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Efficiency of aqueous oleosome extraction from capsicum seeds compared to classical oil extraction

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HIGHLIGHTS

- The yield of oleosome extraction from capsicum seeds was 66.96 wt%
- The total exergy loss for the pre-optimised oleosome process is 31.4 GJ, about twice the value of the conventional route.
- Oleosome extraction yield can be increased to 90 wt%
- Oleosome extraction can be more resource-use efficient compared to oil extraction.

ABSTRACT

The extraction of oil from oilseeds in intact oleosomes is one of the suggested processes that could replace the extraction of oil by pressing and solvent extraction, being milder, environmentally less impactful and potentially more efficient in its use of resources. This study assesses the latter using an exergy assessment of oleosome extraction for food emulsions. The contribution of each part of the process to the overall impact was investigated. Based on current lab-scale data, oleosome extraction has nearly twice the exergy loss compared to the industrial process of oil extraction and industrial assembly of emulsions. The exergy losses of the lab-scale oleosome extraction are currently dominated by the chemical exergy associated with product loss during the separation of oleosomes from the rest of the biomass. This loss is expected to significantly decrease when upscaled to industrial scale. When substituted with industrial material efficiencies, the total exergy loss decreased to nearly a quarter of the original loss, representing oleosome extraction as a potentially more effective and environment-friendly option.

1. Introduction

Since in the coming decades a global population of up to 10 billion must be sustained using the same amount of cropland that is deployed today (Searchinger et al., 2019), developing resource-efficient agri-food processes is essential. Industries are therefore investigating new methods to more completely utilise their raw materials (Valdez-Morales et al., 2021). The extraction of pigments from the pericarp of capsicum fruits leaves the seeds which can constitute 45–50 % of the original dry weight (Chouaibi et al., 2019; Gu et al., 2017), which at present is mostly discarded directly or used as low-value animal feed, leaving an obvious opportunity for better use of the raw material (Lie-Piang et al., 2021).

Traditionally, food processors aim to extract pure components to obtain highly functional and versatile ingredients. However, this approach leads to redundancy and inefficiency, as pure ingredients are usually recombined with other components during product formulation. To reduce the overall footprint, one can therefore extract lower-purity fractions that have similar functionalities to pure ingredients (McClements, 2020).

Classical oil extraction from oil-bearing seeds is typicaly done by pressing followed by solvent extraction. However, one can also extract the oil as an aqueous emulsion fom the seeds. This can be done by steeping the seeds in water, and then pressing the juice. This can for example be done ujsing a twin-screw press (M. J. Romero-Guzmán et al., 2020, b). This aqueous extraction preserves the natural oil droplets, called oleosomes, as well as their function as a natural emulsion. Oleosomes consist of a triacylglycerol core surrounded by a sophisticated membrane of phospholipids and proteins, that protects the oleosomes against external stresses in the seed cell (Tzen, 2012). Phospholipids and

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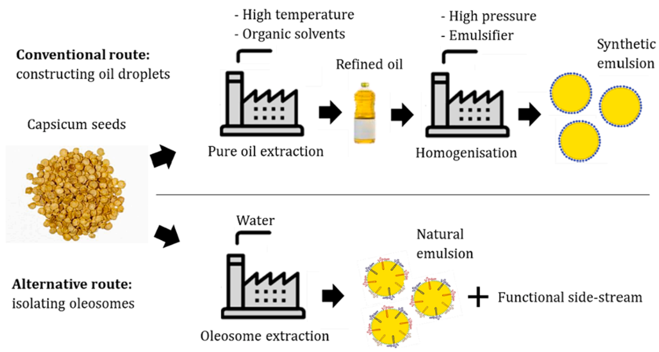

Fig. 1. Conventional and alternative process route for oil-in-water (O/W) emulsions.

proteins arrange themselves at the oleosome interface in a structure similar to synthetically emulsified oil droplets with comparable physicochemical stability (Chen et al., 2012; Nikiforidis, 2019). As oil-in-water emulsions are conventionally have to be prepared by homogenisation, the method is a potential shortcut to obtain a comparable product with lower resource use, as it does not require the use of solvents and does not need the emulsification step at all, since all dairy and most meat analogues are formulated using plant oil in an emulsified form (Kyriakopoulou et al., 2021). Additionally, the mild processing conditions preserve the side stream's functionality, suggesting high sustainability potential (Lie-Piang et al., 2021).

