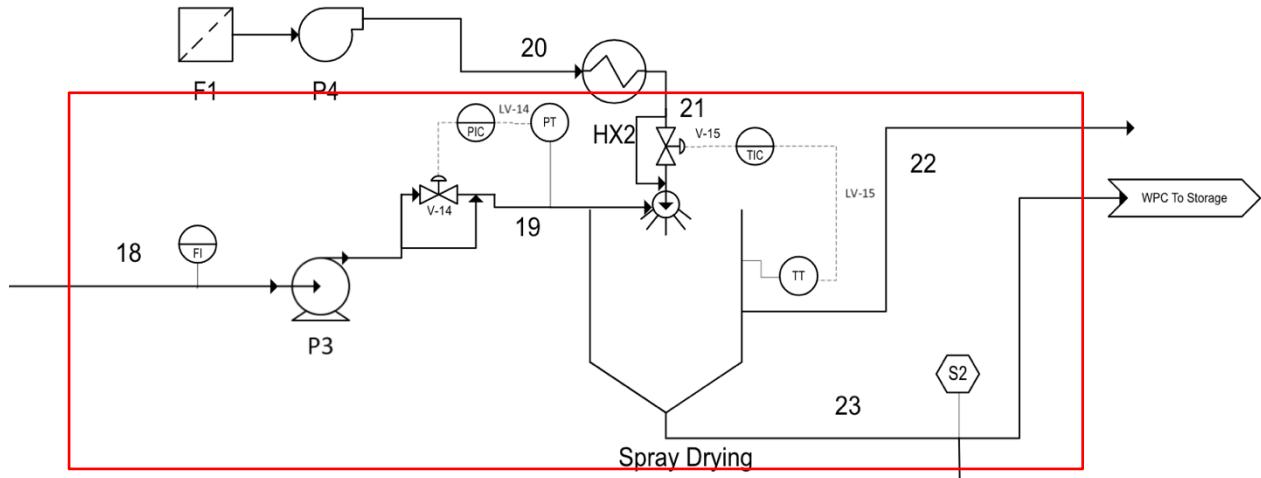


Figure 9: System boundary for spray dryer mass balance

The system boundary around the spray dryer is demonstrated in Figure 9. The mass flowrate of stream 23 can be calculated from the mass after the 93% of water is removed from stream 18. This assumes that only the water is evaporated in the dryer and no solid product is lost.

$$F_{23} = F_{18} - 0.93x_{water,18}F_{18} = 1.04 \text{ t batch}^{-1}$$



The water evaporation rate is determined as the difference in the water inlet and outlet, which is 1383 kg batch<sup>-1</sup>. Assuming an inlet humidity of 0.02 kg water/kg dry air (Masilungan-Manuel et al., 2015), performing a water mass balance and rearranging, the dry air flow rate is given as:

$$G = \frac{1383}{H_2 - 0.02}$$

(Harrison et al., 2015). The outlet humidity, H<sub>2</sub>, needs to be determined. The enthalpy of air is given as:

$$C_{p,s}(T - T_0) + H \times \lambda_0 \quad (5)$$

(Harrison et al., 2015). For air and water mixtures, C<sub>p,s</sub> = 0.24 + (0.4H), and at a datum temperature, T<sub>0</sub>, of 0°C and atmospheric pressure, the latent heat of water, λ<sub>0</sub>, is 597 kcal/kg (Harrison et al., 2015).

It is assumed that the exhaust air temperature is equal to the outlet temperature of the whey stream, hence the exhaust air and outlet whey stream are at 70°C. (Chalermthai et al., 2020). Air is normally heated to 150–250°C for spray drying in the dairy industry (Tetra Pak, 1995), therefore a temperature of 150°C is chosen. The inlet stream enters at standard temperatures of 25°C.

The enthalpy of the protein is determined by the temperature multiplied by the specific heat of the protein, which is assumed to be 1.26 J K<sup>-1</sup> g<sup>-1</sup> (Yang and Rupley, 1979) which is equivalent to 0.3 kcal kg<sup>-1</sup> K<sup>-1</sup>. Setting the total enthalpies in equal to the total enthalpies out, and substituting in the equation for G, H<sub>2</sub> is determined as 0.0522 kg water/kg dry air. From this, the dry air flow rate is determined as 42884 kg batch<sup>-1</sup>. Multiplying this by the respective humidities, this gives a water vapour rate in the air stream of 858 kg batch<sup>-1</sup>, and a water vapour rate out of the air stream of 2239 kg batch<sup>-1</sup>. Adding these values to the dry air rate, the total air flow rates in and out are determined as F<sub>21</sub> = 43742 kg batch<sup>-1</sup> and F<sub>22</sub> = 45123 kg batch<sup>-1</sup>.

Check: F<sub>18</sub> + F<sub>21</sub> ≈ 46172, and F<sub>22</sub> + F<sub>23</sub> ≈ 46163.

These values are the same to 3sf, with any differences being related to rounding errors, or may be due to some of the water remaining in the spray dryer.

All compositions of streams can be found in the stream table (Table 5), and full calculations can be found in Appendix B.

### Solids storage

The 1.04 tonnes of whey powder will be stored until required for the next stage. This volume can be estimated using the density of whey protein isolate, 380 kg m<sup>-3</sup> (Bruno De Carvalho-Silva et al., 2013), which has the closest composition to our product. This gives a volume of 2.75 m<sup>3</sup>, however, the volume should be larger to allow for multiple batch operations at a time.

It is assumed that the powder is cooled in storage to room temperature before proceeding to the plastic making steps.

### Energy balances

#### Ultrafiltration

Assumptions:

- Ambient temperature (298.15 K).
- Retentate and permeate streams at atmospheric pressure.
- Transmembrane pressure of 2 bar.
- Energy requirements mainly consist of the pump requirement for the feed pressure.

Pump 1: Centrifuged liquid whey to be separated using ultrafiltration



The ultrafiltration membrane is operated with a driving force provided by a transmembrane pressure of 2 bar, as this was used in studies for increasing the protein concentration of whey and hence is appropriate (Baldasso et al., 2022). Using the following equation, the feed pressure required can be calculated.

$$P_{TM} = \frac{(P_f + P_r)}{2} - P_p \quad (6)$$

(Cyganowski and Lutz, 2015). The assumption that the desired retentate and permeate streams are operated at atmospheric pressure, 1.01 bar, is made. Using Equation 6:

$$2 = \frac{(P_f + 1.01)}{2} - 1.01$$

$$P_f = 5.01 \text{ bar}$$

The hydraulic power requirement of the pump can be calculated using the following equation.

$$P_h = \frac{Q}{3600\eta} dP \rightarrow E = \frac{V}{3600\eta} dP \quad (7)$$

(Neutrium, 2020)

The volume of the pump (pump 1) feed is calculated to determine the energy requirement of the pump per batch. The volume of the solid component can be estimated using the density of whey protein isolate, 380 kg m<sup>-3</sup> (Bruno De Carvalho-Silva et al., 2013). The water density used is 997.05 kg m<sup>-3</sup> (Beaton et al., 1989).

$$V = \frac{x_{water}F_{10}}{\rho_{water}} + \frac{x_{solids}F_{10}}{\rho_{solids}} = \frac{0.897 \cdot 70000}{997.05} + \frac{(1 - 0.897) \cdot 70000}{380} = 81.95 \text{ m}^3$$

The differential, Equation 7, is then solved to calculate the energy requirement of the pump per batch. It is assumed that the efficiency of the pump,  $\eta$ , is 80% (Exxon Mobil, 2018):

$$\begin{aligned} E &= \int_{P_1}^{P_2} \frac{V}{3600\eta} dP = \left[ \frac{V}{3600\eta} (P_2 - P_1) \right] = \left[ \frac{81.95}{3600 \cdot 0.8} (5.01 - 1.01) \times 10^2 \right] \\ &= 11.38 \text{ kWh} = 40975 \text{ kJ batch}^{-1} \end{aligned}$$

## Diafiltration

With the same assumptions as for ultrafiltration, the feed pressure is 5.01 bar for the diafiltration unit. It is assumed that there are negligible pressure losses between the units, and that stream 14 is pumped to 5.01 bar before the diafiltration membrane.

The hydraulic power requirement of the pump (pump 2) can also be calculated using Equation 7.

The change in density of the stream was assumed to be negligible, hence the mass was assumed to be constant.

The volume entering the pump per batch can be estimated as the sum of the total buffer, F<sub>13</sub>, and the concentrated liquid whey input, F<sub>12</sub>. This neglects the fact that a portion of the inlet stream is to be re-pumped due to the retentate recycle stream. However, as a 20:1 feed to retentate ratio is assumed, and not all the retentate is to be recycled, it is assumed that the volume of the recycle stream per pass is negligible in comparison to the buffer stream, and so the extra volume requirements due to the recycle stream are negligible compared to the total input volume. Therefore, the total mass entering the membrane can be estimated as the sum of the total buffer per batch and the input:



$$= F_{12} + F_{13} = 3.5 + 45.06 = 48.56 \text{ tonnes batch}^{-1}$$

The majority of the mass is the buffer, which is water, so a density of  $997.05 \text{ kg m}^{-3}$  is used (Beaton et al., 1989).

$$V = \frac{48.56 \times 1000}{997.05} = 48.70 \text{ m}^3$$

Equation 7 can then be solved to calculate the energy requirement of the pump per batch. It is assumed that the efficiency of the pump,  $\eta$ , is 80% (Exxon Mobil, 2018).

$$\begin{aligned} E &= \int_{P_1}^{P_2} \frac{V}{3600\eta} dP = \left[ \frac{V}{3600\eta} (P_2 - P_1) \right] = \left[ \frac{48.70}{3600 \cdot 0.8} (5.01 - 1.01) \times 10^2 \right] \\ &= 6.76 \text{ kWh} = 24350 \text{ kJ batch}^{-1}(4sf) \end{aligned}$$

### Spray dryer

The input whey-based feed to the pressurised nozzle of the is assumed to be 50 bar (Park and Haenlein, 2013) and the air enters at atmospheric pressure. This pressure drop provides the energy to atomise the feed. The temperatures are as discussed in the mass balance section.

The energy requirements of this unit are assumed to be the energy required to heat the air sufficiently to evaporate the water from the inlet stream, and the energy required by the pump to create the pressure required by the pressurised nozzle to atomise the feed.

### Pump energy requirements:

Pump 3 requirements can be calculated using Equation 8.

$$V = \frac{x_{water}m}{\rho_{water}} + \frac{x_{solids}m}{\rho_{solids}} \quad (8)$$

As mentioned previously, the water and solids density are assumed to be:  $\rho_{water} = 997.05 \text{ kg m}^{-3}$ ,  $\rho_{solids} = 380 \text{ kg m}^{-3}$ . The pump efficiency is assumed to be 80% (Exxon Mobil, 2018).

$$V = \frac{0.61 \times 2.43 \times 1000}{997.05} + \frac{(1 - 0.61) \times 2.43 \times 1000}{380} = 3.97 \text{ m}^3$$

Substituting into Equation 7:

$$E = \int_{P_1}^{P_2} \frac{V}{3600\eta} dP = \left[ \frac{V}{3600\eta} (P_2 - P_1) \right] = \left[ \frac{3.97}{3600 \cdot 0.8} (50.5 - 1.01) \times 10^2 \right] = 6.82 \text{ kWh} = 24550 \text{ K}$$

### Heat exchanger energy requirements:

The heater duty for the inlet air heat exchanger (excluding heater losses) is given by:

$$Q_{heater} = \dot{m}_g c_{pg} (T_{g,in} - T_{g,a}) \quad (9)$$

Performing a simple heat balance on the continuous dryer:

$$\text{Heat in} = \text{Heat out}$$

$$\begin{aligned} \text{Heat supplied by hot air} &\approx \text{Evaporation load (heat used to evaporate water)} \\ &+ \text{sensible heating of solids (heat used to increase the temperature of the solids)} + \text{heat losses} \\ \dot{m}_g c_{pg} (T_{g,in} - T_{g,a}) &\approx \dot{m}_s (x_{in} - x_{out}) \Delta H_V + \dot{m}_s c_{ps} (T_{g,out} - T_{g,in}) + Q_{loss} \end{aligned} \quad (10)$$

(Kemp, 2012)

Combining these equations, it is obtained that:

$$Q_{heater} = \frac{(T_{g,in} - T_{g,a})}{(T_{g,in} - T_{g,out})} [W_s(X_{in} - X_{out})\Delta H_v + W_s c_{ps}(T_{g,out} - T_{g,in}) + Q_{loss}] \quad (11)$$

Heat losses are typically 5-10% of the heat inlet (Kemp, 2012). Hence, 10% is to be used in this calculation to prevent underestimating the heat requirements.

The mass of the whey stream entering ( $\dot{m}_s$ ) is 2.428 tonnes batch $^{-1}$ , and  $x_{in}$  and  $x_{out}$  are determined as 0.612 and 0.1 respectively from mass balance calculations.  $T_{g,in}$  is 150°C and  $T_{g,out}$  is 70°C as discussed previously. It is assumed that the air is stored at room temperature, 25°C, therefore,  $T_{g,a}$  is 25°C.

As the inlet whey stream enters at 25°C, the latent heat of evaporation of water at standard temperature, which is approximately 2400 kJ kg $^{-1}$ , is to be used (Kemp, 2012). The heat capacity of the whey stream is approximated by the specific heat capacity of protein at 25°C of 1.26 J K $^{-1}$  g $^{-1}$  (Yang and Rupley, 1979), which is a reasonable approximation as protein makes up most of the composition of this stream.

Using Equation 11:

$$\begin{aligned} Q_{heater} &= \frac{(150 - 25)}{(150 - 70)} [(2.42 \times 10^6 \text{ [g batch}^{-1}\text{]} \times (0.612 - 0.1) \times 2400 \text{ [J g}^{-1}\text{]}) \\ &\quad + (2.42 \times 10^6 \text{ [g batch}^{-1}\text{]} \times 1.26 \text{ [J K}^{-1}\text{ g}^{-1}\text{]} \times (70 - 150)) + (0.1 \times Q_{heater})] \\ Q_{heater} &= 1.5625(2.974 \times 10^9 - 243936000 + 0.1Q_{heater}) \\ (Q_{heater} \div 1.5625) &= 2.73 \times 10^9 + 0.1Q_{heater} \\ Q_{heater} &= 5.06 \text{ GJ batch}^{-1} \end{aligned}$$

Therefore, for each batch roughly 5.06 GJ batch $^{-1}$  is required to be supplied to heat the air entering the spray dryer. Hence, the energy requirements for HX2 5.06 GJ batch $^{-1}$ . This value is close to that obtained by literature, as the average energy consumption of a dryer from a survey by the U.K government was determined as 4.87 GJ/tonne of water evaporated (Baker and McKenzie, 2005), and the spray dryer evaporates 1.38 tonnes of water per batch, hence with this source 6.72 GJ batch $^{-1}$  would be required for the spray dryer. This is of the same order of magnitude as the calculated value.

## C: Chemical Processing

### Mass Balances

The chemical processing stage consists of 3 batch reactors with each corresponding to protein dissolution, methacrylation and polymerisation. An outline of the material balances for each of the units is below with more detailed stream breakdowns in the stream table (Table 5).

The conversion for each of the three stirred vessels are listed below and are taken from literature. Due to the novelty of the reactions, the conversion rates listed are taken as an average from publications. These are to be verified with further design. The reactions in each vessel can be conducted at ambient conditions of 1 atm and 25°C, reducing operating costs, as the agitation and the use of initiator and catalyst can ensure a sufficient reaction rate.

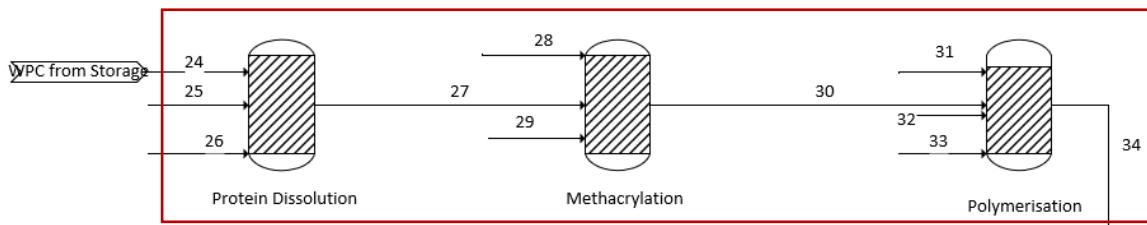


Figure 10: System boundaries for the Chemical Processing section

### Protein Dissolution Tank

Assuming that the pH adjustment by the NaOH solution is sufficient to bring the protein powder solution from pH 6-6.7 to 10-11, far outside of protein isoelectric point of around 4, the protein dissolution extent is taken to be 100%. (Veide Vilig and Undeland, 2017) The protein is left to agitate for 20 minutes to

ensure maximum dissolution in the stirred tank. It is assumed that the protein has completely dissolved and hence all protein is available for the methacrylation reaction.

It is assumed that the inlet whey powder stream to the protein dissolution tank is equal to the whey powder stream entering storage ( $F_{23} = F_{24}$ ). This is 1.045 tonnes batch $^{-1}$ . 1000 L of water and 100 L of 10 M Sodium Hydroxide solution are required per batch (Chalermthai et al., 2020). Using the respective densities of 997.05 kg m $^{-3}$  (Beaton et al., 1989) and 1.33 g cm $^{-3}$  (Merck, 2022e), it is determined that  $F_{25}$  = water stream = 9.971 tonnes batch $^{-1}$  and  $F_{26}$  = Sodium hydroxide stream = 0.133 tonnes batch $^{-1}$ . Full calculations for this can be found in Appendix C.

Though the protein dissolution tank is not a key unit and thus not included within the specification sheets, preliminary sizing was carried out, shown in Appendix C

### Methacrylation Stirred Tank Reactor

The methacrylation reaction occurs randomly on the primary amine groups on protein chains by adding methacrylamide groups onto the amine groups (Chan et al., 2017).

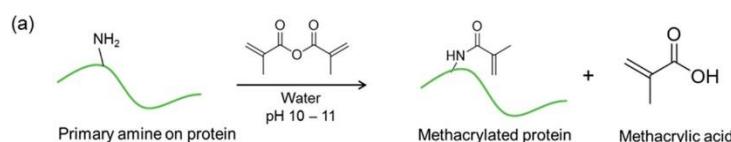


Figure 11: Methacrylation reaction equation

Methacrylated proteins act as macromonomers which later react in a free-radical polymerisation reaction with a co-monomer and initiator/catalyst combo. This reaction occurs under basic conditions, with the addition of 10 M NaOH, to prevent protein precipitation and to balance the acidity brought by the by-product of methacrylic acid. The conversion found for this process is based on literature consisting of functionalisation of methacrylates (Muzammil et al., 2017) and methacrylation of hydrogels (Bencherif et al., 2008) which both have ranges of methacrylation of 71-81% and 14%-90%. This assumption is because the main reaction occurring is a change in the functional groups on the protein N-terminals. To use a conservative estimate, a degree of methacrylation of 80% is assumed and with the reaction left to agitate for 7 hours (Chalermthai et al., 2020), to ensure the highest extent of protein methacrylation.

Additionally, because the highest proportion of protein in the whey powder, 50%, is beta-lactoglobulin the molar mass of the proteins in the solution are assumed to be close to the molar mass of beta-lactoglobulin, 18363 g/mol (Merck, 2022a). Also, the methacrylation is assumed to be occurring on all the protein mass in the methacrylation reactor inlet due to the presence of N-Terminals on all proteins in the inlet. In the methacrylation, methacrylic anhydride ( $M_w = 154.2$  g/mol (Merck, 2022b)) and protein react in mole ratio of 6 methacrylic anhydride/protein (Chan et al., 2017). Finally, the amount of methacrylic acid,  $M_w=86.06$  g/mol (NCBI, 2022b), is found by assuming that the moles of methacrylic acid are equal to the moles of reacting methacrylic anhydride due to the nature of the reaction being a functional group change. These assumptions will be later refined in detailed design.

The dissolved whey powder input into the methacrylation reactor is the sum of the inputs to the protein dissolution tank:

$$F_{27} = F_{24} + F_{25} + F_{26} = 1.04521 + 9.9705 + 0.133 = 11.15 \text{ tonnes batch}^{-1}$$

50 L of methacrylic anhydride and 125 L of 10 M NaOH solution (Chalermthai et al., 2020), are added to this reactor. Using the respective densities at 25°C, of 1.035 g/cm $^3$  (Merck, 2022b) and 1.33 g cm $^{-3}$  (Merck, 2022e) the mass of the methacrylic anhydride stream,  $F_{18}$ , is determined as 0.05175 tonnes batch $^{-1}$ , and the mass of the NaOH stream,  $F_{19}$ , is determined as 0.1663 tonnes batch $^{-1}$ . Full calculations for this can be found in Appendix C.

The limiting reagent of the reaction is assumed to be protein, and the reaction is calculated for an 80% conversion of protein. It is assumed the mass of protein entering the methacrylation reactor (in stream



27) is the same as the mass of protein entering storage (in stream 23). Thus, in stream 27 there are 0.9405 tonnes of protein per batch.

Determining the moles of reacted protein using the molar mass of beta-lactoglobulin and 80% conversion:

$$0.9405 \text{ tonnes} \div 0.018363 \text{ tonnes/mol} * 0.8 = 40.97 \text{ mol reacted } \beta \text{ lactoglobulin}$$

Using the mol ratio to determine the moles of methacrylic anhydride at this conversion:

$$40.974 \text{ mol} * 6 \text{ mol} \frac{\text{methacrylic anhydride}}{\text{protein}} = 245.8 \text{ moles methacrylic anhydride}$$

The mass of unreacted methacrylic anhydride and protein are calculated from the moles of reacted protein and methacrylic anhydride and the corresponding molecular weights:

$$\begin{aligned} 0.9405 \text{ tonnes protein} - (40.97 \text{ mol protein} * 0.018363 \text{ tonnes/mol}) \\ = 0.1881 \text{ tonnes unreacted protein} \end{aligned}$$

$$\begin{aligned} 0.05175 \text{ tonnes methacrylic anhydride} - (245.8 \text{ mol} * 0.0001542 \text{ tonnes/mol}) \\ = 0.01385 \text{ tonnes unreacted methacrylic anhydride} \end{aligned}$$

The mass of methacrylic acid is then found with the assumption that the moles of methacrylic anhydride are the same as the moles of methacrylic acid formed:

$$245.842 \text{ moles methacrylic acid} * 8.61 \times 10^{-5} \text{ tonnes/mol} = 0.0212 \text{ tonnes methacrylic acid}$$

Performing a mass balance on the protein and the reacting species in the methacrylation reactor, the mass of the methacrylated protein leaving the reactor is found:

$$\begin{aligned} F_{30,\text{methacrylated protein}} &= F_{27,\text{protein}} + F_{28} - (\text{methacrylic acid} + F_{27,\text{protein,unreacted}} + F_{28,\text{unreacted}}) \\ &= 0.9405 + 0.05175 - (0.0212 + 0.1881 + 0.01385) \\ &= 0.7691 \text{ tonnes methacrylated protein batch}^{-1} \end{aligned}$$

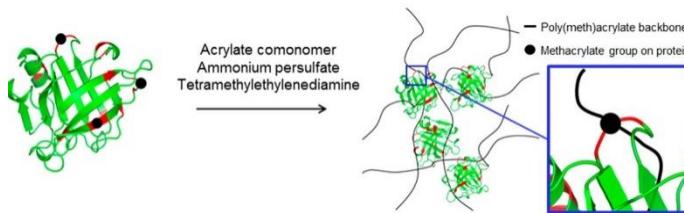
Mass balance checks are done around the methacrylation unit by subtracting outlet components from inlet components, giving 0 as expected.