Applying mild processing conditions results in lower oil yields compared to conventional extraction methods. Twin-screw pressing rapeseeds and centrifuging the extract allowed for an oleosome recovery about 63 wt% (M. J. Romero-Guzmán et al., 2020, b), where organic solvent percolation can achieve oil yields of over 95 wt% (Avram et al., 2014). From a sustainability standpoint, investing in an oleosome extraction process only makes sense if the entire process, including side-stream use, is more resource-efficient than the route following traditional pure oil extraction.

Therefore, the objective of this study is to quantify the resource use of both production routes, Fig. 1, and evaluate the potential of aqueous oleosome extraction to valorise capsicum seed material. The quantification will be performed using exergy analysis. Exergy is a sustainability indicator in which multiple types of resources are expressed into one single unit (the Joule), enabling the comparison of processes using different materials, machines, and fuels (Zisopoulos et al., 2017). The study finalises with a performance prediction based on different optimisation scenarios, providing a suggestion for further studies.

2. Materials and methods

2.1. Materials

Capsicum seeds were provided by Chenguang Biotech Group (Quhzou, China). Besides the collection of seeds from different capsicum varieties, the material contained a small fraction (10 wt%) of red flakes. Further details on storage and harvesting conditions were not provided. The ultra-pure water (MilliQ) was obtained by a Merck Millipore device (Darmstadt, Germany).

2.2. Methods

2.2.1. Aqueous extraction of oleosomes

Raw capsicum seeds were steeped for one hour in ultrapure water. 300 g of raw capsicum seeds were soaked using ultrapure water in a 1:1 ratio (m_{seed}/m_{soak}), stirring every 10 min. The seeds were introduced into a lab-scale twin-screw press (Angel 7500 extractor) without draining, in a step-by-step fashion, collecting two separate fractions: a liquid extract and a solid press cake. The rotational velocity of the screws was 82 rpm. The extract was centrifuged (8000 g, 30 min, 4 °C) (Sorvall Legend XFR, ThermoFisher Scientific, Waltham, MA, USA), and the cream layer was collected. The material was drained from the excess solution using filter paper and the remaining pellet and serum (supernatant) fraction were separated by simple decantation. All experiments were done in triplet, determining the mass of the fractions using an analytical balance.

2.2.2. Characterization of streams

2.2.2.1. Moisture content. To determine the moisture content the sample weight was measured before and after 36 h drying in an oven (Memmert, Memmert GmbH & Co.KG, Schwabach, Germany) at 70 °C. Prior to drying, the seeds were milled and sieved using a pore size of 1.6 mm.

2.2.2.2. Protein content. The serum, pellet, and extract were freeze-dried rather than oven-dried to avoid amino acid loss, as they had a moisture content >60 %. The remaining fractions were dried as described in the moisture content analysis. Protein content was determined using the DUMAS method, combusting dry samples at high-temperature in the range of 800–900 °C, where aspartic acid was used as a standard for the calibration, and a conversion factor of 5.7 was used for the nitrogen content.

2.2.2.3. Lipid content. All fractions were dried as described in the moisture content analysis. Again, the seeds were milled and sieved, now using a pore size of 25 mm. For the other fractions, the solvent contact area was increased by crushing the material into a powder using mortar and pestle. Dry matter lipid content was determined using the Soxhlet method, extracting oil for 14 hr using petroleum ether as solvent (B-811 Buchi Extractor, Switzerland). Oil and protein content were calculated using Eq. (1).

$$\text{oil/protein content (wt\%)} = 100 * \left(\frac{\text{g of extracted oil/protein}}{\text{g of initial sample}}\right) \quad (1)$$

3. Theory and calculation

3.1. Theory

3.1.1. Theoretical pure oil process sequence

The industrial production of pure oil from capsicum seeds has been

Table 1
Heuristics and assumptions used in determining the process sequence for pure oil extraction from capsicum seeds.

The mass flow is continuous.
The goal is large-scale industrial oil production, not the creation of a specialty product.
Alternative technology improving operational efficiency (e.g. supercritical fluids, enzyme or membrane-assisted technology) were not considered.
All process stage (crude oil extraction, refining and emulsion construction) are carried out at the same plant location in direct succession.
The decisions for equipment type and process conditions were based on the physical and chemical properties of the seed when applicable.
When a unit operation was identical for both process routes (i.e. equal exergy losses), it was left out of the analysis.
Some process conditions were obtained from sources that were specified to a single oilseed (e.g. soybean, cotton, sunflower), rather than from general oil processing descriptions. These conditions assumed to be valid for the capsicum process too, without further investigation.

mentioned before, but currently there are no sources available that discuss the specifics of its manufacturing process (Campos-Vega, R., Oomah, B.D., & Vergara-Castaneda, 2020). Therefore, a hypothetical process was constructed combining information from other oilseeds, such as soybean, rapeseed, and sunflower seeds. The heuristics and assumptions used for the design are listed in Table 1.

3.1.2. Exergy

Exergy is a state variable that quantifies the usefulness (potential to do work) of a resource based on the first two laws of thermodynamics (Zisopoulos et al., 2017). It is especially relevant when comparing processes with different mass, fuel and heat flows because all resources are expressed into one single quantity. As it has proven itself as a useful predictor of real-time resource use for industrial processes, such a thermodynamic assessment is a good first step in designing sustainable production chains (Zisopoulos et al., 2017).

Exergy quantifies the potential usefulness of a stream or resource. Thermal exergy differs from thermal enthalpy in the sense that enthalpy simply describes the heat content of a certain flow, irrespective of temperature, where exergy includes the concept of heat quality. It takes into account that a stream with a higher temperature can do more, as it can heat materials to a wider range of temperatures. The quantification is always done in relation to a reference environment, defined by the (local) ambient temperature, atmospheric pressure, relative humidity, and a number of basic substances, e.g. CO_2 and H_2O (in air) (Saidur et al., 2010). The more a resource differentiates from the reference environment, the larger the exergy value. A resource that is in equilibrium with the reference environment has no potential to do work by exchange with this environment and is therefore assigned a zero exergy value.

Within this framework, exergy streams are categorised as follows:

3.1.2.1. Chemical exergy. The standard chemical exergy describes the energy stored in the bonds and structure of molecules, representing the work required to create a substance from basic substances present in the standard environment, e.g. CO_2 and H_2O (in air). For many substances, the standard chemical exergies are tabulated (Morris & Szargut, 1986).

3.1.2.2. Physical exergy. The physical exergy represents the thermal and pressure gradients of streams with respect to the reference environment. Physical exergy includes also other forms of energy, such as kinetic, potential, and surface tension, but in practice, these can often be neglected due to their small size compared to other forms of exergy. Physical exergy includes electrical exergy, which in contrast to other forms is fully utilizable (Zisopoulos et al., 2017), meaning its exergy content is equal to its energy content.

3.2. Calculation

3.2.1. Equations of required utility streams

Based on the theoretical process description the size of the required steam, air, refrigeration fluid and cooling water flows to achieve all heating, cooling, and drying duties were calculated using mass and enthalpy balances, Eqs. (2) and (3),

$$\sum m_{in} - \sum m_{out} = 0 \tag{2}$$

$$\sum (mh)_{in} - \sum (mh)_{out} = 0 \tag{3}$$

where m is the mass (kg) and h is the enthalpy (kJ/kg). The enthalpies of the in and outgoing streams was calculated using Eqs. (4)–(6),

$$h_{solid/liquid/gas} = c_p(T - T_0) \tag{4}$$

$$h_{vapour} = c_{p.liquid}(T_{boil} - T_0) + \Delta h_{ev} + c_{p.gas}(T - T_{boil}) \tag{5}$$

$$h_{moist.air} = x_{air} c_{p.air} T + x_{moisture}\left(\Delta h_{air.moisture} + c_{p.watervapor} . T\right) \tag{6}$$

where c_p is the specific heat capacity (kJ/(kg.°C), T_0 is the temperature of the reference state, Δh_{ev} is the heat of evaporation (kJ/kg) and x is the mass fraction. Vapours are defined as substances that are liquid at ambient temperature (e.g. water), while gases are defined as substances that are in a gas state at ambient temperature (e.g. oxygen). C_p and Δh_{ev} values for the relevant components are listed in Appendix A.

The c_p for seeds and other biomass streams were estimated from its proximal composition according to Eq. (7), based on Ref. (Karel & Lund, 2003).

$$c_p(x_c, x_p, x_o, x_s, x_w) = (1.42 . x_c + 1.549 . x_p + 1.675 . x_o + 0.837 . x_s + 4.187 . x_w) \tag{7}$$

$_c$, x_p, x_o, x_s and x_w are the mass fractions of carbohydrates, proteins, oils, ashes and water, respectively, and c_p is in J/(kg.K).