Salt production by the NaOH and methacrylic acid are assumed to be in solution and not considered in the composition of the outlet stream.

### Polymerisation Stirred Tank Reactor

The polymerisation reaction is carried out using an initiator (ammonium persulfate) and a catalyst (TEMED) with PEGMA,  $M_w=500$  g/mol, as a co-polymer with the methacrylated protein. The reaction occurs in solution and is agitated for 1 hour in a stirred tank reactor. APS and TEMED are assumed to be regenerated in the reaction and thus the initial masses added are equal to the final masses present after polymerisation. PEGMA acts as a co-polymer providing a rubbery soft medium to the rigid medium provided by the methacrylated protein. Thus, through free radical polymerisation, the methacrylated proteins bond to the poly(meth)acrylate backbone, forming a polymer. The ratio of methacrylated protein:PEGMA by mass affect the mechanical properties of the resulting polymer with a balance required between the rubbery and rigid mediums in the polymer. The ratio of 30:70 methacrylated

protein: PEGMA is shown to produce polymers with higher tensile strengths of  $3.8 \pm 0.2$  MPa compared to  $1.9 \pm 0.4$  MPa for lower protein content of 20:80 (Chalermthai et al., 2019).



*Figure 12: Polymerisation reaction diagram*

The methacrylated content entering the polymerisation reactor is calculated as follows:

$$F_{30} = F_{27} + F_{28} + F_{29} = 11.15 + 0.05175 + 0.1663 = 11.37 \text{ tonnes batch}^{-1}$$

2300 L of PEGMA, 92 L of ammonium persulphate (APS) and 4.6 L of TEMED enter the polymerisation reactor (Chalermthai et al., 2020). Using the respective densities at standard conditions of  $1.05 \text{ g/cm}^3$  (Merck, 2022d),  $1.98 \text{ g/cm}^3$  (NCBI, 2022a) and  $0.775 \text{ g/cm}^3$  (Merck, 2022c), the amount of PEGMA entering in stream 31 is  $2.484 \text{ tonnes batch}^{-1}$ , APS in stream 32 is  $0.1748 \text{ tonnes batch}^{-1}$ , and TEMED  $3.565 \times 10^{-3} \text{ tonnes batch}^{-1}$ . Full calculations for this can be found in Appendix C.

The conversion of free radical polymerisation in a batch reactor is taken from literature to be 90% ((Jašo et al., 2013), (Santanakrishnan et al., 2010), (Tefera et al., 1997)). Therefore, the amount of reacted PEGMA is calculated by taking the mass of the methacrylated protein and using the mass ratio of methacrylated protein:PEGMA of 30:70 along with the 90% conversion:

$$0.7691 \times \frac{0.7}{0.3} \times 0.9 = 1.615 \text{ tonnes of PEGMA reacted}$$

The masses of unreacted PEGMA and methacrylated protein are found with a mass balance on the unit. The total mass of polymer is taken to be the sum of the mass of reacted PEGMA and methacrylated protein mass, 2.307 tonnes. However, other impurities such as methacrylic acid, unreacted reagents, and water may also make up some of the polymer mass. These calculations will be refined in individual detailed design of the reactors.

The mass of polymerised content leaving the reactor is then found:

$$F_{34} = F_{30} + F_{31} + F_{32} + F_{33} = 11.37 + 2.415 + 0.1748 + 0.003565 = 13.96 \text{ tonnes batch}^{-1}$$

Compositions of the streams are all listed in the stream table (Table 5) with full calculations given in Appendix C.

### *Energy Balances*

The heat of reaction can be estimated using the bond energy data for the bonds made and bonds broken.

### **Methacrylation reaction**

For the methacrylation reaction, it is assumed that for every mole of methacrylic anhydride used up in the reaction, 1 mol of C-O & N-H bonds are broken and 1 mol of C-N and O-H bonds are formed. The bond energy data for these bonds are shown in Table 8 (Song and Le, 2019):

*Table 8: Bond energy data*

Enthalpy of Breaking Bonds (kJ/mol)		Enthalpy of Forming Bonds (kJ/mol)	
C-O	358	C-N	305
N-H	391	O-H	467



As calculated in the material balance for the methacrylation reaction, the number of moles of methacrylic anhydride that is used up in the reaction ( $n_{MethAN}$ ) is 254.8 mol.

Therefore, the enthalpy of reaction for the methacrylation reaction can be calculated using Equation 12:

$$\Delta H_{rxn} = \Sigma (n_{MethAN} \Delta H_{bonds\ broken}) - \Sigma (n_{MethAN} \cdot \Delta H_{bonds\ formed}) \quad (12)$$

$$\Delta H_{rxn} = 254.84 \times (358 + 391 - 293 - 463) = -5654 \text{ kJ}$$

The enthalpy change in the reaction is negative, hence the reaction is exothermic.

Using the general energy balance for a steady state system:

$$\Delta U + \Delta H + \Delta E_K + \Delta E_P = Q - W_s \quad (13)$$

Assumptions:

- The change in internal energy  $\Delta U$  is equal to zero.
- Changes in kinetic ( $\Delta E_K$ ) and potential ( $\Delta E_P$ ) energies are negligible compared to enthalpy of reaction.
- The shaft work done by the agitator ( $W_s$ ) is negligible.

From these assumptions, Equation 13 simplified to  $Q = \Delta H$ . Hence,  $Q = -5654 \text{ kJ}$ .

This indicates that 5654 KJ of energy will be released during each batch of methacrylation. To maintain a constant temperature of 25 °C within the reactor, a cooling jacket should be added to the reactor. The cooling jacket will remove the 5654 KJ produced by the reaction from the reactor. As the batch time of the methacrylation reaction is 7 hours, the required cooling capacity of the cooling jacket is:

$$\left( \frac{5654 \text{ KJ}}{7 \times 60 \times 60} = 0.224 \text{ kJ s}^{-1} \right) = 0.224 \text{ kW}$$

Considering that the cooling duty required for the methacrylation reactor is minimal compared to the other heat exchanges in this process, the streams are not included in the stream tables (Table 5) and the material balances, but simply show the utility requirements for the reactor. The calculations of cooling requirements will be refined in individual design and more detailed modelling of the cooling requirements over the batch time will be carried out.

### Polymerisation reaction

For the polymerisation reaction, it is assumed that for every mole of PEGMA reacted, 2 mol of C=C bonds are broken and 1mol of C-C bonds are formed. The bond enthalpies are shown in Table 9:

Table 9: Bond enthalpies

Enthalpy of Breaking Bonds (kJ/mol)	Enthalpy of Forming Bonds (kJ/mol)
C=C	614
C-C	347

As calculated in the material balance for the polymerisation reaction, the number of moles of PEGMA used up in the reaction ( $n_{PEGMA}$ ) is 3230.364 mol.

Therefore, the enthalpy of reaction for the polymerisation reaction can be calculated using Equation 14:

$$\Delta H_{rxn} = \Sigma (n_{PEGMA} \Delta H_{bonds\ broken}) - \Sigma (n_{PEGMA} \cdot \Delta H_{bonds\ formed}) \quad (14)$$

$$\Delta H_{rxn} = 3230.364 \times (2(614) - 347) = 2846000 \text{ kJ}$$

The enthalpy change in the reaction is positive, therefore, the reaction is endothermic.

Using the general energy balance equation as given in equation 13 and with the same assumptions as in the methacrylation reaction,  $Q = \Delta H \therefore Q = 2846000 \text{ kJ}$

Therefore, 2845951 kJ of energy will be absorbed by the reaction during each batch of the polymerisation reaction. To maintain a constant temperature of 25 °C within the reactor, a heating jacket should be added to the reactor. The heating jacket will provide the 2845951 kJ of energy required to keep the temperature constant. As the batch time of the polymerisation reaction is 1 hour, the required heating capacity of the heating jacket is calculated as:

$$\frac{2846000 \text{ kJ}}{1 \times 60 \times 60} = 790.8 \text{ kW}$$

Considering that the heating duty required for the polymerisation reactor is lower compared to the other heat exchanges in this process, the streams are not included in the stream tables (Table 5) and the material balances but simply show the utility requirements for the reactor. The calculations of heating requirements will be refined in individual design and more detailed modelling of the heating requirements over the batch time will be carried out.

#### D. Plastic Making

The plastic making section of the process comprises washing of the polymer to remove impurities, centrifugation to remove water, and drum drying to achieve the target bioplastic composition.

Assumptions:

- Ambient temperature and pressure (298.15 K and 1 atm) apply in the washing unit and centrifugation.
- The plastic product is similar to PHB in terms of water requirement for washing.
- Washing removes 80% of impurities, assuming the washing process is comparable to PHA extraction.
- Sedimentation efficiency of 30% in the centrifuge

#### Mass Balances

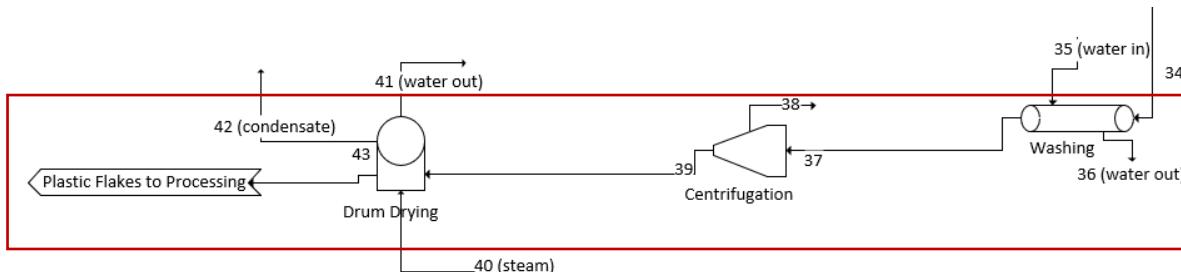


Figure 13: System boundary for plastic processing

#### Plastic washing

In the washer unit, unreacted monomer and other substances are removed, to achieve the desired purity of plastic. Water enters the unit and leaves with the majority of impurities from the polymerised content. The polymerised content stream is the outlet from the polymerisation reactor,  $F_{34} = 13.96$  tonnes batch $^{-1}$ . From the washer stream, the composition of the impurities is not known, as some components may be washed out in greater proportions.

The amount of water required in the washer is calculated from a ratio of polymerised content to water to produce PHB from date seeds; this is 1:1.635 by mass (Yousuf, 2017). Therefore, it is assumed that the cleaning of PHB is similar to the cleaning of our bioplastic. Hence:

$$F_{35} = 13.96 \times 1.635 = 22.82 \text{ tonnes batch}^{-1}$$

To calculate waste from washing, stream 36, the fraction of impurities is added to the water for washing. The polymerised content includes 11.3% impurities, consisting of proteins, fats, carbohydrates, minerals, sodium hydroxide, methacrylic anhydride, methacrylated protein, methacrylic acid, PEGMA, APS, and TEMED. This is taken from the mole fractions in the mass balances performed (Table 5). It



is assumed that 80% of impurities can be removed by washing, based off a similar recovery yield for PHA extraction (Lorini et al., 2021).

Total mass of impurities in stream 34:

$$13.96 \times 0.113 \times 0.8 = 1.262 \text{ tonnes batch}^{-1}$$

Therefore, the waste from washing can be calculated:

$$F_{36} = 22.82 + 1.262 = 24.08 \text{ tonnes batch}^{-1}$$

The cleaned polymer stream, F<sub>37</sub>, can then be found from the impurities removed:

$$F_{37} = 13.96 - 1.262 = 12.70 \text{ tonnes batch}^{-1}$$

Knowing that 20% of the original impurities remain in F<sub>37</sub>, and assuming the water content in the outlet is the same as in the inlet, F<sub>37</sub> has a mass fraction of 0.1812 of polymer. Full calculations for calculations of streams 36 and 37 can be found in Appendix D, and compositions of these streams are given in Table 5.

### Centrifugation

The sedimentation efficiency of the centrifuge is 30% (Chalermthai et al., 2020). Thus, the mass of the centrifuged polymer stream and the centrifuged waste can be determined (the centrifuged waste is predominantly water):

Centrifuged polymer stream:

$$F_{39} = 0.3 \times 12.7 = 3.81 \text{ tonnes batch}^{-1}$$

Centrifuge waste:

$$F_{38} = 0.7 \times 12.7 = 8.89 \text{ tonnes batch}^{-1}$$

The centrifuge reduces the water content of the polymer stream, to 40% (Chalermthai et al., 2020). Therefore, 1.524 tonnes of stream 39 is water, and 2.286 tonnes is the polymer and impurities. The calculations for streams 38 and 39 are given in Appendix D, and compositions are given in Table 5.

### Drum dryer

In the drum dryer, 85% of the water in the centrifuged content is evaporated (Chalermthai et al., 2020). Therefore:

Amount of water removed in drum dryer:

$$F_{41} = F_{39,water} \times 0.85 = 1.524 \times 0.85 = 1.295 \text{ tonnes batch}^{-1}$$

Amount of water in final product:

$$F_{43,water} = F_{39,water} - 1.295 = 1.524 - 1.295 = 0.2286$$

From this water removal, the total product per batch can be found:

$$F_{43} = F_{43,water} + F_{39,polymer \text{ and } impurities} = 0.2286 + 2.286 = 2.515 \text{ tonnes batch}^{-1}$$

The product has a moisture content of 9%, and a solids content (polymer and impurity) of 91%.

### [Energy Balances](#)

#### Drum dryer

Assumptions:

- Isobaric operation at atmospheric pressure
- The plastic product is similar to PHB in terms of specific heat.
- The drum dryer is treated as a counter flow heat exchanger.



- Overall heat transfer coefficient is assumed to lie within the range for steam heating a very viscous fluid. As the plastic is mostly solid, it is treated as a slurry.

Equation 1,  $Q = m c_p \Delta T$ , is to be used, assuming negligible changes of enthalpy due to a constant pressure. Assuming the plastic will have similar specific heat to PHB:

$$c_p = 1.21 + 0.0035T \quad (\text{Righetti et al., 2019})$$

The plastic is heated from 25°C to 72°C (Chalermthai et al., 2020), by steam at 150°C (Bonazzi et al., 1996). Using this temperature difference and the mass of the stream entering the drum dryer, F39, the heat required can be determined:

$$\begin{aligned} Q &= (3810\text{kg})(72 - 25)K \int_{25}^{72} 1.21 + 0.0035T \, dT \\ Q &= (3810\text{kg})(72 - 25)K(64.85 \text{ kJ kg}^{-1} \text{ K}^{-1}) \\ Q &= 1.161 \times 10^7 \text{ kJ} \end{aligned}$$

For a 6-hour drying time:

$$\dot{Q} = \frac{Q}{360 \times 60 \text{ s}} = \frac{1.161 \times 10^7 \text{ [kJ]}}{360 \times 60 \text{ [s]}} = 537.6 \text{ kW}$$

Steam consumption is determined from equation 15:

$$\dot{m} = \frac{\dot{Q}}{h_{fg}} \quad (15)$$

Through extrapolating from steam tables (Beaton et al., 1989) the steam pressure is calculated as 4.765 bar. It is assumed the condensate pressure is at atmospheric conditions. The specific enthalpy of the steam is 2745 kJ kg<sup>-1</sup> (Beaton et al., 1989).

Therefore:

$$\dot{m} = \frac{537.6 \text{ [kW]}}{2745 \text{ [kJ kg}^{-1}\text{]}} = 0.1958 \text{ kg s}^{-1}$$

Hence, the mass of steam per batch can be determined:

$$F_{40} = 0.1958 \text{ kg s}^{-1} \times 360 \times 60 \text{ s} = 4230 \text{ kg batch}^{-1}$$

This will be equal to the mass of condensate out, F<sub>42</sub>.

Using equation 2, the log-mean temperature difference can be determined, assuming a counter current heat exchanger. Assuming  $U = 600 \text{ W m}^{-2} \text{ K}^{-1}$  applies, for steam heating a very viscous fluid (Sinnott Ray K., 2009) and the area of the drum dryer of 12 m<sup>2</sup> (Chalermthai et al., 2020) the condensate temperature can be calculated:

$$\begin{aligned} \Delta T_{lm} &= \frac{537.6 \text{ kW}}{(0.6 \text{ kW m}^{-2} \text{ K}^{-1})(12 \text{ m}^2)} = 74.67^\circ\text{C} \\ \Delta T_{lm} &= 74.67^\circ\text{C} = \frac{(150^\circ\text{C} - 72^\circ\text{C}) - (T_{h,o} - 25^\circ\text{C})}{\ln \frac{(150^\circ\text{C} - 72^\circ\text{C})}{(T_{h,o} - 25^\circ\text{C})}} \end{aligned}$$

Using goal seek,  $T_{h,o} = 96.43^\circ\text{C}$ .



## Key Unit Specification Sheets

The operating temperatures and pressures, flows and energy requirements for the individual units are taken from material and energy balance calculations. Dimensions and material selection for each of these units is to be discussed below.

### Material Selection

The chosen process of producing bioplastic from liquid waste whey is for food packaging applications, thus the materials which are used within the process must be suitable for contact with food. Special attention must be placed to using the material at the recommended temperature range, selecting the appropriate material for the type of food processing, and the material's durability in maintenance and cleaning processes (Krysiak, 2022). As the final plastic product will come into contact with food products in packaging applications, care must be taken to ensure that there is no contamination of the product by the materials of the units in the process (EFSA, 2022). The materials of the equipment used for this process are defined as food contact materials (FCM), thus the FCM should be sufficiently inert so that their properties do not adversely affect consumer health or food quality. This is achieved through the European Food Safety Authority's evaluation of the product safety, testing, and legislation (EFSA, 2022). Currently, the UK has retained EU law in order to regulate FCM (EFSA, 2022)

The most used materials in food processing equipment are variations of stainless steel, as stainless steels provide strong resistance to corrosion associated with the food industry (Dewangan et al., 2015). Although in the food and dairy industry limitations of stainless steels include attack by lactic and malic acids at elevated temperatures, the process streams at a high temperature are only within the pasteurisation process, thus the likelihood of acid attack is much lower within our process (Dewangan et al., 2015). Most stainless steels used in the food industry are those with a quantity of chromium between 9 and 30 percent, with the other components such as molybdenum, nickel and nitrogen contributing to corrosion resistance prevention. Austenitic stainless steel such as AISI 304 are mainly used as they provide the desired mechanical properties with high corrosion resistance, weldability and shaping properties (Dewangan et al., 2015). Additionally, in food grade applications AISI 304 steel is preferred for its cleanability and lack of effect on the flavour and colour effects on the fluids interacting. Ideally, AISI 316 steel would be used in high acidic fluid foods, as the 2-3% molybdenum provides a higher resistance to corrosion. However, this is less utilised in industry due to its high cost. Still, the AISI 304 steel proves to be just as effective in food and dairy applications as AISI 316, especially when dealing with only mildly corrosive media. Austenitic stainless steel is preferred for food and dairy applications due to the properties mentioned above with applications in literature including: pasteurisation, separators, heat exchangers and process tanks in addition to other valves and fittings ((Dewangan et al., 2015), (Santonja et al., 2019)).

As austenitic stainless steel is the most used in the food industry, and because of the regulations and laws mandating the careful consideration of materials in food industry, the chosen material for all process units, except for when stated otherwise, is AISI 304 Stainless steel. This has sufficient resistance to corrosion, and is also inert and resistant to corrosion. By using this material, both food standards are followed and processes such as maintenance and cleaning are simplified while increasing the lifetime of the equipment compared to lower steel grades(Slipnot, 2012)



## Pasteurisation

Specification Sheet			Document Number:					
			Revision:	Status:				
Operation	Sterilisation of liquid whey		Date: 10/03/2022					
Unit	Pasteuriser and Heat Exchanger 1							
Service	Pre-treatment of liquid whey							
Process Data								
Liquid Flow Rate			Power Requirement					
Inlet	100	tonnes batch <sup>-1</sup>	Pasteuriser	16720 kW				
Outlet	100	tonnes batch <sup>-1</sup>	Heat exchanger 1	16760 kW				
Flow Type	Counter-Flow							
Operating Conditions								
Pressure	1.013	bar						
Temperature	61	°C						
Temperature Out	25	°C						
Batch Time	0.5	hours						
Utility Conditions								
Steam	81.3	°C						
	0.49	bar						
	21	°C						
Cooling Water	1.013	bar						
Mechanical Design								
Equipment Type	Two heat exchangers in series							
Heat Exchanger Type	Gasketed Plate Heat Exchanger							
Plate Material	Stainless Steel 304							
Dimension								
Pasteuriser								
Maximum Heat Transfer Area	500 m <sup>2</sup>							
Plate Dimensions	H 2.231	W 0.950		m				
Number of Plates	236			-				
Frame Type	NP			-				
Dimension of Unit	H 2.741	W 0.950	D 1.200	m				
Heat Exchanger 1								
Maximum Heat Transfer Area	1600 m <sup>2</sup>							
Plate Dimensions	H 3.140	W 1.370		m				
Number of Plates	372			-				
Frame Type	NP			-				
Dimension of Unit	H 3.620	W 1.370	D 1.650	m				

(HISAKA, 2022)

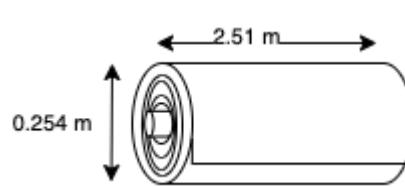
The pasteuriser unit is a simplified design that integrates only two plate heat exchangers inspired by designs produced by HISAKA. The plate pasteuriser is designed to have a minimum residence time of 15 seconds as the liquid whey is heated to 61°C to meet FDA standards; this negates the requirement for a holding tub and corresponding pumps. The pasteuriser will use plates based on the RX-50 design whereas the cooler will use plates based on the larger RX-90 design. This is to achieve the required heat transfer area of 500 m<sup>2</sup> and 1600 m<sup>2</sup> respectively, whilst maintaining a relatively small footprint.



The heat exchangers are gasketed plate types. The gaskets will be polyfluoroethylene (PTFE) cushion gaskets that have been pioneered to withstand corrosion which is a possibility due to the waste liquid whey pH level. The plates are held by a NP type frame which also gives the heat exchangers more room for future expansion. This design will provide easy access for cleaning and maintenance too. (HISAKA, 2022)

## Ultrafiltration

Specification Sheet			Document Number:	
			Revision:	Status:
Operation	Protein concentration		Date: 10/03/2022	
Unit	Ultrafiltration			
Service	Production of whey powder from pre-treated liquid whey			
Process Data				
Liquid Flow Rate			Power Requirement	
Inlet	70	tonnes batch <sup>-1</sup>	Pump	40980 kJ batch <sup>-1</sup>
Retentate	3.5	tonnes batch <sup>-1</sup>		
Permeate	66.5	tonnes batch <sup>-1</sup>		
Operating Conditions				
Feed pressure	5.01	bar		
Retentate pressure	1.01	bar		
Permeate pressure	1.01	bar		
Temperature	25	°C		
Mechanical Design				
Equipment Type	Spiral-wound membrane			
Central tube material	Stainless steel 304			
Membrane material	Polysulfone (PSO)			
Dimension				
Membrane area	76	m <sup>2</sup>		
Length of element*	2.36	m		
Outer diameter of element*	0.262	m		
Number of units	6	-		



The type of UF membrane chosen is a spiral-wound membrane, as UF membranes used in the dairy industry are typically of this format. These modules are composed of flat membrane sheets coiled around a central tube to carry out the permeated fluid, which is key to their low unit cost and success in the dairy industry (Duke and Vasiljevic, 2015).

Most of the stainless steel used in food equipment is of the austenitic AISI 300 series, and approximately 50% of all stainless steel produced is 304 stainless steel (Schmidt et al., 2012). Therefore, this is chosen as the central tube material.

For the membrane material, polysulfone (PSO) was selected, as it has been used in several applications for UF and MF and is practically the only membrane material used in high quantities in the dairy industry (Wagner, 2001).

Standard industrial dimensions for the module diameter go up to 10.3" (Synder, 2022). The packing density of a spiral wound membrane is between 300-1000 m<sup>2</sup>/m<sup>3</sup> (Lee, 2020). Assuming the membrane has a packing density of 600 m<sup>2</sup>/m<sup>3</sup>, and considering this membrane has an area of 76 m<sup>2</sup>, the total module volume required is determined as 0.127 m<sup>3</sup>. As this process is relatively large scale, assuming the module has a diameter of 10.3" (0.262 m), and assuming that the module is cylindrical, the length of the element required is 2.36 m (92.9"). These dimensions are to be further considered, alongside more detailed dimensions in further stages of design.

## Diafiltration

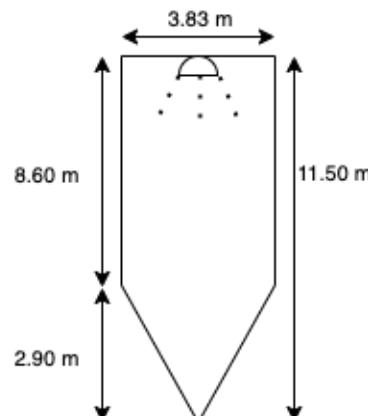
Specification Sheet			Document Number:			
			Revision:	Status:		
Operation	Product concentration		Date: 10/03/2022			
Unit	Diafiltration					
Service	Production of whey powder from ultra-filtrated liquid whey					
Process Data						
Liquid Flow Rate			Power Requirement			
Inlet	3.5	tonnes batch <sup>-1</sup>	Pump	24350 kJ batch <sup>-1</sup>		
Buffer	45.06	tonnes batch <sup>-1</sup>				
Permeate	46.13	tonnes batch <sup>-1</sup>				
Retentate	2.43	tonnes batch <sup>-1</sup>				
Operating Conditions						
Feed pressure	5.01	bar				
Retentate pressure	1.01	bar				
Permeate pressure	1.01	bar				
Temperature	25	°C				
Batch Time	4	Hours				
Mechanical Design						
Equipment type	Spiral wound ultrafiltration membrane					
Membrane material	Polysulfone (PSO)					
Central tube material	Stainless steel					
Dimension						
Membrane area	30.1		m <sup>2</sup>			
Outer diameter*	0.097		m			
Length of element*	1.70		m			

The diafiltration unit was designed similarly to the ultrafiltration unit, the difference occurring with the buffer and recycle stream and the number of membranes required. Only one unit is required due to the lower liquid whey input which is more concentrated than the input into the UF membrane.

Assuming the membrane also has a packing density of 600 m<sup>2</sup>/m<sup>3</sup>, and considering this membrane has an area of 30.1 m<sup>2</sup>, the total module volume required is determined as 0.05 m<sup>3</sup>. As this unit is relatively small scale, it was assumed the module has a diameter of 3.8" or 0.097 m (Synder, 2022). Assuming that the module is cylindrical, the length of the element required is therefore 1.70 m (66.8"). These dimensions are to be further considered in detailed design.

## Spray dryer

Specification Sheet			Document Number:			
			Revision:	Status:		
Operation	Water removal from whey powder		Date:	10/03/2022		
Unit	Spray Dryer					
Service	Production of dehydrated whey powder					
<b>Process Data</b>						
<i>Liquid Flow Rate</i>			<i>Power Requirement</i>			
Inlet	2.43	tonnes batch <sup>-1</sup>	Pump P3	19340 kJ batch <sup>-1</sup>		
Outlet	1.05	tonnes batch <sup>-1</sup>	HX2	5060000 kJ batch <sup>-1</sup>		
<i>Air Flow Rate</i>						
Inlet	24.3	tonnes batch <sup>-1</sup>				
Outlet	25.7	tonnes batch <sup>-1</sup>				
<i>Operating Conditions</i>						
Inlet liquid pressure	50	bar				
Inlet Liquid temperature	25	°C				
Inlet Air Temperature	150	°C				
Outlet Liquid and Air Temperature	70	°C				
<b>Mechanical Design</b>						
Equipment Type	Pressure nozzle Spray Dryer					
Material	Stainless Steel 304					
<b>Dimension</b>						
Equipment Volume	110	m <sup>3</sup>				
Diameter	3.83	m				
Height	11.5	m				



Spray drying takes place in 3 stages: dispersion of the concentrate into very fine droplets, mixing of the finely dispersed concentrate into a stream of hot air which quickly evaporates the water, and separation of the dry milk particles from the drying air. A pressure nozzle atomiser is to be chosen, as it is robust, reliable, well-established and easy to use, justifying their common use within the dairy sector (O'Sullivan et al., 2019). Depending on the facility, the inlet pressure of the liquid can vary from 5 to 30 MPa (Park and Haenlein, 2013). 5 MPa is chosen as the pressure, as lower pressure is desired to decrease energy consumption. This will be reviewed in further stages of the design. Air is to enter co-currently to the product, which is suitable for this process as the air at the higher temperature contacts the particles with the highest humidity, hence protecting the particles from overheating.

From the mass balances for the spray dryer, assuming a molecular weight of wet air out of 28.2 (Harrison et al., 2015), and assuming the ideal gas law applies, the density of the wet air out is around 1 kg/m<sup>3</sup>. This gives a total air flow out of 45122 m<sup>3</sup> batch<sup>-1</sup>. It is assumed that the spray dryer runs for 4 hours at a time (which is reasonable as this would mean processing around 0.6 tonnes in an hour, and spray dryers in industry can process between a few pounds per hour to hundreds of tonnes per hour) (BETE, 2005). Assuming that the particle sizes from the pressure nozzle are around 100 µm (Harrison et al., 2015) the residence time is between 20-35 seconds (Harrison et al., 2015). For conservative time, 35 seconds is to be chosen. Using these values, the volume of the spray dryer chamber required is 110 m<sup>3</sup>. Full calculations for this are given in Appendix E.



The height to diameter ratio for the spray dryer is taken as 3:1 (Chalermthai et al., 2019). Spray dryers are commonly cylindrical with an inverted cone on the base (Santos et al., 2017). Using dimensions from literature of a spray dryer with a similar height to diameter ratio, the height of the cylindrical section is  $\frac{3}{4}$  of the total height, and the height of the cone section is  $\frac{1}{4}$  of the total height (Anandharamakrishnan et al., 2010). With this information, the diameter of the spray dryer is determined as 3.83 m, the total height 11.5 m, the cone height is 2.9 m and 8.6 m for the cylindrical height. Full calculations are given in Appendix E.

### Methacrylation Reactor

Specification Sheet			Document Number:	
			Revision:	Status:
Operation			Date: 10/03/2022	
Unit			Methacrylation	
Service			Addition of methacrylate functional group onto proteins	
Process Data				
Batch Inlet & Outlet			Power Requirement	
Total Inlet	11.32	tonne batch <sup>-1</sup>	Cooling Jacket	0.224 kW
Total Outlet	11.32	tonne batch <sup>-1</sup>		
Operating Conditions				
Pressure	1	atm		
Temperature	25	°C		
Batch Time	7	Hours		
Mechanical Design				
Equipment Type	Stirred Batch Reactor			
Reactor Material	Stainless steel			
Dimension				
Reactor Volume	17.76		m <sup>3</sup>	
Diameter	2.54		m	
Height	4.26		m	
Mixing*				
Number of Baffles	4		-	
Baffle Width	0.2		m	
Agitator Speed	1750		rpm	
Agitator Type	6 Bladed Ruston Turbine			
Agitator Width	0.8		m	
Agitator Depth (from bottom of tank)	0.8		m	
Agitator Power	0.01-0.03**		kW/m <sup>3</sup>	



\* Dimensions taken from literature guidelines (Couper et al., 2012a)

\*\*taken from literature as the range from (Towler and Sinnott, 2013)

Stirred tank reactors are not designed to operate fully filled, with most reactors designed to operate at 60% to 70% full (Towler and Sinnott, 2013). Therefore, the volume of 1 batch going into the methacrylation reactor was found, and then divided by 0.6 to find the true volume for the 60% filled reactor. For the methacrylation, this gave a total volume of 17.76 m<sup>3</sup> for a cylindrical reactor. The diameter and height of this reactor was then determined using the cylindrical stirred tank optimal configuration of L/D of 1 (Couper et al., 2012b). Full calculations for this can be found under Appendix F.

For the design of the stirrer and the decision to add baffles, the desired level of mixing was considered. A well-mixed vessel is crucial for the maximum extent of the methacrylation reaction to be achieved, therefore, the addition of a stirrer was necessary.

To determine the type of stirrer, the viscosity of the reactor contents was considered. The liquid viscosity is taken to be approximately 2.63 mPa s at 25 °C, which is the density of WPC solutions of 10 weight %, corresponding to the dilution in protein dissolution phase (González-Tello et al., 2009). From the agitator selection guide in Sinnott and Towler Chapter 15, the chosen agitator should be a turbine or propeller at 1750 rpm. This has a range of agitator power requirements of 0.01-0.03 kW/m<sup>3</sup> as determined for homogeneous reactions in Sinnott and Towler Chapter 15 rules of thumb (Towler and Sinnott, 2013). Thus, a 6 bladed Ruston turbine was selected with dimensions as recommended by Chemical Process Equipment, Third edition, with blades of width D/3 and depth of D/3 from the bottom of the tank.

Baffles should be added to aid mixing and prevent vortex forming. From literature, Baffle width should be 1/12 of the diameter of the vessel with four baffles in total at each quadrant of the cylinder. Thus, baffle width should be 0.2m. (Couper et al., 2012a)

Full calculations can be found in the Appendix F.

## Polymerisation reactor

Specification Sheet			Document Number:			
			Revision:	Status:		
Operation	Chemical Processing		Date: 10/03/2022			
Unit	Polymerisation					
Service	Polymerisation of methacrylated protein					
<b>Process Data</b>						
<i>Batch Inlet &amp; Outlet</i>			<i>Heating Jacket</i>			
Total Inlet	13.960	tonne batch <sup>-1</sup>	Heating Capacity	790.8 KW		
Total Outlet	13.960	tonne batch <sup>-1</sup>				
<i>Operating Conditions</i>						
Pressure	1	atm				
Temperature	25	°C				
Batch Time	1	hour				
<b>Mechanical Design</b>						
Equipment Type	Stirred Batch Reactor					
Reactor Material	Stainless steel					
<b>Dimension</b>						
Reactor Volume	25.574		m <sup>3</sup>			
Diameter	2.69		m			
Height	4.49		m			
<b>Mixing*</b>						
Number of Baffles	4		-			
Baffle Width	0.2		m			
Agitator Speed	1750		rpm			
Agitator Type	6 Bladed Ruston Turbine					
Agitator Width	0.9		m			
Agitator Depth (from bottom of tank)	0.9		m			
Agitator Power	0.01-0.03**		kW/m <sup>3</sup>			

\* Dimensions taken from literature guidelines (Couper et al., 2012a)

\*\*taken from literature as the range from (Towler and Sinnott, 2013)

Similarly to the methacrylation reactor, according to literature, stirred tank reactors are not designed to operate fully filled, with most reactors designed to operate at 60% to 70% full (Towler and Sinnott, 2013). Therefore, the polymerisation reactor had a volume of 25.574 m<sup>3</sup> for a cylindrical reactor. This



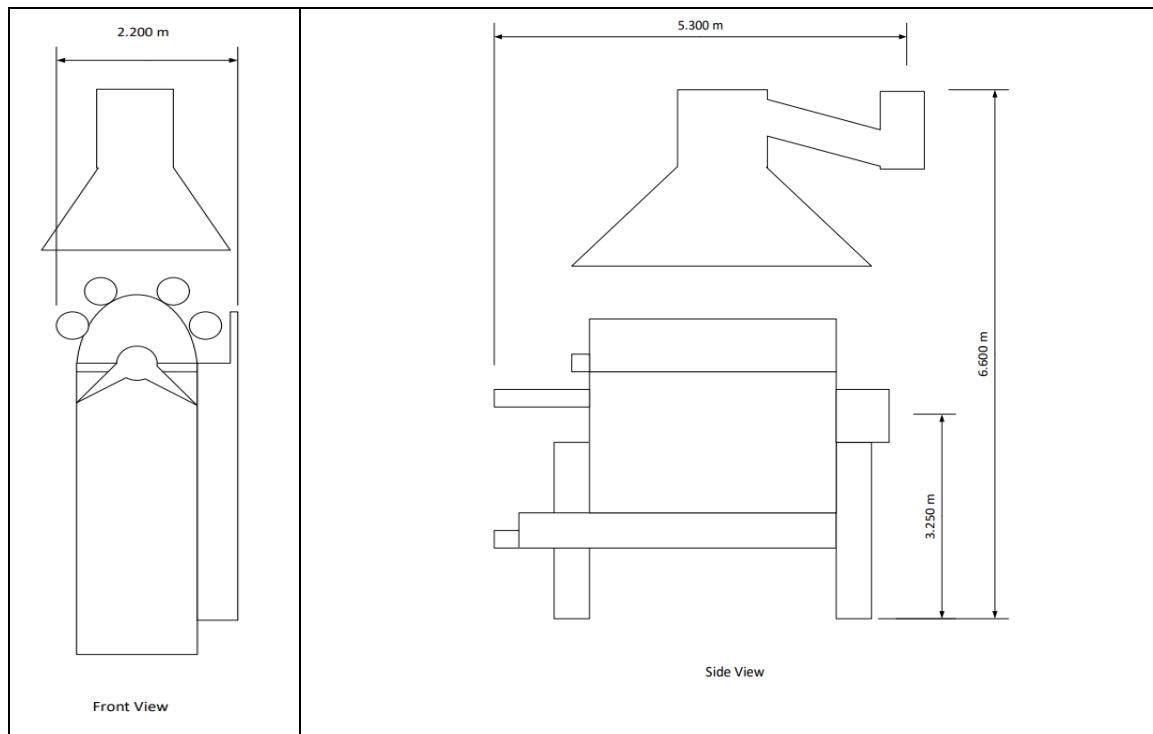
was also to have an optimal L/D value of 1 (Couper et al., 2012b), hence the height and diameter of the reactor could then be determined. More detailed calculations can be found under Appendix G.

The liquid viscosity is assumed to be the same in the polymerisation as for the methacrylation reactor. As this determines the agitator type, the agitator for this polymerisation reactor is the same as for the methacrylation reactor. The number of baffles and the baffle width is also the same as in the methacrylation reactor.

Further calculations can be found in the Appendix G.

## Drum dryer

Specification Sheet			Document Number:						
			Revision:	Status:					
Operation	Plastic Making		Date: 10/03/2022						
Unit	Drum Dryer with Knife								
Service	Production of dried plastic flakes through evaporation								
<b>Process Data</b>									
<i>Bioplastic</i>			<i>Power Requirement</i>						
Inlet	3.81	tonnes batch <sup>-1</sup>	Drive	33	kW min				
Outlet	2.515	tonnes batch <sup>-1</sup>	Power	60	kW max				
<i>Steam/Condensate</i>									
Inlet	4.23	tonnes batch <sup>-1</sup>							
Outlet	4.23	tonnes batch <sup>-1</sup>							
<i>Operating Conditions</i>									
Pressure	1	atm							
Bioplastic In	25	°C							
Bioplastic Out	72	°C							
Steam In	150	°C							
Water Out	96.43	°C							
Batch time	6	hours							
<b>Mechanical Design</b>									
Equipment Type	Single Drum Dryer Heat Exchanger								
Material	Type 304 Stainless Steel								
<b>Dimension</b>									
Equipment Volume	76.96		m <sup>3</sup>						
Drum Diameter	1250		mm						
Drum Length	3000		mm						
Drying Surface Area	12		m <sup>2</sup>						
Number of Applicator Rolls	4		-						
Applicator Roll Diameter	240		mm						
Unit Length	5300		mm						
Unit Width	2200		mm						
Unit Height	6600		mm						
Drum Heart Line	3250		mm						
Total Weight	32		tonnes						



Dimensions are based on two different drum dryer models: Andritz Gouda drum dryers model E 10/30 and 15/30 (ANDRITZSeparation, 2014). The 10/30 model has area  $9.4 \text{ m}^2$ , whereas the 15/30 model has area  $14.1 \text{ m}^2$ . The required drum dryer area is  $12 \text{ m}^2$ , which is roughly between the models. Thus, dimensions are taken as approximately between those of the models. The designed dryer has a diameter of 1250 mm, the average between both models, and a drum length of 3000 mm, which is the same for both models. For the rolls design, both models have 4 rolls and the diameter is taken as 240 mm, which is the average between the models. A similar approach is taken to determine unit length, width, and height, as well as other dimensions such as weight. Design of the drum dryer is based on the Andritz Gouda models, and includes a vapour hood to remove evaporated water.



## Safety and Operability

Safety should be considered throughout the entirety of the design process to minimize hazardous consequences affecting the personnel of the process plant in addition to the surrounding areas.

This process involves utilising waste whey from cheese manufacturers in Somerset, which is a region in the UK with a large agricultural and livestock presence. Thus, the overall plant safety should also be considered to minimise proximity of livestock to hazardous process units. Danger to staff and personnel was considered throughout this process by choosing units and processes which minimised hazardous process conditions such as high temperature and pressure, for example by using catalyst and activator combination to make the reactions during chemical processing occur at atmospheric temperature and pressure. Additionally, the only units occurring at high temperatures and pressures are the pasteurization, spray drying, and drum drying units in the process which all operate at temperatures below 200°C and pressures of 50 bar which are both attributed to utility streams. Reaction vessels are also sized at 60% filled according to industry recommendations to allow for overfilling. Other hazards such as reagent toxicity and flammability are also considered and safeguards devised to mitigate the related consequences especially within the plant layout, making sure that reagents are placed down-wind of ignition sources. Hazards such as those related to batch operations due to heavy lifting are addressed with a special emphasis placed on staff training and ethical working conditions. Other hazards such as the knives present in the drum dryer are mitigated with a suitable start-up and shut down strategy, discussed later in the process. With these considerations the process is largely an inherently safe process with further hazards mitigated through control and alarm systems.

The evaluation in this project of safety is structured through a preliminary PFD (Figure 4) which is assessed with the aid of a HAZID exercise. The HAZID is carried out in reference to various process nodes as highlighted in the PFD (Figure 4). The HAZID then informs the choice of a relevant hazardous node of the process for further evaluation. This is then analysed in a HAZOP workshop with the design team and safeguards are added to mitigate any hazards and operability considerations.



## Hazard Identification

*Table 10: Hazard Identification (HAZID) for the process*

Guideword	Hazard	Consequence	Safeguards	Comments
Natural Disasters (All)	Earthquakes  Severe weather  Floods	Equipment/infrastructure damage/failure  Economic loss due to production loss and repair costs  Utility failure	Reinforcements on units and a geographical survey on location before construction  Emergency shutdown plan for each scenario.	Staff training on the Emergency Action Plan and regular emergency drills.  Evacuation protocols in place.  Regular inspections of structural integrity
Location (All)	Loud mechanical noises  Emissions  Wildlife	Noise pollution  Air pollution  Injury of cattle	Ensure location is chosen far from housing or cattle fields.  Minimise emissions  Fence off plant to local surroundings	Discuss the plant layout with local residents/businesses and ensure their opinion is taken into consideration in the design phase
Plant layout (All)	Confined spaces  Proximity hazards (eg electrical source near water)	Emergency escape routes may be restricted  Ignition, explosion	Designated routes that everyone on-site is aware of  Strategic design: ensure consideration is taken to allow reasonable space between equipment	Hazards discussed taken into consideration in plant layout design
Toxic chemicals	PEGMA – Irritant (C)  Ammonium persulphate – oxidiser, irritant (C)	Chemical rashes and irritation when in contact with skin and inner membranes  Mild allergic reactions	Personnel PPE.  Alarms to notify when spills have occurred	Staff training on reagent risks and safety protocols.  First aid training and on site first aid supplies.



	Sodium hydroxide – caustic and corrosive (C)	Corrosion of equipment	Clear signs describing hazards	Acquire suitable materials for transport/storage
Mechanical equipment	Sharp blade in drum dryer (D)  High pressures of UF membrane and DF membrane (B)	Personnel injury from serious cuts  Impact injuries to personnel Membrane degradation and fouling	Hazard zones with clear signage  Cut-resistant gloves for personnel  Ensure isolation of equipment during maintenance, pressure alarms	Regular maintenance and checks to equipment
Utility Streams	High temperature steam inlet for drum dryer and pasteurisation unit (A, D)	Burns to personnel	Hazard zones with clear signage  Protective gloves when handling steam pipelines and provide insulation, temperature alarms	First aid training and supplies on site
Sources of ignition	Electrical equipment (All)  Pumps (All) and heat exchangers (All)  Onsite smoking (All)  Mechanical sparks (All)	Fire damage  Injury to personnel  Explosion  Equipment damage	Regular electrical safety testing  No smoking signs  Fire safety equipment  Fire doors  Ventilation	Regular maintenance  Site audits  Fire safety training and drills



Sources of flammables	PEGMA (C)	Fire	Keep away from ignition sources  Monitor valve and pipe condition and functionality	Location of storage containers
Release of inventory	Valve leaks (All) Tank leaks (All)	Personnel injury from slips  Hazardous reagent release  Loss of product yield	Storage in closed containers  Cleaning up spills immediately  System shutdown/unit isolation for repairs	Regular maintenance of equipment  Incident reporting procedure to prevent further leaks
Effluent disposal	Plastic washing (D) Separation units (A, B, D) Environmental impact (A, B, D) Transportation (Pre-A, Post-D)	Spillage  Damage to aquatic life and land contamination  Floods on site	Safe disposal strategy  Waste treatment partner  Safe transportation	Follow legal disposal protocols and regulations



Electrical Hazards	Pumps (All) Heat Exchanges (All?) Control systems (All)	Failure of pumps causing system delay  Incorrect heating affecting products  Alarm and control failure  Fires as above in ignition sources	PAT testing  Away from water  Insulated cables  Covered switches	Regular maintenance and inspection of electrical equipment  Safety protocols and training
Heavy Objects	Product removal and solids handling (B->C, D)  Maintenance and equipment removal and replacement (All)	Human injury  Equipment damage  Loss of yield	Safe handling procedures  Only trained professionals  Clear surrounding area  First aid  Use of appropriate equipment	No comments

Key:

- A: Pre-treatment of waste liquid whey, which includes the pasteurisation and centrifugation (1) units
- B: Production of whey protein powder from whey, which includes ultrafiltration, diafiltration, spray drying and storage units
- C: Chemical processing of the whey protein powder, which includes protein dissolution, methacrylation and polymerisation
- D: Plastic making, which includes washing, centrifugation (2) and drum drying

The HAZID indicates that stages C and D of the process are associated with the most hazards. However, many of the hazards in stage D are related to the drum dryer, which is a more mechanical process unit, and so chemical engineering expertise will be fairly limited to perform a HAZOP on this unit. Therefore, a HAZOP is to be carried out on the polymerisation reactor unit in stage C of the process, as this unit is associated with the most input chemicals, such as PEGMA, ammonium persulfate and TEMED and so the risks associated need to be evaluated.