3.2.2. Default heating and cooling mechanisms

Heating and cooling operations were simplified by assuming co-current heat exchangers. Counter-current heat exchangers are more energy-efficient (Boom, 2022; Knissel & Peußner, 2018).

For heating <80 °C, steam of 100 °C is condensed at atmospheric pressure. The heat of condensation released by the phase change is the only heat that is exchanged, meaning that the condensate exits at 100 °C and 1 atm, and is assumed to be re-boilde into steam.

For heating >80 °C, steam of $T_{p,end}$ + ΔT_{min} is condensed at the saturation pressure. Here, $T_{p,end}$ is the temperature of the product upon exiting a unit operation. The ΔT_{min} is 20 °C and ensures heat transfer rates remain sufficiently high for industrial settings (Léonard et al., 2016). The heat of condensation released by the phase change is the only heat that is exchanged, meaning the condensate exits at the same temperature as the steam enters.

For cooling <50 °C, liquid ammonia enters at its boiling point of –33.3C, vaporises, and leaves at the same temperature (Ayub, 2006). Only the heat of evaporation is exchanged, and the vapor is recondensed in a compressor. The required electricity is calculated by dividing the total heat removed by its coefficient of operation, which is estimated at approximately 2.0 for industrial refrigerators (Bansal & Martin, 2000; Boom, 2022).

For cooling >50 °C, cooling water from a storage tank at ambient temperature enters the heat exchanger and heats up to 40 °C. The existing cooling water is returned to the storage tank, where it cools down to ambient temperature by conduction through the tank walls.

3.2.3. Air drying

The temperature decrease as a result of moisture uptake is predicted by the adiabatic lines in a conventional Mollier diagram (Air drying with Mollier diagram). For effective drying without recondensation, the moisture in the air cannot exceed 60 % of its maximum moisture-holding capacity (RH <60 %) (Boom, 2022). Assuming drying air is provided at a temperature of 140 °C and the environmental air moisture content (w_0) is 0.008 kg water/kg air (Boom, 2022), following the adiabatic line to RH = 60 % gives an air moisture content (w_{out}) of 0.0495 kg/kg. The amount of drying air required then follows from Eq. (8).

$$m_{air} = (m_{product.in} . x_{w.in} - m_{product.out} . x_{w.out}) / (w_{out} - w_0) \tag{8}$$

3.2.4. Makeup water

The steam condensing in the heat exchangers is recycled to the boilers. After giving off its heat, the condensate is discharged and lowered from the load pressure to the system's condensate pressure. As a result, steam flashes and is exhausted into the environment. The lost material is equalised by a stream called makeup water, which enters the boiler at ambient temperature, meaning the heat required to recreate the steam increases. The amount of flash steam from the condensate is

Table 2
List of standard chemical exergies.

Material	Standard chemical exergy (b_0) (J/kg)	Ref.
Water (l)	5.000E + 04	(Morris, 1986)
Water (g)	5.278E + 05	(Morris, 1986)
Lipids	4.309E + 07	(Boom, 2021)
Proteins	2.535E + 07	(Boom, 2021)
Carbohydrates	1.764E + 07	(Boom, 2021)
Ash (K_2CO_3)	3.164E + 04	(Van Donkelaar et al., 2016)
Hexane (l)	4.774E + 07	(Morris, 1986)
Hexane (g)	4.779E + 07	(Morris, 1986)
NaOH	1.873E + 06	(Ayub, 2006)
H_3PO_4	9.143E + 05	(Ayub, 2006)
Diatomaceous earth (SiO_2)	1.365E + 05	(Ayub, 2006)
Ammonia	1.984E + 07	(Ayub, 2006)
Succinic acid	1.363E + 07	(Morris, 1986)
Mushrooms (oyster)	1.826E + 07	(Oluwafemi et al., 2016)
Enzyme	2.253E + 07	(Van Donkelaar et al., 2016)
Soy protein isolate (SPI)	2.41E + 07	(Benjamin et al., 2014)
Natural gas (methane)	5.18E + 07	(Morris, 1986)

calculated by Eq. (9),

$$x_{mw} = \frac{h_{c,1} - h_{c,2}}{\Delta h_{ev}} \quad (9)$$

here x_{mw} is the amount of makeup water (% of condensate), $h_{c,1}$ is the enthalpy of the condensate inside the heat exchanger (kJ/kg), $h_{c,2}$ is the enthalpy of the after the heat exchanger (kJ/kg), and Δh_{ev} is the heat of evaporation (kJ/kg) of the flash steam.