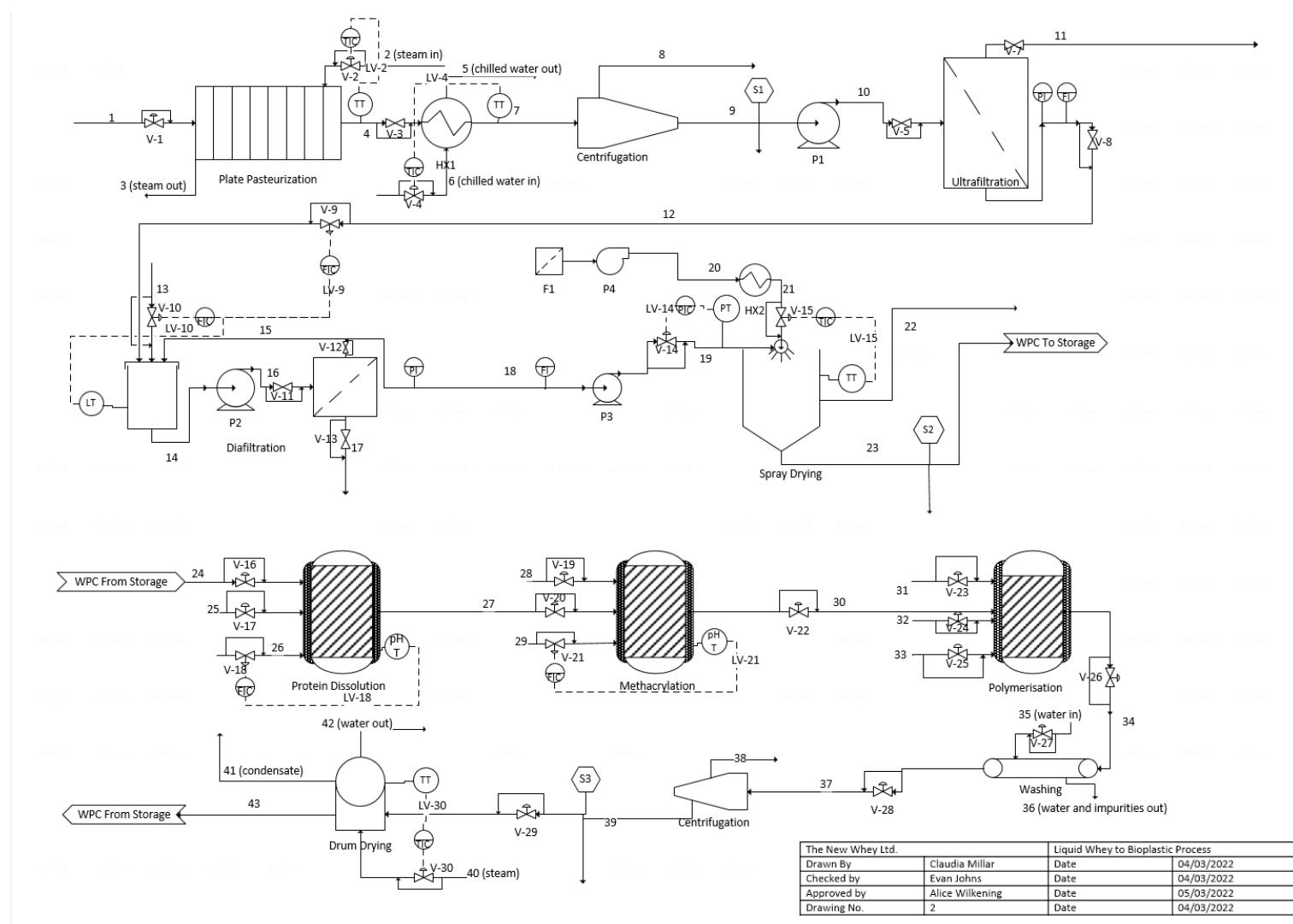
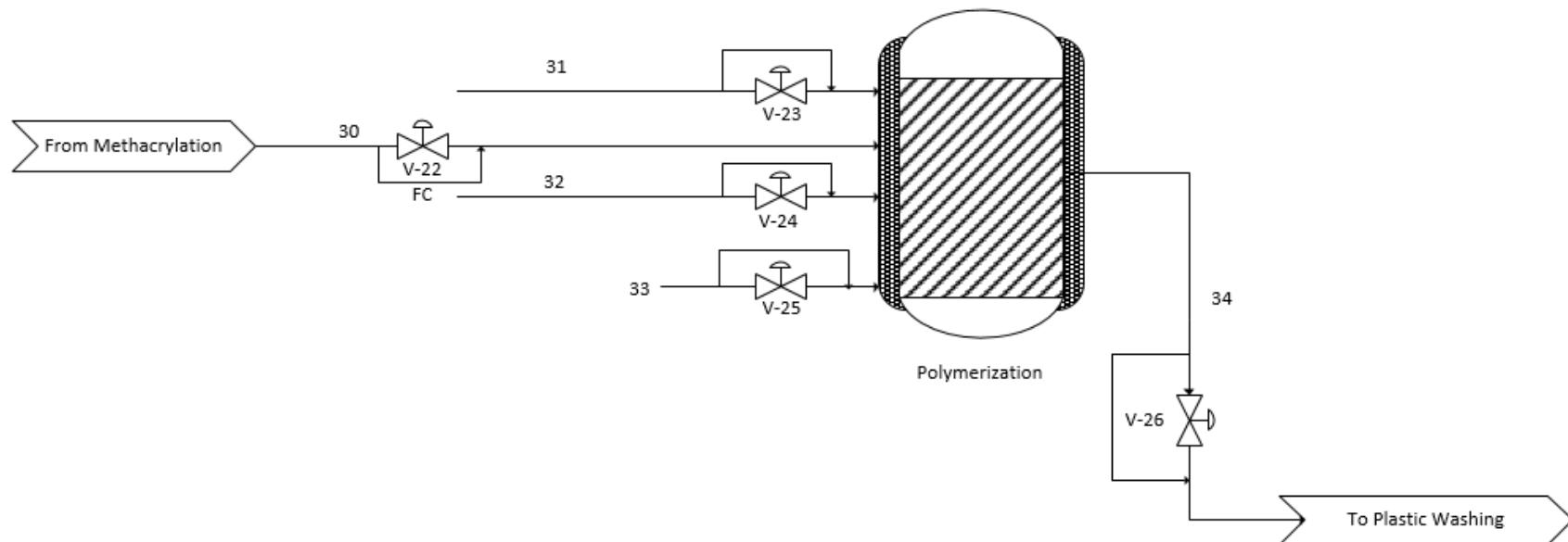


Figure 14: P&ID

## Unit Specific P&ID



The New Whey Ltd.		Liquid Whey to Bioplastic Process	
Drawn By	Claudia Millar	Date	10/03/2022
Checked by	Emily Woodhall	Date	10/03/2022
Approved by	Alex Raneri	Date	10/03/2022
Drawing No.	3	Date	10/03/2022

Figure 15: Individual unit P&ID



## HAZOP

Table 11: HAZOP for the polymerisation reactor

Case No.	Parameter	Guideword	Deviation	Cause	Consequence	Action /Safeguard	Severity	Likelihood	Risk
1	Temperature	More	Temperature of stream 30 too high	Exothermic methacrylation reaction upstream	Denatured protein which reduces product quality	Temperature transmitter Temperature indicator control Temperature high alarm  All connected to stream 30. Fail close if temperature too high  Heat exchange jacket on reactor with temperature transmitter, temperature indicator control, flow indicating control	3	2	6
2		Less	Temperature of polymerisation reactor too low (temperature of stream 34 too low)	Endothermic polymerisation reaction	Slower rate of polymerisation reaction leading to lower conversion of bioplastic  More heating required in downstream utilities to reach final product	Temperature controls connected to heat exchange jacket utility to correct if temperature lower than set point with temperature indicator, temperature	3	2	6



						indicator control, flow indicating control				
3	Flow	No	No flow in stream 30	Failure of valve 22  Piping blockage upstream  Operator failure due to exhaustion between batches	No reaction leading to lower production rate  Process delay	Bypass on valve  Regular maintenance of pipes and valves  Operational checks and inspections  Rotating shifts for operators	3	2	6	
4		No	No flow in stream 31	Same as Case No.3 except valve 23	No reaction due to lack of co-polymer leading to lower production rate  Process delay	Same as Case No 3	3	2	6	
5		No	No flow in stream 32	Same as Case No.3 except valve 24	No reaction due to lack of initiator leading to lower production rate  Process delay	Same as Case No 3	3	2	6	
6		No	No flow in stream 33	Same as Case No.3 except valve 25	Slower rate of reaction leading to lower production rate	Same as Case No 3	3	2	6	
7		More of	More flow of stream 30	Valve 22 fails open  Control / operating failure of valve	Ratio of co-polymers in products altered which affects mechanical	Fail close on valve 22  Flow transmitter and indicator	2	2	4	



			22	properties of product Unreacted PEGMA leading to greater impurities in product	controller on stream 30 Regular maintenance of valves Operational checks and inspections Rotating shifts for operators				
8	More of	More flow of stream 31	Same as Case No.7 except valve 23	More APS in reactor leading to greater impurities in product	Fail close on valve 23 Flow transmitter and indicator controller on stream 31 Regular maintenance of valves Operational checks and inspections Rotating shifts for operators	2	2	4	
9	More of	More flow of stream 32	Valve 24 fails open Control / operating failure of valve 24	More TEMED in the reactor leading to greater impurities in the product	Fail close on valve 24 Flow transmitter and indicator controller on stream 32	2	2	4	



					Regular maintenance of valves Operational checks and inspections Rotating shifts for operators				
10	More of	More flow of stream 34	Higher flow of streams 31 and/or 32 and/or 33	Greater processing required in downstream increasing utilities and costs  Lower product quality due to higher impurities	Flow transmitter and flow indicator control for streams 31 and/or 32 and/or 33  Sampling point on stream 34	2	2	4	
11	Less of	Less flow of stream 31  Control / operating failure of valve 23  Entry pipe blockage	Valve 23 fails close	Ratio of co-polymers in products altered which affects mechanical properties of product  Lower product yield if insufficient co-polymer for reaction	Flow transmitter and flow indicator control for stream 31  Regular maintenance of valves  Operational checks and inspections  Rotating shifts for operators	3	2	6	
12	Less of	Less flow of stream 32	Valve 24 fails close	Lower product yield due to lack of initiator	Same as for Case No 3	3	2	6	



			Control / operating failure of valve 24							
			Entry pipe blockage							
13	Less of	Less flow of stream 33	Valve 25 fails close  Control / operating failure of valve 25  Entry pipe blockage	Lower rate of reaction resulting in lower product yield	Same as Case No 3	3	2	6		
14	Less of	Less flow of stream 34	Less flow of streams 31 and/or 32 and/or 33	Loss of batch if composition is incorrect (inadequate product quality) Insufficient product produced leading to loss of profits	Flow transmitter  Flow indicator control  All for streams 31,32,33,30 Sampling point on stream 34	3	2	6		
15	Fire	Present	Fire in the plant  Flammable reagents (PEGMA) near ignition sources  Smoking or other ignition sources	Possible explosion  Damage to reactor  Loss of product	Fire safety protocols onsite  High pressure alarms linked to pressure relief valve and bursting disk  High pressure indicators to shut off inlet flows if pressure too high	4	1	4		



16	Pressure	More	More pressure in reactor	Same as for Case No 15	Same as for Case No 15	Same as for Case No 15	4	1	4
17	Level	More	More level in the reactor	Flow deviations of inlet stream(s)	Spillage or leaks causing injury to personnel  Fire if fluid contact with electrical equipment  Increased agitator power required due to greater volume  More flow of stream 33 with consequences discussed above	Level transmitter on reactor  Level indicator control Level high alarm  Level high cut off  Add tolerance in reactor sizing to allow for excess level Clean up spillages immediately	3	2	6
18		Less	Less level in the reactor	Flow deviations of inlet stream(s)	Less flow of stream 33 with consequences as in Case No 7, 14	Level transmitter on reactor  Level indicator control  Level low alarm Level transmitter All connected to valves with respective flow controllers	3	2	6
19	Composition	Different from	Composition of reactor contents / stream 34	Flow deviations of inlet stream(s)  Incorrect operating temperature	Decreased product quality  Possible loss of batch resulting in lower product yield	Sampling point on stream 34 during batch time where correctional action can be	3	2	6



					Greater processing requirements downstream to remove impurities	taken to adjust inlet flows of streams 30,31, 32,33.				
20	Operation and maintenance	No	No process operations	Power/utility failure Worker shortage / strikes	No product produced resulting in loss of profit	Back-up power supply  Ethical working conditions and liaise with workers union  Hire and train sufficient staff	4	1	4	
21		No	No maintenance	Maintenance not scheduled	Greater hazards Equipment failure Inadequate product quality	Develop operations and maintenance philosophy: plan for regular maintenance	4	1	4	
22		Other Than	Insufficient process operations and maintenance	Worker shortage Delays caused by maintenance  Supply chain delays	Greater hazards/ process errors due to lack of staff. Lower production rate leading to loss of profit	Ensure bypasses are introduced on all valves so process can run alongside maintenance  Schedule maintenance between batches to minimise downtime	4	2	8	
23	Utilities	No	No power / electricity	External power cuts/outages	Failure of control systems due to lack of electricity. Consequences as Case No. 1-21	Back-up power supply	4	1	4	

24	Instrument air	No	No air supply to control systems	Malfunction in air supply due to piping, fouling , and/or lack of lubrication	Failure of control and alarm systems Greater process risks caused by lack of control in reactor	Regular maintenance and replacement of actuators	3	1	3
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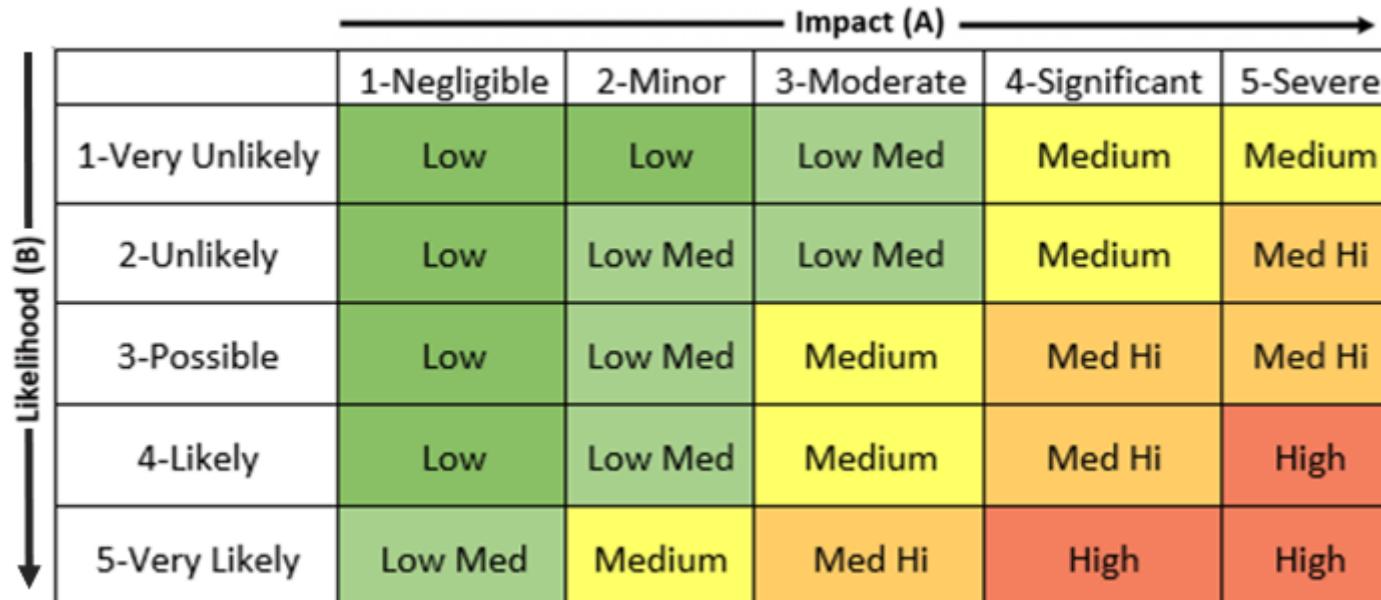


Figure 16: Risk Ranking Matrix

In industry, it is important that the HAZOP is carried out by a multi-disciplinary team. The HAZOP leader who will prepare the study and lead discussions relating to the study is to be affiliated with the process/ operations being analysed. A secretary will prepare any worksheets, record discussions and prepare the HAZOP reports. A project engineer, process engineer, electrical engineer, safety engineer, operating team leader and maintenance engineer for the company are also valuable in a HAZOP, as for efficient running of the process at least one person for each relevant discipline associated with the project should be aware of the associated hazards and contribute to risk minimisation methods, with each person bringing a different area of expertise that will ensure all hazards are considered.

The HAZOP was conducted by the entire design team during a workshop where the chosen guidewords were followed throughout the process with considerations of different deviations in temperate, flow, level, composition, operations and maintenance, utilities, pressure, instrument air and fire. Safeguards were devised to mitigated consequences and later applied to the P&ID, Figure 13.

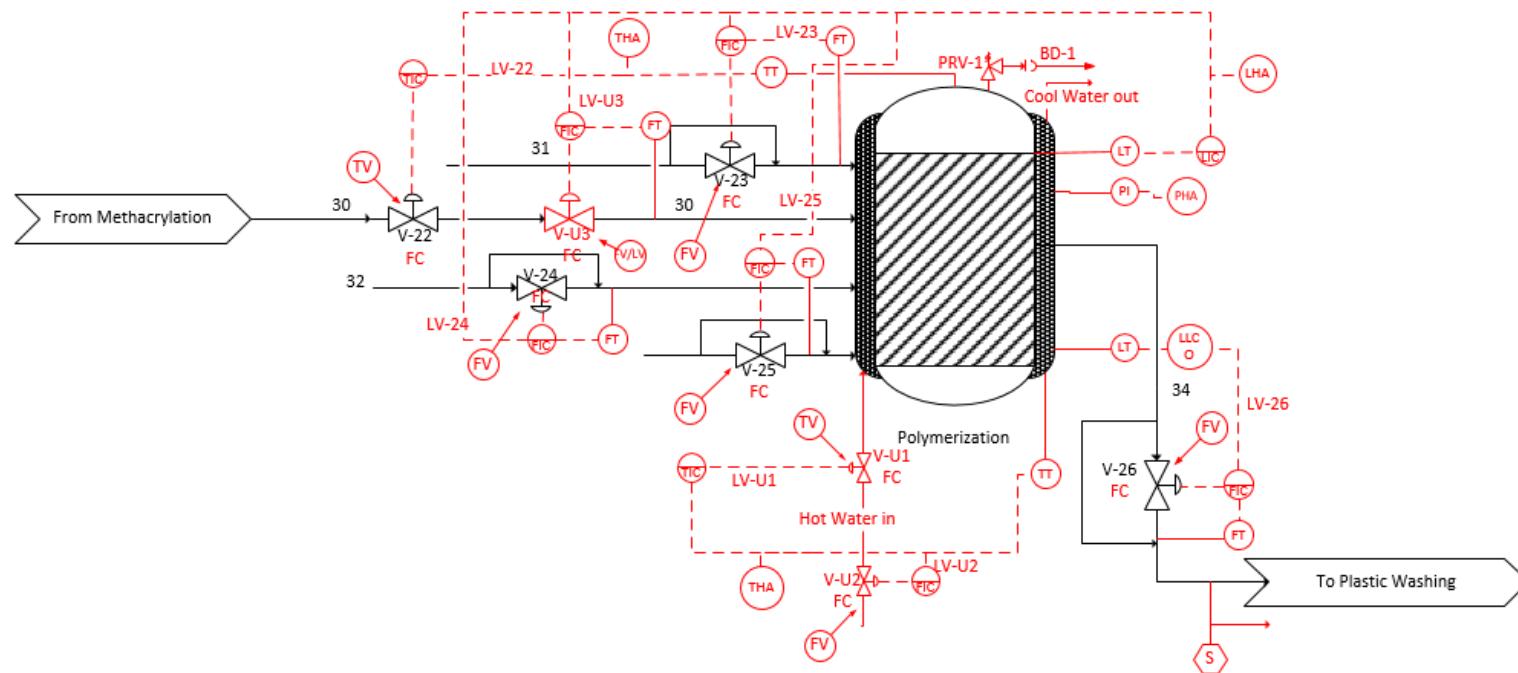


The HAZOP conducted above is aimed to assess the hazards and operability of the most hazardous node in the process, taken to be the polymerisation reactor in Process step C due to the presence of the most chemical components in the process, PEGMA, TEMED, APS, Methacrylic Anhydride, Methacrylic acid and other components as detailed in the stream table (Table 5). A risk ranking matrix (Figure 14) was then used to evaluate the severity or impact and likelihood of each hazard in a semi-quantitative manner based on experience of the design team and process knowledge. The final score or colour of the hazard was then used to prioritise mitigations including temperature and pressure control and alarm systems along with flow and level controls and alarms.

The main aim of the HAZOP was to protect against elements of process safety and operational safety. In cases 1-2 for deviations of temperature in the reactor, the main objective was to mitigate any increase in temperature cause by the upstream methacrylation reaction and the decrease in temperature caused by the endothermic polymerisation. This was done by adding temperature controls on the initial P&ID, Figure 13 on stream 30 from the methacrylation reaction (LV-22) and connecting this to a temperature transmitter and temperature high alarm on the reactor so that the temperature of the stream does not ever increase past 60°C, which begins to fall outside the temperature ranges of the reaction and causing denaturing of proteins. Additionally, temperature indicator control and temperature high alarms were added onto the heating jacket so that the flowrate of heating utility can be varied based on the temperature of the reactor to keep it at ambient temperature, 25°C, (LVU-1 and LVU-2). In cases 3-14, for Flow deviation, and 17-19, for Flow and composition Deviation, the safeguards added to the P&ID included an extensive system of flow indicator controls and transmitters connected to level transmitters and high level alarms in order to mitigate overfilling of the reactors from the inlet valves. The valves V-U3, V-23, V-24, and V-25 (LVU-3, LV-23,LV-24, LV-25) were all included in this additional flow and level integrated control system with level high alarms in order to ensure that the right proportions of reagents are added per batch. A level low alarm and a level low cut off was also added to stream 34, V-26, in order to prevent any accidental underfilling leading to wrong composition in the batch, LV-26. Finally, to mitigate risks from Fire and Pressure case 15 and 16, a pressure indicator, pressure high alarm, pressure relief valve (PRV) and bursting disk were added with the PRV-1 to be rated at 10% above system operating pressure, 1.11 bar as recommended from engineering practice (Sinnott and Towler, 2005). Bursting disk, BD-1, is added for additional insurance in case of liquid blockage in the PRV. All valves were set to fail closed to minimize loss of batch due to wrongful inputs into the vessel.

For operational safety, various mitigations were addressed to facilitate smooth running of the batch reactor. These including factors such as: ethical working environment, fire safety training, and staff training on procedures to ensure batch operations are sufficiently staffed. Additionally, operations and maintenance were also considered with a need for a comprehensive operations and maintenance strategy to ensure maintenance is carried out to prevent valve and pipe blockages in the system leading to hazardous consequences due to equipment failure. Finally, instrument air failure and utilities failure were considered with most mitigation strategies addressed in other guidewords along with the need of backup power supply and scheduled maintenance to prevent deterioration of systems.

## Revised P&ID



The New Whey Ltd.		Liquid Whey to Bioplastic Process	
Drawn By	Claudia Millar	Date	11/03/2022
Checked by	Emily Woodhall	Date	11/03/2022
Approved by	Alex Raneri	Date	11/03/2022
Drawing No.	4	Date	11/03/2022

Figure 17: Revised individual P&ID



## Start-up and Shutdown Procedures

Proper Start-up and Shutdown procedures are vital in ensuring plant safety and optimising process yield and efficiency, this section will outline the steps necessary in for optimal plant operations (Criterion Technologies, 2008).

### Start-up

Start-up can pertain to a restart after a planned/emergency shutdown or the initial start-up of a unit in the process. Identical guideline and instructions must be followed for both scenarios.

#### Reactor Vessels

It must be ensured that all vessels are thoroughly cleaned and emptied of any contaminants before they are connected to feed pumps. The vessel used for the batch polymerisation reaction must be completely clear of any sources of ignition during cleaning and filling stages. Individual vessels must also be inspected by trained staff members to identify and rectify any issues with vessel condition and specification. Reactor level should be monitored and slowly moved to operating levels, with reactor temperature maintained at ambient levels. When safe operating levels have been established, the reactor should be slowly moved from a feed/recycle system to on-spec operations when required conversion is achieved and the process moves to steady state.

#### Filtration membranes

All membranes must be thoroughly cleaned and disinfected before operation to achieve maximum throughput throughout the process. Membranes must then be inspected by a trained professional to ensure there are no faults with the capacity to lead to loss of pressure in the unit. The membrane unit must then be slowly moved to operating pressure as feed is moved back onto spec.

#### Drying vessels and centrifuge

All vessels utilising elevated temperatures via hot fluids must be carefully inspected by a trained professional to maintain safety standards when starting up. Vessels are then cleaned, and any fluid flow entryways must be checked and cleared. Units are then moved to on-spec feed as a feed/recycle system is redundant.

#### Plate pasteuriser

The pasteurisation unit must be inspected for faults by a trained professional, plate conductivity and location must be same as specification to ensure high efficiency during use. The unit is then cleaned and disinfected before feed is introduced. Unit temperature must be then slowly increased to operating temperature of 61°C to ensure the pasteurisation process is operating at optimal efficiency.

### Shutdown

#### General preparation

Plant or battery limits must be set closed and isolated of all but essential workers. Any fluids in filled vessels must be drained or vented to a predetermined area. All vessels must then be purged with an inert gas before deinventoryation can occur. In the case of maintenance of a specific unit or piece of equipment, they must be isolated and cleaned as directed in equipment protocols. All units to be entered must be at atmospheric pressure before entry.

#### Reactor vessels

Vessels must be completely emptied with products routed to off-spec. Any heating/cooling elements must be switched off and at ambient temperature before any maintenance can be performed. Flow is then halted, and vessels pumped out to low points, or in cases of equipment replacement, emptied. If



a trained worker is to enter the vessel, it must be full emptied and disinfected of any feed fluids for human safety.

Plant shutdown must be avoided unless completely necessary for plant safety or required maintenance had been scheduled.

All procedures were checked by a group of process engineers and distributed among all plant employees.

## Plant Layout

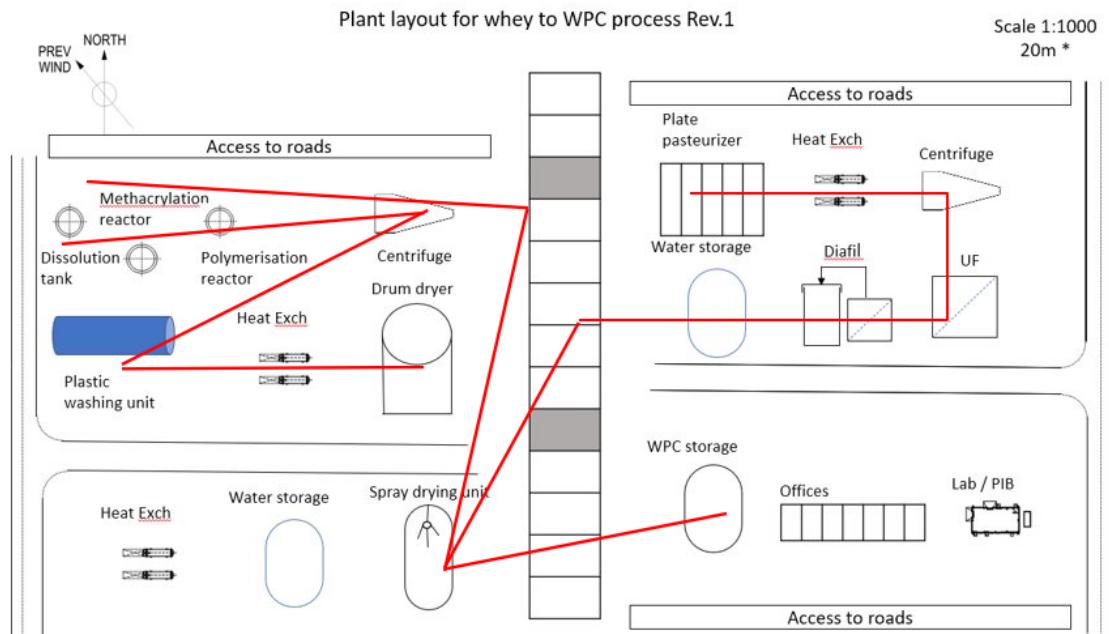


Figure 18: Initial plant layout with piping connections

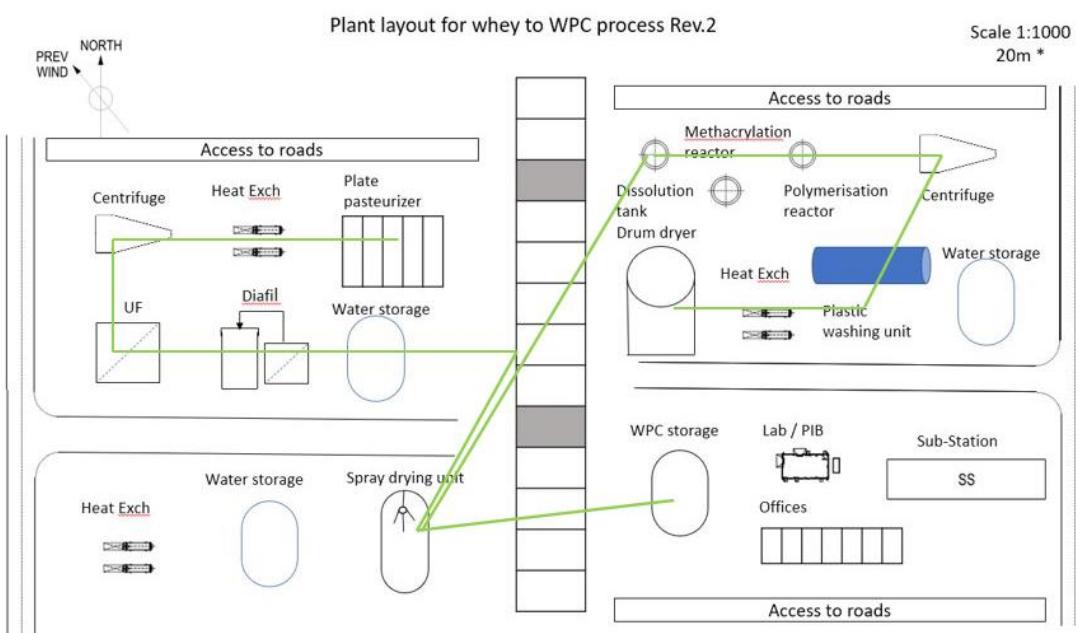


Figure 19: Revised plant layout with minimized piping



The plant layout for the process was created using general industry standard considerations for plant design. The main points used in the design were: safety, prevailing wind direction, process requirements, constructability and maintenance and minimization of CAPEX and OPEX costs. Safety was considered within the plant by spacing each process unit using ideas of inherently safe design. The location of each process unit was decided with any units with a chance of catastrophic malfunction placed a sufficient distance away from any office spaces or labs to prevent any loss of life or human injury in the case of unit failure. Individual units were also spaced relative to each other with inter-unit interactions considered, so in the case of malfunction downstream consequences are minimized. Ample emergency access and evacuation roads were also chosen in the interest of plant safety, ensuring the workers were safe to leave the plant in emergency and to help any required firefighting efforts. Process requirements were also used in the plant design, with units placed in groups pertaining to a certain node of the process, minimizing pipe lengths across the plant as well as the amount of pipe crossings. This is shown by the initial plant layout Figure 17 before revision, where safety is considered but not pipe crossings, then Figure 18 which is the revised final plant layout with a much lower quantity of pipe crossings. Decreased pipe lengths and crossings affect the CAPEX and OPEX of the process, as shorter average pipes result in lower process losses in pumping and material requirements, the shorter pipes also lead to decreased CAPEX as less length of pipe is purchased. Prevailing wind location was one of the most important considerations in the design of the plant mostly as this cannot be controlled. Due to this, it was decided to place units with potential fume release at the top edge of the plant (the reaction vessels), to safeguard plant workers from harm. It was also decided to ensure any sources of ignition were not downstream of the reactors preventing any chance of the spread of fire. Maintenance and constructability were maintained via multiple avenues, the placement of roads throughout the plant, facilitating access to the units during operations and streamlining the batch nature of the process. Pipe lengths were kept to a minimum increasing the ease of plant construction with less need to run long piping around the plant.

## Economic Analysis

As mentioned in the introduction the Techno-economic assessment (TEA) (Chalermthai et al., 2020) for a similar process to our chosen one estimated that the CAPEX for the process would be £30.12 million and the OPEX £3453 per tonne of product. However, it is predicted that these cost estimates will be different to the estimates made by this TEA. The main reason for this is that the TEA used a software to calculate their costs while ours were done by hand which is far less accurate and gives a larger amount of error.

### Capital cost estimation

#### Equipment purchase cost

Table 12 shows the equipment purchase costs (EPC) of all major process units, which were estimated using a mixture of 'Rule of Thumb' data from textbooks, and prices of similarly designed equipment in online marketplaces. Values were adjusted using CEPCI (Chemical Engineering plant cost index) values to account for the time value of money and get present values for the equipment costs.

The CEPCI value for 1989 is 320.0 (Garrett, 1989), the CEPCI value for Feb 2007 is 512.4 (Lozowski, 2007) and the most recent CEPCI value from Sept 2021 is 754.0 (CEPCI, 2021).

Table 12: Purchase Costs for all major Process Units

Process Unit	Reference EPC (£ k)	Reference	Reference Date	Present EPC (£ k)
Pasteurisation	338.3	(Garrett, 1989)	1989	797.2
Centrifuge 1	1,770	(Garrett, 1989)	1989	4,170
Ultrafiltration	13.92	(Woods, 2007)	2007	20.49
Diafiltration	5.515	(Woods, 2007)	2007	8.115
3X Pumps	0.7919	(Ebara Pumps, 2022)	2022	0.7919
Spray Drying	1527	(Woods, 2007)	2007	4493
Storage Tank	1.527	(Garrett, 1989)	1989	3.597
Protein Dissolution	42.03	(Garrett, 1989)	1989	99.04



Methacrylation	43.06	(Garrett, 1989)	1989	101.5
Polymerisation	49.21	(Garrett, 1989)	1989	115.9
Washing	1.989	(IndiaMart, 2022)	2022	1.989
Centrifuge 2	49.37	(Garrett, 1989)	1989	116.3
Drum Drying	167.6	(Woods, 2007)	2007	246.6

Therefore, the Total Equipment Purchase Cost (TEPC) is £10.17 million.

#### Other costs:

The other costs included in the capital cost were estimated as a fraction of the TEPC (Garrett, 1989). Table 13 shows the costs of each component of the total capital cost. The total capital cost is calculated to be £31.03 million, which is around 3 times the TEPC.

*Table 13: Costs for Each Component of the Capital Cost*

Component	Fraction of TEPC	Cost (£ m)	Percentage of Total Costs
TEPC	1.000	£10.17	32.79
Piping & Instrumentation	0.250	£2.544	8.197
Electrical & Utilities	0.400	£4.070	13.12
Misc. Plant Construction	0.250	£2.544	8.197
Buildings	0.500	£5.087	16.39
Land	0.100	£1.017	3.279
Engineering	0.300	£3.052	9.836
Contractors Fee	0.100	£1.017	3.379
Contingency	0.150	£1.526	4.918
<b>Total CAPEX</b>	<b>3.050</b>	<b>£31.03</b>	<b>100.0</b>

#### Operating costs:

Operating costs were calculated based on prices for the utilities and raw materials required. The required quantity of each, in tonnes, or kWh per batch, across each relevant unit was calculated from mass and energy balances. Assuming 448 batches per year, the total operating cost per annum could be calculated from the total raw material and utility requirements per batch. The price of each material or utility was found per cubic metre, tonne, or kWh.

The total operating cost was calculated to be £3.084 million per year. Table 14 shows the annual costs of purchasing the raw materials and Table 15 shows the annual cost of utilities. The costs per tonne of the raw materials were taken from Chalermthai et.al (Chalermthai et al., 2020), the cost per kWh of electricity from (Department for Business, 2013), the costs per tonne of steam from (TLV: A Steam Specialist Company, 2022), and the cost per m<sup>3</sup> of water was from (Ofwat, 2022) and (Wessex Water, 2022).

*Table 14: Operating Costs for Purchasing Raw Materials*

Material	Process Water	NaOH	Methacrylic Anhydride	TEMED	PEGMA	APS
Mass per Batch (Tonnes)	55.03	0.2993	0.05175	0.003565	2.415	0.1748
Mass per Annum (Tonnes)	24650	134.1	23.18	1.597	1082	78.31



Price of Material	Water (£ m <sup>-3</sup> )	NaOH (\$ tonne <sup>-1</sup> )	Methacrylic Anhydride (\$ tonne <sup>-1</sup> )	TEMED (\$ tonne <sup>-1</sup> )	PEGMA (\$ tonne <sup>-1</sup> )	APS (\$ tonne <sup>-1</sup> )
	1.97	300.00	8,000.00	4,200.00	3,000.00	600.00
Annual Cost (£k)	48.80	30.70	141.6	5.121	2,478	35.87
Total Cost of Raw Materials (£mil)			2.740			

Table 15: Operating Costs for Utilities

Utility	Electricity Consumption (kWh batch <sup>-1</sup> )	Steam Consumption (tonnes batch <sup>-1</sup> )	Water Consumption (Tonnes batch <sup>-1</sup> )
Total per batch	1905	16.66	147.6
Total per annum	853500	7464	66140
Price of Utility	Electricity (£ kWh <sup>-1</sup> )	Steam (£ tonne <sup>-1</sup> )	Water (£ m <sup>-3</sup> )
	0.1433	12.20	1.970
Annual Cost (£k)	122.3	91.06	130.9
Total Cost of Utilities (£k)		344.3	

#### Income from sales:

As previously calculated, the mass of plastic produced in a year is 1126.7 tonnes. It is assumed that the selling price of the plastic produced is £5.34 per kg, as given in the TEA for this process. (Chalermthai et al., 2020)

A certain portion of our product will be sold back to the local cheese producers at a discounted price, as they will be giving us their waste whey for free. Since 9 tonnes of whey is produced for every 1 tonne, if the cheese producers give us 44800 tonnes of whey as assumed in the introduction, the mass of cheese will be 1/9<sup>th</sup> of this, 4978 tonnes. It was assumed that 1 g of plastic packaging is used per 100g of cheese. Therefore, the mass of plastic required by the cheese producers will be 49.78 tonnes. This will be sold to the cheese producers at a 70% discount, which is £3.74 per kg. The remaining bioplastic will be sold at the standard price.

The total annual income from sales will be £5.646 million. The annual gross profit will be £2.562 million.

5% (£0.1281 million) of our profits will be given to our partner company who will be producing plastic film from our final product. Therefore, our remaining annual income will be £5.518 million, and our remaining annual profit will be £2.434 million.

#### Plant lifetime:

Chemical plants usually have a lifetime of 25 to 50 years (Smith and DuPont, 1999), we have assumed that our plant lifetime is within this range at 35 years.

#### End of Project:

The following assumptions were made about the plant, building and land value at the end of the project:

- The plant has no value at the end of the project, and plant disassembly and disposal will cost £800k (EWMI, 2022).
- The value of the buildings will decrease by 1% of the original value every year.
- The value of the land will stay constant.



### Other Assumptions:

- The tax rate is 30% and the after-tax discount is 7% as stated in the project brief.

### Net Present Value:

Figure 20 shows the cumulative discounted cash flow diagram for the project. The NPV at the end of the project is -£2.673 million.

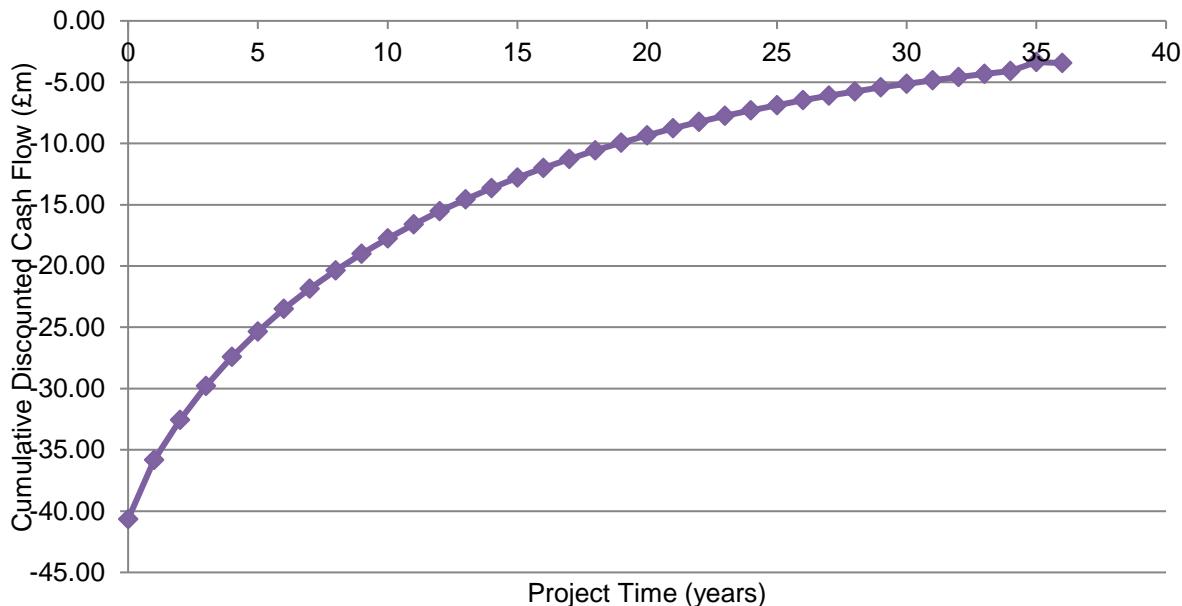


Figure 20: Cumulative Discounted Cash Flow Diagram for the project

Therefore, it is expected that the project will not be economically feasible unless some changes are made. Some possible changes that could be made to increase the final NPV of the project are:

- Finding a cheaper alternative to PEGMA.
- Running more batches per year.
- Selling the product for a higher price.

### Economic Sensitivity Analysis

A sensitivity analysis was done to determine the how changing different parameters affects the profitability of the project.

Cheaper alternative copolymer: The first parameter tested was the price of the copolymer used. The cost of purchasing the PEGMA copolymer is the largest part of the operating cost. Therefore, finding a cheaper alternative copolymer to use would greatly decrease the operating costs. The price of copolymer price was set to 5%, 10%, 25% and 50% of the cost of PEGMA. The final NPV and payback time (if the project breaks even) were then calculated for each of these values. Table 10 shows the final NPV and payback time for each of the chosen copolymer prices, and Figure 21 shows the relationship between the copolymer price and the final NPV. From interpolation of Figure 21, the cost of the copolymer needs to be reduced to below £2.175 million for the project to be economically feasible. The TEA does not mention any possible cheaper, alternatives to PEGMA; therefore, research would need to be done on a range of different options for a cheaper copolymer to find the best option.