3.2.5. Exergy calculation

3.2.5.1. Chemical exergy. An overview of relevant standard chemical exergies is presented in Table 2. For a stream containing biomass, the chemical exergy was approximated by summing the protein, lipid, carbohydrate, water, and ash fractions multiplied by their respective chemical exergies.

3.2.5.2. Physical exergy. The thermal and pressure exergies are calculated using Eqs. (10) and (11), in which the ideal gas law was used to estimate the pressure for non-steam gases, Eq. (12). For steam, pressures values were inserted from a conventional steam table (Ejiogu & Fiori, 1987).

$$B_{thermal} = mc_p(T_p - T_{amb})\left[1 - \frac{T_{amb}}{T_p - T_{amb}}\ln\left(\frac{T_p}{T_{amb}}\right)\right] \quad (10)$$

$$B_{pressure} = nRT_{amb}\ln\left(\frac{p_p}{p_{atm}}\right) \quad (11)$$

$$pV = nRT \quad (12)$$

B is the exergy (J), T_{amb} and T_p are the ambient and product temperature (°C), n is the amount of moles, R is the gas constant (J/K.mol), p_p and p_{atm} are the product's and atmospheric pressure (Pa) and V is the volume (m^3).

3.2.6. General assumptions and constants used

The list of the general assumptions and constants used in the calculations are shown in Appendix A. The default model to describe a unit operation is that of a continuously stirred-tank reactor (CSTR), meaning the temperature and pressure of exiting streams is equal to the temperature and pressure inside the equipment.

Table 3
Component balance aqueous oleosome extraction from capsicum seeds.

Component	Composition (%) [(a)]					
	Capsicum seeds	Extract	Cake	Oleosomes	Serum	Pellet
Moisture	7.72 ± 0.19	71.65 ± 0.15	36.03 ± 2.28	50.16 ± 0.98	84.26 ± 2.92	66.60 ± 3.25
Lipids	17.37 ± 0.91	10.87 ± 0.26	9.08 ± 0.16	37.84 ± 0.16	2.08 ± 0.01	8.30 ± 0.12
Protein	16.43 ± 0.16	6.01 ± 0.08	10.64 ± 0.13	6.15 ± 1.11	4.17 ± 0.05	6.56 ± 0.12
Other [(b)]	58.48	11.47	47.18	5.25	9.5	16.89
% of total mass	100	44.35 ± 1.21	46.53 ± 1.32	7.85 ± 0.34	19.53 ± 0.62	12.58 ± 0.58

[(a)] Values are mean ± SD of three replicates.
[(b)] *No experiments done, so no standard deviation*

4. Discussion

4.1. Compositions and yields of oleosome extraction

The composition of the raw material and streams during oleosomes extraction are depicted in Table 3. The lipids and moisture contents are in good agreement with previous studies (Benjamin et al., 2014; Chouaibi et al., 2019; Embaby & Mokhtar, 2011; Yılmaz et al., 2015), but the protein content is generally a few percentages higher in the reported literature. The lipid content is 17.4 wt%, which is considered low compared to other oilseeds but falls within the range reported in the literature for different capsicum varieties (13.6 % – 26.7w%). This is explained by the fact that the raw material supplied by Chenguang contains a 12 wt% capsicum peels.

The component balance was created using the data from the 300 g seeds soaking in a 1:1 ratio, as this parameter combination allowed for the lowest material loss in the equipment used (9.12 wt%). Twin-screw pressing of the capsicum seeds resulted in an extract containing 55.74 % of the starting oil, with 11.2 % lost in the machine residue. In previous papers, oleosome yield is expressed as the difference between the oil in the starting material and the oil in the cake fraction (Avram et al., 2014). Using this approach, the oleosome yield was 66.96 %, which is comparable to the twin-screw oil yield from soybeans (65–70 %) (Rosenthal et al., 1998), but still significantly lower than the yield from maize germs (78 wt%) and rapeseeds (82.8w%) (Avram et al., 2014; Nikiforidis & Kiosseoglou, 2009). In the absence of data on an industrial-sized process, the oil yield of 55.74 % is used as a basis for the component balance, meaning the oil left in the machine residue is considered a loss.