Table 16: Final NPV's and Payback Times for different Copolymer Costs

	Annual Copolymer Price (£mil)	Payback Time (years)	Final NPV (£mil)
Original	2.48	-	-2.67
5% Reduction	2.35	-	-1.58
10% Reduction	2.23	-	-0.48
25% Reduction	2.11	34	0.62
50% Reduction	1.24	18	8.29

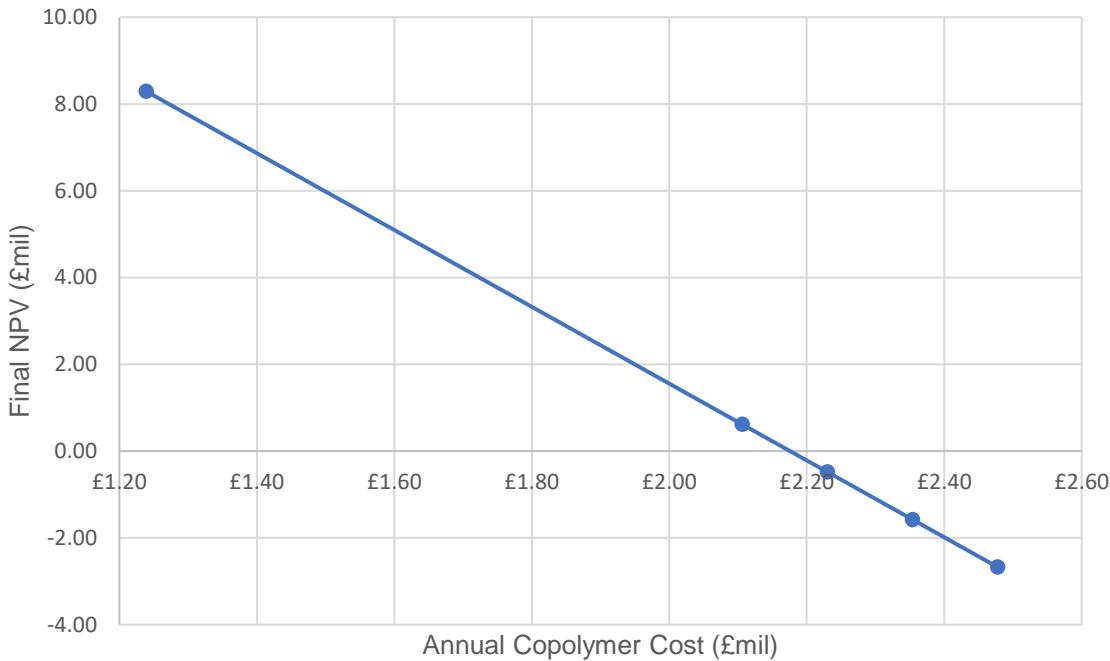
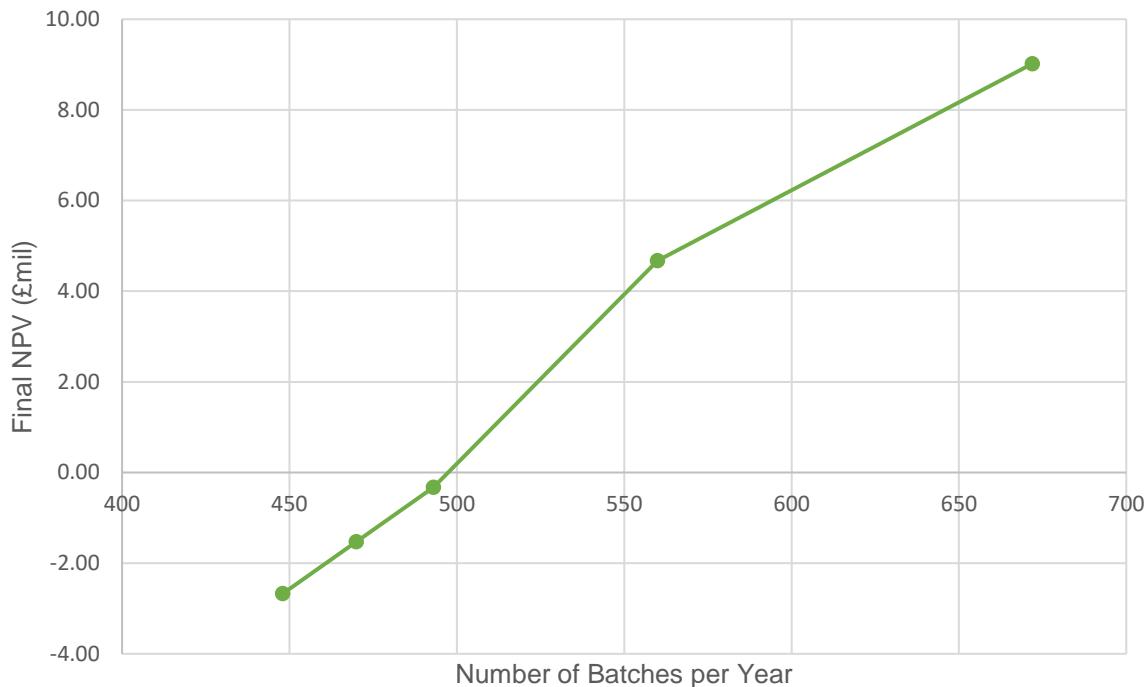


Figure 21: Relationship between the Annual Copolymer Cost and the Final NPV

Increasing the number of batches per year: The next parameter that was tested is the annual number of batches. A greater number of batches coincides to a greater quantity of plastic production per year, so the annual income will increase. However, the operating costs will also increase as the annual number of batches increases. The number of batches was set to 5%, 10%, 25% and 50% greater than the original number of batches. The final NPV and payback time (if the project breaks even) were calculated for each of these values. Table 11 shows the final NPV and payback time for each of the chosen annual number of batches, and Figure 22 shows the relationship between the annual number of batches and the final NPV. From interpolation of Figure 22, the annual number of batches needs to be increased above 500 for the project to be economically feasible.

Table 17: Final NPV's and Payback Times for different Annual Numbers of Batches

	Number of Batches per year	Payback Time (years)	Final NPV (£mil)
Original	448	-	-2.67
5% Increase	470	-	-1.52
10% Increase	493	-	-0.32
25% Increase	560	22	4.68
50% Increase	672	17	9.02

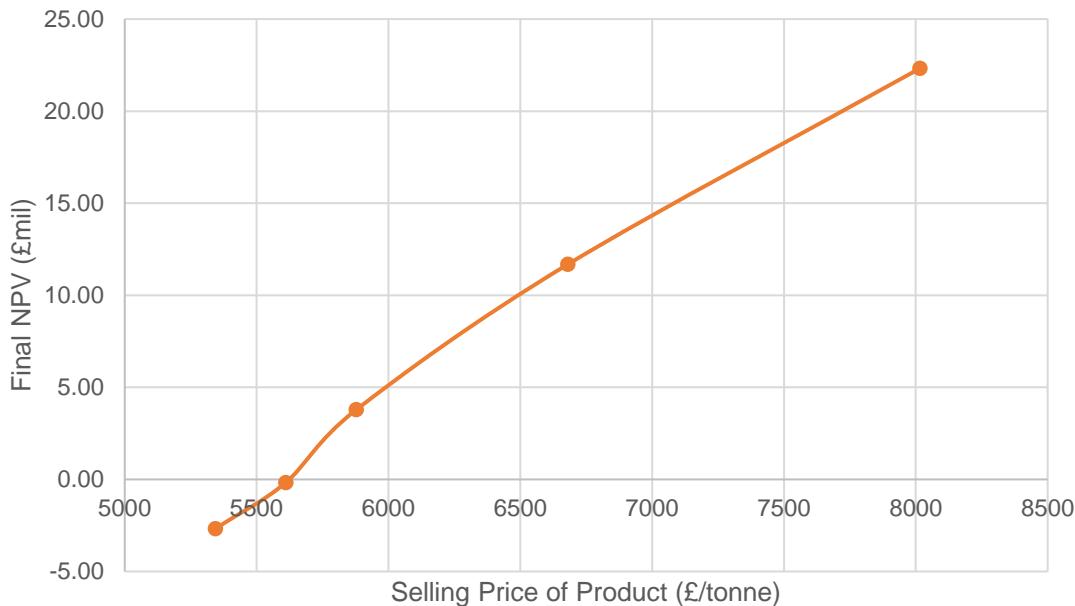


*Figure 22: Relationship between the Annual Number of Batches and the Final NPV*

Increasing the selling price of the product: The final parameter that was tested was the selling price of the product. A greater selling price will lead to the annual income increasing. The selling price of the product was set to 5%, 10%, 25% and 50% greater than the original selling price of the product. The final NPV and payback time (if the project breaks even) were calculated for each of these values. Table 12 shows the final NPV and payback time for each of the chosen product selling price, and Figure 23 shows the relationship between the product selling price and the final NPV. From interpolation of Figure 23, the product selling price needs to be increased above £5600k per tonne for the project to be economically feasible. As mentioned by the TEA, the selling price of £5344 is based on the price of plastic produced from algae biomass. As the mechanical and thermal properties of our plastic will be greater than the algae-based plastic, it can be expected that the selling price of our plastic will be greater. The TEA estimated that the plastic could be sold for as much as £8015 per tonne (Chalermtai et al., 2020), which as shown in Table 18, would greatly increase the profits of the project.

*Table 18: Final NPV's and Payback Times for different Product Selling Prices*

	Product Selling Price (£/tonne)	Payback Time (years)	Final NPV (£mil)
Original	5344	-	-2.67
5% Increase	5611	-	-0.17
10% Increase	5878	24	3.78
25% Increase	6679	15	11.67
50% Increase	8015	10	22.32



*Figure 23: Relationship between Final NPV and Product Selling Price*

## Environmental Impact Assessment

The environmental impact of this process is to be considered from the sourcing of the inputs into the system, the operations of the process and the waste created from the process.

### Environmental impact of system inputs

As the process plant location is situated near dairy farms in Somerset, the environmental impact associated with transport of the liquid whey is neglected, whereas if whey powder was utilised as the raw material, transport requirement would be more significant. However, the use of other inputs to the system such as methacrylic anhydride, PEGMA, sodium hydroxide, APS and TEMED will all require transport to the process site. This transport requirement is associated with burning fossil fuels, which will have impacts associated with global warming potential, abiotic depletion, acidification, and human toxicity. To minimize this, these chemicals will aim to be sourced as close as is possible to the site. We would also choose producers that are associated with the lowest emissions and have sustainable practices.

Steam and water inputs into the system will diminish water resources. Furthermore, steam is to be produced from the boiling of water onsite. Use of fossil fuels to produce this steam will also contribute to abiotic depletion, disturbance to vegetation and soil and air pollution due to drilling land for these resources, acidification of water systems due to large volumes of contaminated water being produced, greenhouse gas (GHG) emissions and human toxicity due to presence of heavy metals and other chemical intake through inhalation, ingestion or skin contact (Chalermthai et al., 2021). To minimise these effects, the plant should use electric boilers for the steam and use a renewable energy supplier.

A life cycle assessment (LCA) study on this process identified that PEGMA was a major contributor to environmental damages (Chalermthai et al., 2021) as PEGMA consists of ethylene oxides, which are derived from fossil-based sources. The impacts of fossil fuels are discussed above. Ethylene oxides are also extracted through the sea (Chalermthai et al., 2021) which may lead to water degradation and reduction in biodiversity. The environmental benefits of the production of the whey protein bioplastic can be enhanced if PEGMA is renewably sourced, its quantity reduced as a co-polymer, or a substitute determined. This is to be investigated with further research.

Methacrylic anhydride also contributes significantly to environmental impacts of the process, due to the presence of acetic anhydride and methacrylic acid, as methacrylic acid is derived from hydrolysis of



methacrylamide sulphate, or from commercial isobutene production plants (Chalermthai et al., 2021) and acetic anhydride is mainly produced by thermal cracking of acetic acid to ketene, followed by reaction with additional acetic acid (Lewis, 1997).

### **Environmental impact associated with the process**

In a life cycle assessment (LCA) that was carried out from the whey powder to the bioplastic production using the same method followed for this project, the energy requirements were determined as 2.9 MJ/kg of plastic produced (Chalermthai et al., 2021). This was lower than for other plastic production methods, for example PLA production required 53 MJ/kg, PP 74 MJ/kg and PHB 42.9 MJ/kg (Chalermthai et al., 2021). However, this does not take into consideration the energy requirements upstream to purify and concentrate the liquid whey into the powder and does not consider the further processing requirements of converting our product into a film before it is to be of use. Furthermore, as this method is still relatively novel, certain chemical and physical properties may not be directly comparable, hence is difficult to compare energy consumption and other environmental impacts.

All units utilise electricity during the process. The use of fossil fuels for this electricity production has impacts as discussed above, and the plant using electricity from a renewable energy supplier can reduce these consequences. Ultrafiltration requires high energy inputs for the pressure against the membranes, alongside use of large amounts of cleaning agents which can degrade the membrane material and generate effluents possibly damaging to the environment (Bacenetti et al., 2018). Nevertheless, spray drying accounts for a large proportion of energy consumption of the process, as in comparison to membrane filtration, which from literature requires 0.014-0.036 kJ/kg of water evaporated, a 1 stage spray dryer requires 4.9 MJ/kg water evaporated (Ramírez et al., 2006). To minimise energy consumption as much as possible, an energy pinch analysis should be carried out by optimising heat recovery systems, energy supply methods and process operating conditions. This will be considered further in the detailed stages of design, although as the overall process operates at relatively mild temperatures and pressures through most units indicating its lower energy consumption requirements compared to many conventional processes.

It is also important to note that although the site is conveniently situated near cheese farms to minimise transport requirements, construction of a process plant of this scale changes the land use of this area. This implies soil disruption including contamination of land that may wash into water ways and may result in relocation of any farm animals that were previously situated on this land. The construction and operation of the plant will also result in greater noise and air pollution effects to local residents.

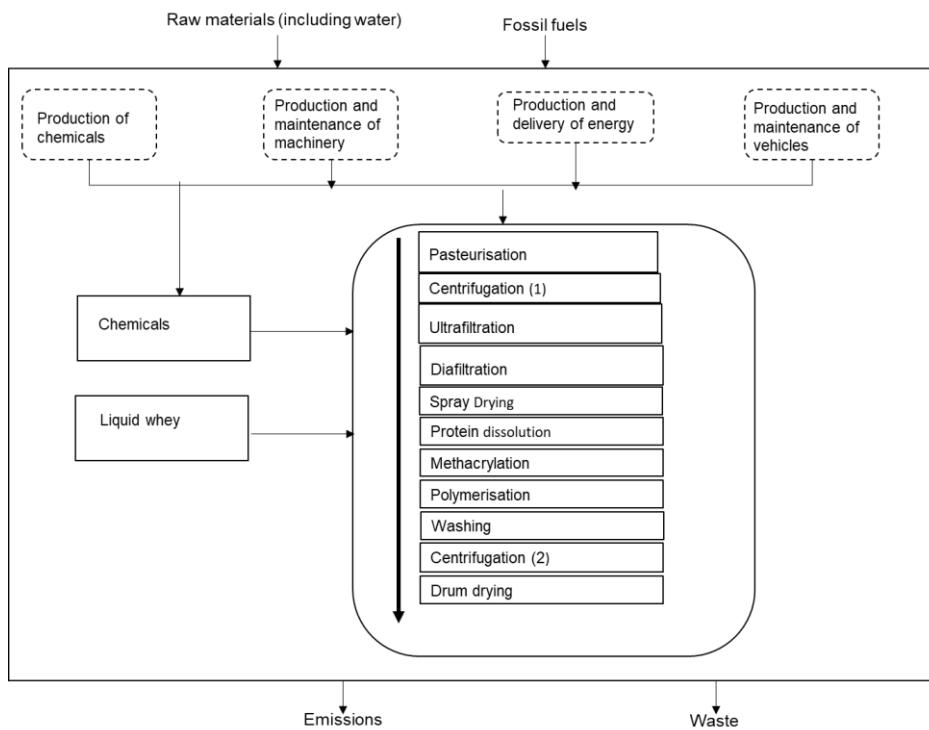
### **Environmental impact of waste streams**

The process also produces a variety of waste streams. The first centrifugation unit has a solid waste stream containing fats, carbohydrates, and minerals. The Ultrafiltration (UF) and Diafiltration (DF) units produce wastes containing proteins and smaller fats, minerals, and carbohydrates. To reduce the quantity of waste, the permeate streams from the membrane can be taken for further processing in to produce lactose, as this can be recovered directly from concentrated residues from whey ultrafiltration: lactose is crystallized, and crystals are separated using centrifugation followed by drying in a spray dryer (Santonja et al., 2019). However, this would result in further energy requirement. The remaining liquid can be dried or used as such as animal feed. The high salt content in the minerals gives these minerals limited use.

The spray drying and drum drying unit have water outputs. A water recycle system should be investigated on site to minimize the water requirements. For example, water exiting the spray dryer can be reused when entering the system again as steam or as the buffer solution for the diafiltration unit.

The washing unit produces a waste stream of impurities from the reactors, including unreacted PEGMA, whey, methacrylic anhydride, sodium hydroxide, APS and TEMED. This waste must be sent off as aqueous waste to a treatment site, which corresponds to transport requirements, alongside further emissions involved in the treatment process. Even after treatment, some of this waste must be disposed of, which could cause water emissions associated with environmental issues such as eutrophication and terrestrial ecotoxicity.

## Life Cycle Assessment (LCA) of the process



*Figure 24: System boundary for the cradle-to-gate life cycle assessment for production of whey protein plastic.*

In the more detailed stages of the design, a LCA could be carried out for the process. Until further research is carried out onto the biodegradability of the product, it is not possible to carry out a cradle-to-grave analysis and instead a cradle-to-gate analysis can be carried out. The system boundary for this is given in Figure 24.

To carry out this assessment, the inputs and outputs to the system are to be quantified, and major impact categories are to be selected. For example, the LCA carried out for the whey powder to bioplastic part of this process (Chalermthai et al., 2020) considered the following impact categories: abiotic depletion (measured in kg of Antimony equivalent), acidification (measured in terms of SO<sub>2</sub> equivalent), global warming potential (expressed in kg of CO<sub>2</sub> equivalent), ozone layer depletion (measured in kg of CFC-11 equivalent), photochemical oxidation (measured in kg of ethylene equivalent), human toxicity (measured in kg of 1,4-dichlorobenzene (1,4-DB) equivalent), and ecotoxicity (measured separately as kg of (1,4-DB)). Hence, from each of the inputs and outputs of the system these can be effectively quantified in relation to each of the impact categories. The relative environmental impact can also be determined by comparing the impact of conventional plastics to the whey plastics for each category.

### Safety considerations

To minimise the impact on local residents, it is important that actions proposed in the HAZID and HAZOP are implemented. The plant should be enclosed, and waste should be properly treated to ensure no waste from the site or chemical inputs is released into the surroundings. Chemicals utilised in the process pose a hazards to workers, such as: PEGMA, which is a skin irritant and is combustible at a flash point of 113°C (Merck, 2022d), sodium hydroxide can severely irritate the skin and eyes and is corrosive to tissue, (National Institute for Occupational Safety & Health, 2021), TEMED is highly flammable and can cause skin burns and eye damage (National Diagnostics, 2010) and ammonium persulphate is an oxidizer and an irritant (NCBI, 2022a). These chemicals also pose a risk to locals, as flammability/combustibility could lead to fire if there was a source of ignition. The construction of this plant in a rural area will correspond with a greater quantity of vehicles in the area, which poses a greater likelihood of accidents in the area involving locals and farm animals, and so workers should be encouraged to drive safely into the area and abide by speed restrictions. It is also important to consider



the total land requirements for the site, and how this relates to the proximity of residential areas. Following this, a detailed risk analysis should be carried out and those who live nearby the plant should be informed of the associated risks. Nevertheless, as discussed previously the process is of relatively low risk due to inherently safe design.

## Sustainability

*Consider three pillars (environmental, societal and economic) and their impacts locally, regionally and globally and UN sustainability goals*

Bio-based plastics are produced either from first-generation or second-generation feedstocks. First-generation feedstocks typically correspond to readily fermentable sugars such as corn, sugarcane and edible vegetable oils (Rosenboom et al., 2022). Although some studies suggest that it is possible to sustainably co-produce biomass for both food and fuel (and thus also for bio-based materials), first-generation biomass is controversial, due to ethical concerns about potential competition with food resources, especially in local settings (Rosenboom et al., 2022). Even though only 0.02% of global agricultural land use is currently devoted to producing precursors for bioplastics, utilising second-generation biomass is a more sustainable approach, as these non-edible biowastes would otherwise go to waste (Rosenboom et al., 2022). In the case of whey, one of the main environmental impacts is associated when whey is not used for the manufacture of new products and is released directly into waterways without any treatment. The high polluting power of whey is due to the organic substances present including protein and lactose; thus whey can cause destruction of flora and fauna due to high BOD which has high concentrations (Amaral and Silva, 2021). The BOD is estimated to be 100 times more than of domestic sewage (Amaral and Silva, 2021). Nevertheless, environmental legislation prohibits the disposal of whey without efficient treatment, thus dairy products agribusinesses must obligatorily perform treatment of effluents before final disposal (Amaral and Silva, 2021). This is extremely challenging for small to medium-sized industries as this requires high-cost investments which makes them end up acting illegally or wasting this valuable product (Amaral and Silva, 2021). Hence, utilising waste whey as our feedstock aligns with SDG2 of zero hunger, as it prevents competition with food sources associated with first-generation feedstocks, and SDG12 of responsible consumption, as it is preventing waste. This also aligns with the COP26 agenda of a reduction of waste, as the plant is to utilise 44800 tonnes of waste whey a year as the feedstock.

Furthermore, construction of this plant creates jobs to those in the surrounding areas and minimises the burden on smaller scale cheese producers to deal with the abundance of whey and can create a circular economy by using the waste and feeding it back into the cheese businesses for packaging purposes. This aligns with SGB8 to promote sustained, inclusive and sustainable economic growth and with SDG12.

Utilising whey protein as a co-polymer for the plastic produced reduces the reliance on fossil fuels for plastic production, as conventional plastics are entirely fossil fuel based. This aligns with SDG13 of climate action and the agenda of COP26 of moving away from petroleum-based products. However, in comparison to other bioplastics such as PHA and PLA which are 100% bio-based, our product is less sustainable in terms of its composition, with 70% being made from PEGMA which is derived from fossil fuels.

COP26 also aimed to eliminate single-use plastics. For this to happen, this product must be recyclable. As this is a relatively novel process it is not certain whether this plastic can be processed in recycling plants, and thus this should be investigated further.

## Societal Impacts

Societal impacts of the process have been considered in screening, selection and design. The creation of the process allows for jobs to be generated and opens opportunities for small cheese-making companies. The response to this opportunity was to design the process to use locally sourced cheese whey and select a location nearby various small cheesemakers in Ditcheat, Somerset. This supports the local economy in various ways: providing bioplastic at a reduced price to the cheesemakers to wrap their cheeses, using the waste whey which cheesemakers usually pay to dispose of, and generating



interest in the companies and communities involved are among the benefits. The local economy can benefit further by the company employing locally where possible and hiring local drivers to transport the whey from different farms. The production of bioplastic from waste feedstocks rather than feed grown or produced specifically to prevent bioplastic is that the latter takes up space which could be used to produce food, which contributes to world hunger. The production of the bioplastic from waste whey may generate interest in Ditchheat, drawing attention to the town both from the environmentally conscious consumer and the researcher in the field of bioplastic. The economy of the town could benefit, and local cheesemakers would gain a positive reputation. With the aid provided by the project, these local producers would be able to compete with large dairy corporations where they usually would not. Large corporations may not be generating value-added products from waste, and although they may sell dairy products cheaply, the local cheesemakers would have this advantage. In using waste to generate plastic to wrap the cheese, a circular economy is created, thus the use of fossil-fuel derived plastic can be avoided. Minimising the use of non-degradable plastics benefits the health of animals, as well as natural beauty and the cleanliness of towns and roads. The generation of jobs gives opportunities to local workers, as well as combatting unemployment rates in rural areas. As this is a novel process, the introduction of this into a rural area may generate interest in STEM subjects amongst local children, who may otherwise not be introduced to the field. It may influence the future generation towards holding sustainable values, which is critical in a world where our actions have damaged the environment.

Negative societal impacts of the process involve promotion of the petrochemical industry, as PEGMA is involved. Furthermore, with a greater proportion of the population becoming vegan, it is important to consider the possible objection of this project due to its direct connection and promotion of the dairy industry.

## Ethics

An ethical consideration based on the Statement of Ethical Principles (Engineering Council and Royal Academy of Engineering, 2014) is implemented at every stage of the process screening, selection and design.

### 1. Honesty and integrity

Honesty and integrity were upheld in process screening and selection, through admitting the faults of the bioplastic. These include using PEGMA, which is fossil-fuel derived, and the fact that it is a novel process, thus the extent of the biodegradability of the plastic is to be investigated. Openness, fairness, honesty and integrity must be upheld through design and into operation. This is achieved through acting in a reliable and trustworthy manner, which consists of ensuring the product meets required quality and biodegradability standards, whilst being produced from the advertised feedstock of waste cheese whey. The processes used to produce the bioplastic must be as described, thus avoiding deception. Engineers must be aware of how they affect others and respect their privacy, rights and reputations. This consists of, for example, accepting variations in available whey from the cheesemakers, respecting the demands of these and other suppliers of raw materials involved. Conflicts of interest must be mentioned; those with conflicting interests must feel secure in declaring these. Confidentiality and respect for others must be felt by all individuals involved. Corrupt practices and professional misconduct shall be prevented, by making anti-corruption explicit in company culture through a zero-tolerance policy on bribery and corruption.

### 2. Respect for life, law, the environment and public good

Respect for life and the environment were upheld in process screening and selection, through selecting waste whey as a feedstock, avoiding its disposal in nature and the adverse environmental effects associated. Respect for public good was demonstrated in selecting the location of Ditchheat, a small village, and working with local cheesemakers, thus helping the local economy as opposed to working with large corporations. Respect for the law was upheld through adherence to environmental regulations. Respect for life, law, the environment and public good are to be upheld further through adequate health and safety measures, checks and maintenance, consideration of the public and conservation of resources. Health and safety and awareness of hazards is of critical importance, adherence to this is possible due to a thorough HAZOP. Laws must always be abided by, thus



awareness of this must be upheld by all individuals involved in the company. Data protection, the protection of personal and intellectual property, and cyber security must be ensured through antivirus software. The quality of the site must be maintained through regular checks and maintenance. Public good must be considered in any decisions made. Adverse effects must be avoided, such as by disposing of any substance correctly, and minimising carbon footprint by employing locally where possible. Resources must be used sparingly, to avoid waste wherever possible. The reputation of the company must be upheld through adherence to these principles.

### 3. Accuracy and rigour

Accuracy and rigour throughout the process design were upheld through careful and justified calculations. Throughout operation, accuracy and rigour are paramount. Employees must always act with care, carrying out checks thoroughly and regularly, ensuring the correct amounts of substances are used, as well as the correct temperatures and pressures. Each employee must only perform their given role as to ensure competency or perform a role under competent supervision. Competency must be maintained through knowledge in new developments in the field. Similarly, any discoveries made must be reported to further knowledge in the process. Everyone involved must commit to avoid misleading others, through honesty, accuracy and objectivity.

### 4. Leadership and communication

Through process screening, selection and design, leadership was demonstrated through taking initiative to work and arrange group meetings. Leadership and communication must be upheld through operation by individuals taking responsibility. Awareness of issues the process may pose for society must be demonstrated. Everyone must be willing to listen to the concerns of others. Diversity and equality must be upheld through taking a zero-tolerance approach to discrimination. The benefits of the bioplastic must be advertised to the public to promote awareness of waste reduction and biodegradable plastic. Any statements made by the company must be truthful and objective. Any statements that cause professional concern must be challenged.

## Optimisation

For the pasteurisation unit, the liquid whey must be pasteurised at 61°C for at least 15 seconds to ensure that the microorganisms that are in suspension of the fluid are denatured to meet FDA regulations. The plate pasteuriser has been overdesigned to ensure that this occurs, however, the residence time of the fluid flowing through the heat exchanger at that temperature has not been calculated accurately. To allow for this, the pasteuriser has been designed to operate for 15 minutes. This has inflated the heat transfer area and the mass flow rate of steam required to maintain the fluid at 61°C. Steam is an expensive utility which would be preferred if used in moderation. To mitigate this problem, further calculations can be made to calculate the actual residence time needed for the liquid whey to be at 61°C in the heat exchanger. A practical way to ensure pasteurisation is completed is to integrate a holding tub for the heated liquid whey to sit in for 15 seconds. Both methods would see a decrease in the heat transfer area. Therefore, it will negate the cost of installing a larger heat exchanger than necessary and reduce the consumption of steam for this process unit. Also, the design has assumed ideal conditions and fouling of the plates have not been considered. Further calculations into fouling correction of heated liquid whey must be made to ensure the efficiency of the pasteuriser is not hindered in any way during its operation throughout its lifetime. Stainless steel 304 has been chosen as the material for the construction of the plate pasteuriser to meet FDA regulations, however, further research in literature could benefit the design with a food industry appropriate material but with superior heat transfer properties. This would most likely reduce the size of the unit and the cost of construction, if a less expensive material is utilised.

For the ultrafiltration unit, a constant rejection coefficient was assumed throughout the process for each of the components. This is an unlikely assumption due to fouling effects which degrade the membranes. Therefore, to optimise this unit it is important to track any performance deterioration and model this into the mass balance equations, and factor in when membrane replacement and chemical cleaning is required. A transmembrane pressure was decided based on literature; however, a range of pressures could be considered for this, and the relationship between the feed, retentate and permeate pressure



should be investigated to determine the optimum split that results in the lowest energy requirements. The pump energy requirements should also be investigated further, and sizing should be further refined to further optimise the length and diameter of the module, as well as consideration of further detail in the design such as the diameter of the inner tube, the thickness of the feed spaces, the thickness of the membrane, the thickness of the product channel, the thickness of the spacer, sizing of the spiral wound membrane holders and material used for this.

Similar assumptions were made for the diafiltration unit. The rejection coefficients were assumed to be the same as for ultrafiltration and constant throughout the process, ignoring the effect of any fouling that may occur. In further design, this would be optimised to include the increase of fouling throughout the process and its effect on the pressure required to maintain the flux. The fouling would be modelled to track the performance of the unit. The regularity of membrane cleaning and replacement could also be calculated, which would increase the accuracy of the OPEX calculations. The transmembrane, permeate and retentate pressures were all assumed to calculate the required feed pressure. However, further research and experimentation is required to explore the relationship between these variables to determine the optimum split resulting in the lowest energy requirements, as in ultrafiltration. This will affect the pump energy requirements calculated, as the pressure required will not be assumed constant. The density of the retentate and recycle stream was assumed to be constant to facilitate mass balance calculations for the buffer stream. However, the aim of the unit is to concentrate the protein concentration in the retentate, so the recycle stream will not have a constant density. Therefore, in further design, the exact composition of the recycle will be modelled to show the change in composition. This will allow a more accurate total buffer mass to be calculated. The number of recycles will also be refined, to find an optimum balance between minimising water consumption and maximising whey protein purity. Sizing should be further designed to optimise the dimensions of the module, such as the diameter, length, diameter of the inner tube, the thickness of the feed spaces, the thickness of the membrane, the thickness of the product channel, the thickness of the spacer, sizing of the spiral wound membrane holders and material used for this. The tank for the buffer solution can also be included in the design.

Spray drying is a complex operation with a variety of variables including air flow rate, air humidity, temperature and feed rate influencing the process, with many of these variables being interlinked. An air inlet humidity is assumed; however, a variety of humidity's could be considered. Ideally, the air inlet humidity should be as low as possible for our process, as this results in a lower outlet temperature which is required for further process steps. Greater moisture may also lead to the product adhering to the chamber walls more and so may result in a loss of yield. However, this should also be adjusted in accordance with other parameters to ensure the final product moisture is as required. The inlet air temperature was also set, but a range of inlet temperatures should be investigated, balancing the requirement for the product to not become denatured at temperatures too high with costing and product yield, as a greater temperature corresponds to quicker drying and less loss of product adhering to the chamber walls. The size of the whey powder particles required should also be investigated further, as this effects the required residence time. The rate at which the inlet feed was fed into the spray dryer per batch and the inlet pressure of the feed was set; a model should be developed to evaluate the optimum combination of inlet feed rate, air flow rate, air inlet temperature, inlet pressure and chamber volume which results in the lowest costs. The amount of heat loss also needs to be evaluated further to get a more accurate heat duty requirement for the inlet air stream, and further sizing needs to be performed to determine the required thickness and the optimum ratio of the cone volume and cylindrical volume. Losses of product in the outlet air stream as well as from adherence to the chamber walls also needs to be considered in the mass balances.

In the protein dissolution unit, the isoelectric point is assumed to be overcome by the rise in pH from NaOH and thus dissolving all the protein present, making it all available for reaction. The whey powder is also diluted by water to form a 10% by weight solution of whey powder in water.

In the methacrylation reactor, various assumptions were made which can be refined and re-evaluated in detailed design. Firstly, the methacrylation was assumed to occur on all protein, as the protein was assumed to be a largely composed of  $\beta$  lactoglobulin which is the primary reacting species. From literature, the conversion of the methacrylation reaction was taken to be 80%, with mole ratio of



methacrylic anhydride/protein of 6. Additionally, the amount of methacrylic moles produced in the reaction was taken to be the same as the moles of methacrylic anhydride reacted. The molecular mass of the protein was taken to be the same as the molecular mass of  $\beta$  lactoglobulin. The cooling duty for the reactor was assumed to be so minimal that negligible cooling water is needed. The salt formation by methacrylic acid and NaOH was also neglected in composition of the outlet stream. Finally, the reactor was assumed to be well mixed, no side reactions were considered, and the reaction was assumed to occur at standard temperature pressure (STP).

In the polymerisation reactor, the polymerisation is assumed to occur at a 90% conversion by mass with a reacting ratio by mass of 30:70 methacrylated protein:PEGMA. This is due to the lack of information on mole ratios in the reaction. The reaction was also assumed to occur at STP and in a well-mixed reaction with no side reactions or by products. The reaction is concluded to be endothermic through the bond enthalpies for the estimated bonds formed and broken in the reaction. The heating duty is then calculated and assumed to again be minimal to disregard the need for much heating water. APS and TEMED are taken as catalysts and initiator species that are consumed and then regenerated at 100% efficiency, meaning that the volume of APS and TEMED going in is the same as that going out of the reactor.

In the drum dryer, dimensions were assumed based on an average between two different models, one of area  $9.4\text{ m}^2$  and the other  $14.1\text{ m}^2$ , as the area required for the drum dryer is  $12\text{ m}^2$ . Optimisation could involve more detailed calculations to achieve more accurate dimensions, and optimum sizing may involve saving space and material requirements. The specific heat of the plastic could be determined through experimentation, rather than assuming the specific heat of PHB applies, and the required amount of water for the washing should be further investigated. Furthermore, more detailed calculations should be carried out to identify the proportion of impurities in the final product, as this was not determined. fSteam temperature could be optimised to determine whether lower temperatures are sufficient, thus saving on utility costs and environmental impact. Overall heat transfer coefficient could be determined through experimentation, or otherwise different values could be investigated, as the range assumed applicable to the plastic is between  $300$  and  $900\text{ W m}^{-2}\text{ K}^{-1}$ . The value chosen in initial design was  $600\text{ W m}^{-2}\text{ K}^{-1}$ , although this was an arbitrary choice, and further investigation is required to provide an optimised design. Temperature rising due to friction between the blade and the plastic or drum were neglected; whether this is justified may require research. Design of the vapour hood, which removes evaporated water, may be undertaken.

## Conclusion

The use of waste whey as the input to this process prevents use of a first-generation feedstock for bioplastic production, which is associated with competition with the food industry. In comparison to other methods of producing bioplastics from waste whey, such as through fermentation, this is a more simplified process with fewer process units. The process effectively utilises waste that smaller dairy farms may have otherwise had issues with treating/ disposing of and will provide jobs to stimulate the local economy. In comparison to conventional plastics, the use of fossil fuels is reduced, with 30% of the plastic being non-fossil fuel based. Ambient temperatures and pressures throughout the majority of the process provide an inherently safe design, but the many chemicals involved pose the greatest risks. With the number of batches and selling product price considered, the project does not break even throughout the plant lifetime, indicating that it is not economically feasible unless cheaper chemicals are utilised, more batches are carried out or the product is sold at a higher price. Therefore, to further improve this process, more research should be done into determining a safer more sustainable alternative to the co-polymer PEGMA, as this corresponds to many of the environmental impacts and hazards of the process, and it is responsible for a large proportion of the OPEX for the process. The biodegradability and the properties of the product should also be investigated further, and the design of the units further refined to ensure optimum operation of the plant.

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## Appendices

### Appendix A – Mock survey with mock answers

1. **How old are you? (18-25, 26-40, 40-55, 56+)**  
A variety of ages would be included in the survey.
2. **What is your profession? (technical/industry professional, consumer, environmental stakeholder )**  
A variety of professions would be included in the survey.  
**Bioplastics come in various forms based on their feedstock and their disposal method. The graph below shows the definition with combinations of characteristics biodegradable, non-biodegradable, bio-based and fossil-based. The following questions relate to the production of bioplastics and aim to get your opinion on different characteristics of these bioplastics as a consumer.**
3. **How important is having recyclable/biodegradable packaging to you, on a scale of 1-5?**  
On average, the majority of people are aware of the need of alternative packaging to plastics due to the global news showing the negative effects of plastic. We would expect the average answer to be 4 or 5, any anomalies may be due to worries about effectiveness.
4. **How important is having a bio-based (feedstock comes from renewable sources) package to you on a scale of 1-5?**  
We would expect the average answer to be 4 or 5, as most people are aware of the need to move away from non-renewable sources such as crude oil.
5. **How much extra would consumers be willing to pay for a product in bio-based packaging? (20p more, 50p more, £1 more, >£1 more)**  
There is likely to be a range in this question as the younger generations may be willing to pay more extra than older generations. This could be because of differences in financial priorities (I.e. providing for a family) or even societal impact (due to current sustainable trends). Expected to be 20p/50p more.
6. **Do you have any concerns about the implementation of bioplastics as packaging?**



Some concerns may be expressed about the functionality of the product, understanding of how they can be recycled and whether they will affect the shelf-life/quality of food.

If you are an technical/industry professional the following questions apply.

**7. What quantity of biopolymer/bioplastic is required yearly for your industry application? (1 tonne, 100 tonnes, 1000 tonnes, >1000 tonnes)**

In the UK it is estimated that five million tonnes of plastic is used every year, nearly half of which is packaging (Smith, 2022) Assuming 44.3% plastic used is in packaging (British Plastics Federation, 2017), this amounts to 2.22 million tonnes per year.

Sixty-five per cent of pollution from branded packaging in the UK can be attributed to 12 companies - Coca-Cola, PepsiCo, Anheuser-Busch InBev, McDonalds, Mondelez International, Heineken, Tesco, Carlsberg Group, Suntory, Haribo, Mars and Aldi (Malloy, 2021). Assuming an even share this gives them each 0.12 million tonnes a year. Asda for example produces 73,995 of waste per year.

Smaller companies could range anywhere from 1 tonne to 1000 tonnes depending on size.

**8. How important on a scale of 1-5 is transparency of bio-plastics?**

Expected answer of 3 or 4 as most companies would prefer visibility of the product in the packaging. However, many items such as mushrooms, snacks and frozen foods tend not to have clear packaging so it is not always necessary.

**9. How important on a scale of 1-5 are water resistant qualities of bio-plastic?**

5 – to be able to work as food packaging it needs to be water resistant to protect the item and the preserve it.

**10. Is rigid plastic or flexible plastic more desirable? 1 being rigid 5 flexible scale 1-5**

3 or 4 expected, most rigid plastics these days are recyclable whereas flexible films and packages are not. This question will depend on the type of item in mind.

**11. What form would you be looking to buy the plastic in; flakes, pre-made film or pellets?**

Depending on whether a company already has a partner who forms their products they may prefer it as the raw flakes instead of the film. Some may prefer pellets which would require minimal further processing.

If you are an environmental stakeholder answer the following questions apply.

**12. How much of a problem is recycling contamination on a scale of 1-5?**

5 expected, it causes major problems with the system, meaning around 4% of recycling is rejected due to contamination.

**13. Would industrially compostable or recyclable bioplastics solve the contamination issue? Yes or no or other**

Would expect no or other. The bioplastics would still need to be separated from the other plastics to be composted or recycled.

**14. How concerned are you about land competition between food and bio-plastic feedstocks on a scale of 1-5?**

Expected average of 4, there is concern about the use of possible food sources to create bio-plastics, as there is also the UN zero hunger goal to consider. Some bio-plastics like this one however use waste streams as a feedstock which avoids this problem.

**15. How much of a problem is “green-washing”?**

Expected average of 5, as it is misleading to consumers and causes problems with recycling as consumers think it can go in with the normal waste.

If they are supermarkets/other packaging industrial users

**16. Is rigid or flexible plastic used more in your business? (scale 1-5)**

**17. What weight of plastic do you use per year?**

900,000 tonnes of plastic packaging on shelves/year in all UK supermarkets (Greenpeace, 2019)

**18. How much of stock is own label?**

54% of supermarket sales are own-brand (Bold, 2014)

**19. How important is transparency of bioplastic in your business?**

Transparency is desired in consumer goods as it enables the packaging to show the food which is being displayed, however it is not so important that it will decrease the functionality of the packaging likely scores would be 3 or 4.

**20. How important are barrier properties to gas/vapor/aroma of bioplastic in your business?**

Very important as food spoilage must be prevented likely 4/5

**21. How important is lack of water permeability of bioplastic in your business?**



Very important as food spoilage must be prevented by water input and desiccation of the product, likely 4/5

**22. How important are thermal properties of bioplastic in your business?**

Would be important for defining which bioplastics are suitable for microwaveable/heat resistant applications likely around 3 in score.

**23. How important is the weight/thickness of packaging? (scale 1-5)**

The weight will be important for transportation of the plastic packaging and supermarkets will be eager to reduce costs in order to make the transportation of the packages both environmentally and cost friendly.

**24. Is a recyclable or compostable packaging more desirable?**

Though recyclable packaging might seem worse than compostable, some compostable packaging is only able to be composted in industrial composting plants, making programs such as packaging collections necessary for supermarkets, increasing costs and resource needed. Recyclable packaging also encourages the circular economy and discourages single-use plastics.

**25. How is packaging labelled?**

In order to ensure proper recycling it is important that the plastic is certified and labelled by the relevant government bodies to ensure that environmental benefits are not negated by wrongful disposal

**26. Do you have a packaging take-back program in place?**

Important for the same reason as 27 and 28

**27. What length of shelf-life should packaging be able to withstand without losing properties?**

Durability of plastic must be able to withstand shelf life and also at home storage without food spoilage, likely 4/5.

## Appendix B – Mass Balances for the spray dryer

$$\begin{aligned} \text{Water evaporation rate} &= \text{Water inlet} - \text{Water outlet} = \\ &= x_{\text{water},18} F_{18} - x_{\text{water},23} F_{23} = (0.612 \times 2.43) - (0.1 \times 1.045) = 1383 \text{ kg/batch} \end{aligned}$$

Water mass balance:

$$\text{Rate of water evaporation} = \text{Dry air mass rate} \times (\text{Final humidity} - \text{Initial humidity})$$

$$G(H_2 - 0.02) = 1383, G = \frac{1383}{H_2 - 0.02} \text{ kg dry air/batch}$$

Enthalpy of air inlet at a temperature of 150°C:

$$\text{Enthalpy of air in} = [0.24 + 0.46(0.02)]150 + 597(0.02) = 49.32 \frac{\text{kcal}}{\text{kg dry air}}$$

Enthalpy of air outlet at a temperature of 70°C:

$$\text{Enthalpy of air out} = [0.24 + 0.46H_2]70 + 597(H_2) = 16.8 + 629.2 H_2 \frac{\text{kcal}}{\text{kg dry air}}$$

Enthalpy of entering feed at a temperature of 25°C, considering the protein specific heat capacity of 0.3 kcal kg<sup>-1</sup> K<sup>-1</sup> (Yang and Rupley, 1979) and water specific heat capacity of 1.0 kcal kg<sup>-1</sup> K<sup>-1</sup> (Harrison et al., 2015). This assumes a constant heat capacity with temperature. The inlet feed is around 60% water and 40% solid, as indicated in the stream table (Table 5). Since the specific heat of the dry solids is known, the enthalpy of the solids and liquids is based on the weight of the dry solids:

$$\text{Enthalpy of entering feed} = (0.3 \times 25) + \left(1 \times 25 \times \frac{60}{40}\right) = 45 \frac{\text{kcal}}{\text{kg dry solids}}$$

Enthalpy of the product leaving the dryer at a temperature of 70°C (the product stream is around 90% solids and 10% water):



$$\text{Enthalpy of product leaving dryer} = (0.3 \times 70) + \left(1 \times 70 \times \frac{10}{90}\right) = 28.8 \frac{\text{kcal}}{\text{kg dry solids}}$$

Equating the rate of enthalpy in and the enthalpy out gives, multiplying the enthalpies determined by the corresponding flow rates:

$$49.32G + 45(0.9 \times 1045) = (16.8 + 629.2H_2)G + 28.8(0.9 \times 1045)$$

Substituting the equation for G given above into the equation, H<sub>2</sub> is determined as 0.0522. Therefore:

$$G = \frac{1383}{0.052 - 0.02} = 42883 \text{ kg dry air/batch}$$

$$\text{Rate of water vapour out} = 0.0522 \times 42884 = 2238.6 \text{ kg water/batch}$$

## Appendix C – Mass Balances per Batch for Node C

### Stream 24: Whey protein powder input

$$F_{24} = 1.04521 \text{ tonne/batch}$$

Density of whey powder: 0.38 g cm<sup>-3</sup> (Bruno De Carvalho-Silva et al., 2013)

If the density of WPC is taken to be 0.391 g cm<sup>-3</sup> then the volume occupied by the powder will be

$$1.04521 \text{ tonne/batch} \div 0.391 \text{ tonne/m}^3 = 2.673 \text{ m}^3/\text{batch}$$

### Stream 25: Water

10,000 L batch<sup>-1</sup> water = 10 m<sup>3</sup> batch<sup>-1</sup> water

Density of water = 997.05 kg/m<sup>3</sup> (Beaton et al., 1989).