The oleosome-rich fraction obtained after centrifuging the extract contained 34.36 % of the starting oil, which is considerably lower compared to the 63.3 % obtained for rapeseeds (Avram et al., 2014). The yield increased from 29 to 59 % to 65 % for soybean oleosome extraction after re-centrifuging the residues (Campbell et al., 2011).

4.2. Mass flow of the potential industrial extraction of oleosomes

Although the process still requires optimisation, it has been shown that intact oleosomes can be extracted on an industrial scale (Abdullah et al., 2020). For this, the steeped seeds will be processed in a continuous twin-screw press, available for throughputs up to 250 tonnes per hour (Stord International AS). The subsequent oleosome purification is achieved by a decanter centrifuge, an equipment type commonly used to separate light liquid phases, heavy liquid phases, and solids (Alfa Laval), and the obtained oleosome-rich cream is combined with water in an agitated mixer to complete the emulsion. All processes are carried out at ambient conditions (20 °C and 1 Atm).

Contrary to conventional extraction where high-temperature desolventising results in a partial darkening and solidification of the meal (Sessa et al., 1976), the cake obtained by twin-screw pressing is

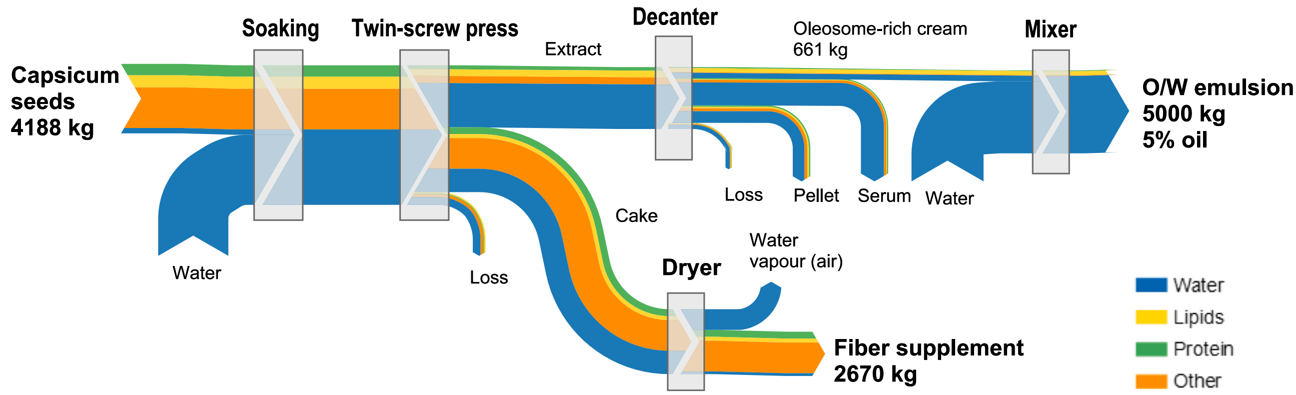

Fig. 2. Component balance for O/W emulsion production from capsicum seed oleosomes. Drying air not visualised as that would dwarf other streams.