The mass of water in stream 15, 9.9705 tonnes per batch, was calculated by using the density of water, 997.05 kg m<sup>-3</sup> at 25 °C and the amount of water needed per batch, 10 m<sup>3</sup> water.

$$F_{25} = 997.05 \text{ kg/m}^3 \times 10 \text{ m}^3/\text{batch} = 9970.5 \text{ kg/batch}$$

### Stream 26: Sodium Hydroxide (Merck, 2022e)

100 L of 10 M Sodium Hydroxide Solution = 0.1 m<sup>3</sup>

- Density of 10 M NaOH solution at 20 °C= 1.33 g/cm<sup>3</sup> = 1.33 tonne/m<sup>3</sup>
- pH = 14

Using the density of NaOH at 20 C, 1.33 tonnes m<sup>-3</sup>, and the amount of NaOH needed to reach a protein solution pH of 8 or 9, 0.1 m<sup>3</sup> of 10 M NaOH, the mass of NaOH required per batch was found 0.133 tonnes per batch NaOH.

$$F_{16} = 0.1 \text{ m}^3 \times 1.33 \text{ tonne/m}^3 = 0.133 \text{ tonnes/batch NaOH}$$

### Total Volume Occupied by liquids in Protein dissolution unit:

$$0.1 \text{ m}^3 + 10 \text{ m}^3 + 2.673 \text{ m}^3 = 12.773 \text{ m}^3 \text{ or } 12,773 \text{ L}$$

Stirred tank reactors are not designed to operate completely filled, 60% to 70% full is more typical. (Towler and Sinnott, 2013)

Thus the stirred vessel for protein dissolution volume is selected below:

$$12.773 \text{ m}^3 / 0.6 = V = 21.28 \text{ m}^3$$



Cylindrical Stirred Tanks optimal geometry should lie at a liquid level to diameter ratio of 1 (L/D=1) (Couper et al., 2012b)

$$\pi \times \frac{D^2}{4} \times D = 12.773 \text{ m}^3$$

$$D = 2.53 \text{ m}$$

Then, adding the additional headspace of 60% filled vessel, so that the total volume is 21.28 m<sup>3</sup>, the height of the vessel H is found

$$\pi \times \frac{2.53^2}{4} \times H = 21.28 \text{ m}^3$$

$$H = \frac{4}{\pi \times 2.53^2} \times 21.28 \text{ m}^3 = 4.23 \text{ m height}$$

Thus, the vessel should have a diameter of 2.53 m and height of 4.23 m.

#### Stream 27: Dissolved whey protein powder

$$\text{Total mass inlet} = F_{24} + F_{25} + F_{26} = 1.04521 + 9.9705 + 0.133 = 11.1471 \text{ tonnes/batch}$$

#### Stream 28: Methacrylic Anhydride

50 L (= 0.05 m<sup>3</sup>) of Methacrylic Anhydride is added to the dissolved whey thus the mass of methacrylic anhydride is calculated using the density at 25°C, 1.035 tonnes m<sup>-3</sup>, 0.05175 tonnes batch<sup>-1</sup>.

Density: 1.035 g/mL = 1.035 tonnes/m<sup>3</sup> (Merck, 2022b)

pH: 4 (European Chemicals Agency, 2022)

$$F_{18} = 1.035 \text{ tonnes/m}^3 \times 0.05 \text{ m}^3 = 0.05175 \text{ tonnes/batch}$$

#### Stream 29: NaOH

125 L of 10 M NaOH solution is added to prevent the methacrylic acid produced in the reaction from causing protein precipitation by lowering the pH. Using the same density as above, the mass of NaOH per batch is found

$$125 \text{ L} = 0.125 \text{ m}^3 \text{ NaOH}$$

$$F_{19} = 0.125 \text{ m}^3 \text{ NaOH} * 1.33 \text{ tonne/m}^3 = 0.16625 \text{ tonne/batch}$$

#### Stream 31: PEGMA (liquid) (Merck, 2022d)

2300 L (2.3 m<sup>3</sup>) of PEGMA is added

- Density at 25°C = 1.05 g/mL = 1.05 tonne/m<sup>3</sup>
- pH = 7 (Same as water)

$$F_{21} = 1.05 \text{ tonnes/m}^3 \times 2.3 \text{ m}^3 = 2.484 \text{ tonnes/batch}$$

#### Stream 32: Ammonium Persulphate (APS) (powder) (NCBI, 2022a)

92 L = 0.092 m<sup>3</sup>

pH=1-2

Density=1.98 g/cm<sup>3</sup> = 1.98 tonne/m<sup>3</sup>

$$92 \text{ L APS} \times 1.98 \text{ tonnes/m}^3 = 0.1748 \text{ tonnes APS/batch}$$



### Stream 33: TEMED (Merck, 2022d)

$$4.6 L = 0.0046 m^3$$

- Density at 20 °C = 0.775 g/mL = 0.775 tonne/m<sup>3</sup>

$$F_{23} = 0.0046 m^3 \times 0.775 \text{ tonne}/m^3 = 3.565 \times 10^{-3} \text{ tonnes}/batch$$

### Polymerisation reaction calculations

The polymerisation is assumed to have a conversion of 90% from literature as specified in the report and the chosen ratio of methacrylated protein:PEGMA by mass is taken to be 30:70. By using the mass of methacrylated protein, the mass of PEGMA reacted can be found using the mass ratio.

$$0.769 \text{ tonnes methacrylated protein} * 0.9 * 0.3/0.7 = 1.615 \text{ tonnes PEGMA}$$

Then, the mass of unreacted methacrylated protein and unreacted PEGMA is found.

$$\begin{aligned} 0.769 \text{ tonnes methacrylated protein} - 0.769 \text{ tonnes methacrylated protein} * 0.9 \\ = 0.0769 \text{ tonnes unreacted protein} \end{aligned}$$

$$2.415 \text{ tonnes PEGMA} - 1.615 \text{ tonnes PEGMA reacted} = 0.7998 \text{ tonnes unreacted PEGMA}$$

The mass of polymerised content is taken to be the sum of the PEGMA and methacrylated protein reacted.

$$0.692 \text{ tonnes methacrylated protein} + 1.615 \text{ tonnes PEGMA} = 2.307 \text{ tonnes polymer}$$

Mass balances for the rest of the components of the stream are within the stream table (Table 5).

### Stream 34: Polymerised content

Sums of streams 30, 31, 32, and 33

$$F_{34} = 11.36671 + 2.415 + 0.1748 + 0.003565 = 13.960075 \text{ tonnes}/batch$$

## Appendix D – Mass balance calculations for node D

### Washing

Fraction of impurities in wash out (stream 36):

$$x_{impurities,36} = \frac{F_{impurities,36}}{F_{36}} = \frac{1.262 \text{ tonnes}}{24.08 \text{ tonnes}} = 0.05241$$

Therefore, the water fraction in wash out is:

$$x_{water,36} = 1 - 0.05241 = 0.9476$$

As 80% of the impurities are removed in the washer waste, 20% of the impurities remain in the polymer stream.

Fraction of impurities in washed polymer stream (stream 37):

$$x_{impurities,37} = \frac{F_{impurities,37}}{F_{37}} = \frac{13.96 \times 0.113 \times 0.2}{12.7} = 0.0248$$

Assuming no water content from the inlet stream is lost in the washer waste, the water in stream 34 is the same as in stream 37. Therefore:

Fraction of water in washed polymer stream (stream 37):



$$x_{water,37} = \frac{F_{water,37}}{F_{37}} = \frac{13.96 \times 0.722}{12.7} = 0.794$$

Therefore, the fraction of polymer in the washed polymer stream (stream 37) is calculated as:

$$x_{polymer,37} = 1 - x_{impurities,37} - x_{water,37} = 1 - 0.0248 - 0.794 = 0.1812$$

### Centrifuge

Flow of water in stream 39:

$$F_{water,39} = 0.4 \times 3.81 = 1.524 \text{ tonne/batch}$$

Hence, the mass of water in the centrifuge waste, stream 38, is determined as:

$$F_{water,38} = F_{water,37} - F_{water,39} = (13.96 \times 0.722) - 1.524 = 8.555 \text{ tonnes/batch}$$

The remaining mass of stream 38 is composed of polymer and impurities:

$$F_{polymer \text{ and } impurities,38} = F_{38} - F_{water,38} = 8.89 - 8.555 = 0.355 \text{ tonnes/batch}$$

## Appendix E – Sizing of the spray dryer

Determining total flow of wet air, assuming the molecular weight of dry air to be 28.3 g/mol (Harrison et al., 2015), the pressure is atmospheric, and the outlet temperature of 70°C.

$$\rho = \frac{P \times M_W}{R \times T} = \frac{1[\text{atm}] \times 28.3[\frac{\text{g}}{\text{mol}}]}{82.06 \left[ \frac{\text{cm}^3 \text{atm}}{\text{mol K}} \right] \times 343.15 [\text{K}]} = 1.005 \times 10^{-3} \frac{\text{g}}{\text{cm}^3} = 1.005 \frac{\text{kg}}{\text{m}^3}$$

From this, the total volumetric flow of wet air can be determined from the dry mass air flow and water vapour mass flow out:

$$\frac{42884 + 2238.6 \left[ \frac{\text{kg}}{\text{h}} \right]}{1.005 \left[ \frac{\text{kg}}{\text{m}^3} \right]} = 45122 \frac{\text{m}^3}{\text{batch}}$$

Using a residence time of 35 seconds and assuming a batch time of 4 hours:

$$v = 45122 \left[ \frac{\text{m}^3}{\text{batch}} \right] \times \frac{1}{3600 \times 4} \left[ \frac{\text{batch}}{\text{s}} \right] \times 35 [\text{s}] = 110 \text{ m}^3$$

$$h = 3D, h_{cylinder} = \frac{3}{4} \times 3D = \frac{9}{4}D, h_{cone} = \frac{1}{4} \times 3D = \frac{3}{4}D$$

*Total volume = volume of cylindrical section + volume of cone section*

$$110 = \pi r^2 h_{cylinder} + \frac{1}{3} \pi r^2 h_{cone}$$

Substituting in values and rearranging:

$$0 = 1.9625D^3 - 110$$

Solving this cubic equation, the only real solution is D = 3.83 m. Therefore, the diameter is 3.83 m, the total height 11.5 m, the height of the cylindrical section 8.6 m and the height of the cone section 2.9



## Appendix F - Sizing of Methacrylation reactor

The methacrylation vessel should be a stirred reactor, designed much like the protein dissolution vessel with 60% filled with liquid and a liquid level to diameter ratio of 1 (L/D=1). Because the extent of methacrylation is crucial for the later polymerisation reaction, as the methacrylation forms the monomers that are then polymerised with PEGMA the agitation of the mixture is crucial once the methacrylic anhydride is added. (Chan et al., 2017)

The NaOH is added after the methacrylic anhydride reacts with the protein as methacrylic acid produced by the reaction can cause protein precipitation due to the lowering of the solution pH

The total volume handled by the methacrylation vessel is the sum of streams 17, 18 and 19.

Stream 27: 12.773 m<sup>3</sup> (from protein dissolution)

Stream 18: 0.05 m<sup>3</sup> (Methacrylic Anhydride)

Stream 19: 0.125 m<sup>3</sup> (NaOH)

Total volume:

$$12.773 + 0.05 + 0.125 = 12.948 \text{ m}^3$$

Stirred tank reactors are not designed to operate completely filled: 60% to 70% full is more typical.

Cylindrical Stirred Tanks optimal geometry should lie at a liquid level to diameter ratio of 1 (L/D=1) (Couper et al., 2012b).

If the vessel is only 60% full and the liquid height to diameter ratio is one, finding the diameter:

$$\sqrt[3]{\frac{12.948 \text{ m}^3 \times 4}{\pi}} = D = 2.54 \text{ m}$$

Then adding the additional headspace and finding the height

$$\frac{12.948}{0.6} = 17.76 = \pi \times \frac{2.54^2}{4} \times H$$

$$H = 4.259 \text{ m} = 4.26 \text{ m}$$

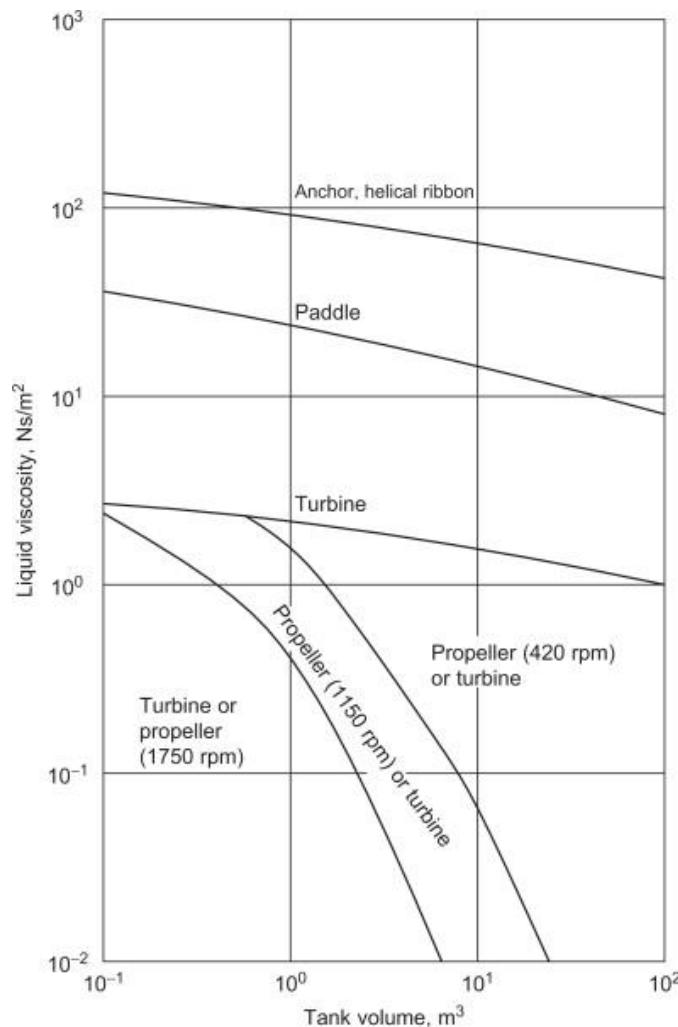
Thus, the height of the vessel should be 4.26 m and diameter of 2.54 m.

Baffles should be added to aid mixing and prevent vortex forming. From Literature, Baffle width should be 1/12 of the diameter of the vessel (Couper et al., 2012a) with four baffles in total at each quadrant of the cylinder. Thus, Baffle width should be 0.2m.

A stirrer should also be added to facilitate mixing and ensure a well mixed condition to maximise methacrylation. For selection of the stirrer, the viscosity of the liquid and the volume of the vessel should be taken into account using the agitator selection guide, Figure F1: (Couper et al., 2012a)

The liquid viscosity is taken to be about equal to that of 2.63 mPa s or 0.00263 Ns/m<sup>2</sup> at 25 °C which is the density of WPC solutions of 10 weight %, corresponding to the dilution in protein dissolution phase(González-Tello et al., 2009).

Thus, the selected agitator should be a turbine or propeller at 1750 rpm



To promote a well mixed vessel, and due to the low viscosity of the solution, a 6 bladed Rushton turbine shall be used ( disk with vertically mounted plates) with a width of  $D/3 = 0.8 \text{ m}$  and placed at a depth of 0.8 m from the bottom of the tank, as per stirred tank design recommendations (Couper et al., 2012a).

*Figure F1: Agitator Selection Chart*

## Appendix G – Sizing of Polymerisation Reactor

Total Volume in polymerisation reactor from mass balance sum of streams 30,31,32, and 33:  $12.948 \text{ m}^3 + 2.3 \text{ m}^3 + 0.092 \text{ m}^3 + 0.0046 \text{ m}^3 = 15.3446 \text{ m}^3$

Following the same process as for the methacrylation reactor:

Finding the diameter (equal to liquid level):

$$\sqrt{\frac{15.3446 \text{ m}^3 \times 4}{\pi}} = 2.69 \text{ m}$$

Finding the height of the stirred tank when the vessel is 60% full

$$\frac{13.0516}{0.6} = 25.574 = \pi \times \frac{2.69^2}{4} \times H$$



$$H = 4.49 \text{ m}$$

Thus the tank should be 2.69 m in diameter and 4.49 m in height.

As in the methacrylation reactor, baffles will be added with a width of  $D/12= 0.2$  m wide and as tall as the liquid level. Again and for the same reasons as above, a 6 bladed Rushton turbine shall be used (disk with vertically mounted plates) with a width of  $D/3= 0.9$  m and placed at a depth of 0.9 m from the bottom of the tank, as per stirred tank design recommendations (Couper et al., 2012a)



## Appendix H: Design Project Gantt Chart

Figures H1 and H2 shows the Gantt chart that we used to plan and delegate tasks over the course of the design project.

Task No	Task	Responsible	08-Feb	09-Feb	10-Feb	11-Feb	14-Feb	15-Feb	16-Feb	17-Feb	18-Feb	21-Feb	22-Feb	23-Feb	24-Feb	25-Feb	26-Feb	27-Feb
	Regular Meeting	All	Done	Done		Done					Done		Done					
	Supervisor Meeting	All			Done					Done				Done				
	Lectures	All	Done											Done	Done			
<b>1 Scoping Report</b>	All													Done				
1.1 Market Need Research	AW,CMC,FU								Done									
1.2 Technological Research	AR,EV,EJ,JOT								Done									
1.3 Economics and Risk Analysis	All										Done							
1.4 Consolidate information	All															Done		
1.5 Write Report/ Reference	All																	Done
<b>2 Group Report</b>	All																	
2.1 Executive Summary	AW, CMC																	
2.2 Introduction	AW,EV																	
2.3 Process Design	All																	
<b>2.3.1 Pre-Treatment of Whey</b>	FU																	
2.3.1.1 Mass Balance	FU																	
2.3.1.2 Energy Balance	FU																	
2.3.1.3 Process Conditions	FU																	
2.3.1.4 Stream Table	FU																	
2.3.1.5 Specification Sheet	FU																	
2.3.1.6 Material Selection	FU																	
<b>2.3.2 WPC Production</b>	AW, EV																	
2.3.2.1 Mass Balance	AW, EV																	
2.3.2.2 Energy Balance	AW, EV																	
2.3.2.3 Process Conditions	AW, EV																	
2.3.2.4 Stream Table	AW, EV																	
2.3.2.5 Specification Sheet	AW, EV																	
2.3.2.6 Material Selection	AW, EV																	
<b>2.3.3 Chemical Processing</b>	EJ, CMC																	
2.3.3.1 Mass Balance	EJ, CMC																	
2.3.3.2 Energy Balance	EJ, CMC																	
2.3.3.3 Process Conditions	EJ, CMC																	
2.3.3.4 Stream Table	EJ, CMC																	
2.3.3.5 Specification Sheet	EJ, CMC																	
2.3.3.6 Material Selection	CMC																	
<b>2.3.4 Production of Plastic</b>	AR																	
2.3.4.1 Mass Balance	AR																	
2.3.4.2 Energy Balance	AR																	
2.3.4.3 Process Conditions	AR																	
2.3.4.4 Stream Table	AR																	
2.3.4.5 Specification Sheet	AR																	
2.3.4.6 Material Selection	AR																	
2.4 Refine PFD	CMC																	
2.5 PFD	EJ															Done	check	
2.6 General P&ID	CMC																	
2.7 HAZID study	All																	
2.8 Node P&ID	CMC																	
2.9 HAZOP	All																	
2.10 Plant Layout	JOT																	
2.11 Economic Analysis	EJ, FU																	
2.12 Environmental Impact	EW, AR																	
2.13 Start-up & Shut-down	JOT																	
2.14 Sustainability	EW, AR																	
2.15 Conclusions	EW																	
2.16 Reference list	CMC																	
2.17 Final editing	All																	
<b>3 Presentation</b>	All																	
3.1 Introduction	AW																	
3.2 Market Need Research	AW																	
3.3 Choosing Options	EV																	
3.4 The Process	FU																	
3.5 Mass & Energy Balances	FU																	
3.6 Economics	EJ																	
3.7 Safety & Operability	CMC																	
3.8 Plant Layout	JOT																	
3.9 Environmental Impact	AR																	
3.10 Create Slides	All																	

Figure H1: Gantt chart from 8<sup>th</sup> Feb to 27<sup>th</sup> Feb



*Figure H2: Gantt Chart from 28<sup>th</sup> Feb to 22<sup>nd</sup> March*



## Appendix I: Meeting Diary

Table I shows the group meeting diary for the duration of the group design project.

*Table I: Meeting Diary*

Meeting Number	Date	Time	Areas of Discussion	Attendance	Result
1	08/02/2022	13:00	Preliminary research, agenda for meeting with supervisor and initial thoughts on the project.	All team members attended either online or in person apart from one unavoidable absence.	Team commitment activity and required activity for the first supervisor meeting was completed. Initial thoughts and research discussed.
2	09/02/2022	10:00	Further discussed any doubts we had on the project and the agenda for first meeting with supervisor.	All team members attended online apart from one unavoidable absence.	Split group into market research team and technology research team. Finalised agenda for first supervisor meeting.
3	10/02/2022	15:00	First meeting with supervisor. Discussed progress and initial questions and thoughts.	Apologies from Claudia, Emily and Jordan	A Gantt chart is required. Initial questions answered.  Meeting chair notetaker and apologies should be included in supervisor meeting agendas.
4	11/02/2022	10:00	Feedback from first supervisor meeting. Initial Gantt chart creation.	All members present online	Draft Gantt chart created, and provisional deadlines set.
5	14/02/2022	12:00	Progress update and discussion of how to compile all research into scoping report	All members present either online or in person	Discussion of the research carried out so far and how we'll compile it into the scoping report
6	16/02/2022	10:00	Progress update and discussion of tasks following.	Apologies from Alex and Jordan	Check over material done for scoping report and if time, begin research on risk and economics



			Prep for meeting with Carmelo		
7	17/02/2022	14:00	Second meeting with Supervisor	All members present either online or in person	Discuss option chosen and project scoping report.
8	21/02/2022	10:30	Group meeting to discuss progress.	Evan, Emily, Claudia and Alice. Apologies from Alex, Fahim and Jordan	Split process into sections and delegated between members. Finalise scoping report for submission.
9	23/02/2022	11:00	Group meeting, discuss finalising	Apologies from Jordan.	Discussed next steps in design after scoping report.
10	24/02/2022	2:00	Supervisor meeting to discuss feedback from scoping report.	Apologies from Jordan.	Discussed improvements required and next steps.
11	28/02/2022	10:00	Group meeting before supervisor meeting.	Apologies from Fahim and Jordan.	Discussed P&ID and mass and energy balances.
12	28/02/2022	2:00	Supervisor meeting to ask questions about mass and energy balances.	Apologies from Jordan.	Increased understanding about work required.
13	2/03/2022	10:00	Start HAZID	Apologies from Evan.	Completed first draft of HAZID.
14	2/03/2022	3:00	Full group meeting to discuss mass balance complications.	All members present.	Solved complications and assigned new tasks.
15	3/03/2022	10:00	Supervisor meeting to HAZID and P&ID.	All members present.	Corrections required discussed.
16	4/03/2022	10:00	Mass and energy balance discussion.	All members present.	Made further progress



17	7/03/2022	10:00	HAZOP	Apologies from Fahim.	Completed HAZOP.
18	8/03/2022	2:00	Supervisor meeting to discuss HAZOP and mass balances.	Apologies from Jordan and Alex.	Queries about mass balances and HAZOP have been answered.
19	11/03/2022	12:00	Presentation	All members present	Decided which group member would present different topics during the presentation
20	14/03/2022	10:30	Supervisor meeting to discuss presentation	Apologies from Fahim and Jordan	Received feedback from supervisor on recommended changes to make to presentation
21	18/03/2022	10:15	Progress update and plans for finalising report	All members present online	Plan to have all content written up by Saturday night (19/03/2022)
22	20/03/2022	12:10	Proof reading and final editing	Alice, Emily, Claudia and Evan present online	Plan to have report ready to be submitted by Monday (21/03/2022) night