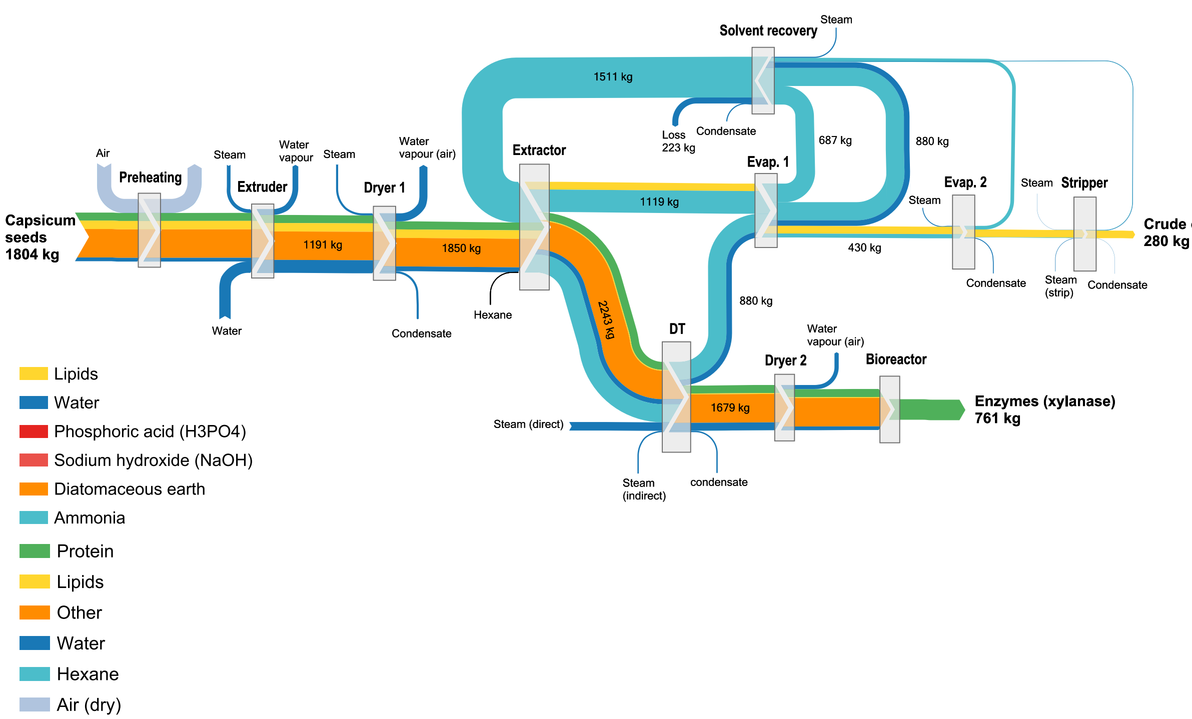

Fig. 3. Component balance for crude oil extraction from capsicum seeds. Drying air and cooling water not visualised as that would dwarf other streams.

subjected only to mechanical stresses. This results in materials of good quality, which could be directly used for food. Capsicum seed meal, dried to the moisture content of 6.2, will has similar macromolecular meal composition with oat bran (Talukder & Sharma, 2010). Oat bran is included for up to 20 % in the formulation of corn-extruded snacks and up to 10 % in dietary chicken patties to improve dietary quality, without compromising sensory attributes (Makowska et al., 2015; Talukder & Sharma, 2010). Based on the macromolecular composition alone, it is assumed the capsicum meal can be used as a fiber supplement for similar applications.

Based on the side stream assumptions and the compositional data presented in Table 3, the component balance diagram was constructed in Fig. 2. For the current oleosome yields, the required amount of seeds processed to obtain 5 tonnes of (5 % oil) emulsion is 4188 kg. Additionally, 2670 kg of the fiber supplement is produced.

The only location where thermal energy is required is in drying the cake from a moisture content of 36.0 to 6.20 %. Knowing the cake mass is 3914 kg, the total amount of removable water is 1244.7 kg, which requires approximately 30.000 kg of 140 °C air. The air is not visualised in the mass diagram as it would dwarf other streams.

Knowing the mass flows, the required electric power was approximated using general values from literature. For producing one tonne of seeds, the twin-screw-press and the decanter consume 14.7 MJ and 3.1 MJ of electricity (GEA Westfalia Separator Group GmbH; Stord International AS), totaling to 74.3 MJ for the production of 5 tonnes of emulsion. For now, an average was taken from the values mentioned in the respective sources, but the real electrical consumption might be deviating due to differences in material properties and system throughput. The value for the mixer was neglected as it was negligible compared to decanting and twin-screw pressing.

4.3. Mass flow of the conventional process applied ot extract oil and fabricate emulsions

A hypothetical process to extract pure oil from capsicum seeds was constructed based on a literature review, using the design heuristics described in Table 1. The resulting flow diagram with the required operating conditions is shown in Fig. S1. A general description of the

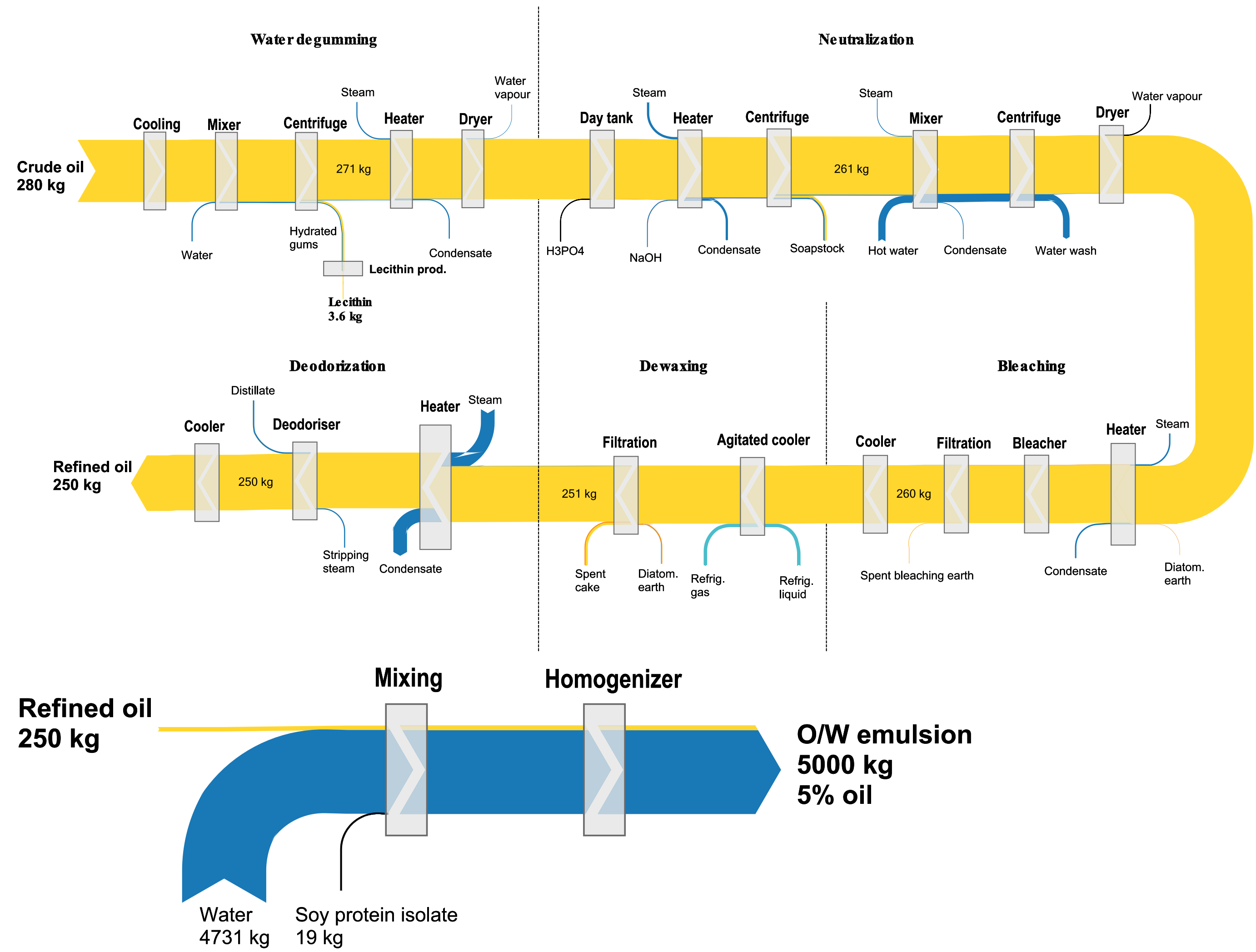

Fig. 4. A) component balance for crude capsicum oil refining. B) Component balance for droplet construction. Both diagrams use a different scale.

Table 4
Electrical energy required for the conventional process.

Unit operation	MJ/tonne seeds	MJ/5 tonne emulsion	Ref.
Extruder	107.4	193.7	(Rittner 1984)
Extractor	4.0	7.2	(Juristowszky 1983)
DT	53.5	96.5	(Desolventizer Toaster Dryer Cooler)
Stripping column	0.1	0.2	(Latondress 1984)
Degumming			
- centrifuge	1.4	2.4	(Latondress 1984)
- vacuum dryer	0.1	0.2	(Latondress 1984)
Neutralisation			
- centrifuge 1	1.4	2.6	(Latondress 1984)
- centrifuge 2	1.3	2.4	(Latondress 1984)
- vacuum dryer	0.1	0.2	(Latondress 1984)
Bleaching	0.1	0.2	(Musediq Adedoyin et al., 2012)
Dewaxing	5.9	10.6	(a)
Deodorisation	0.5	0.9	(Musediq Adedoyin et al., 2012)
Homogenisation	78.9	142.3	(Lekkerkerker dairy food and equipment)
Total	**254.8**	**459.6**	

(a) resulting from refrigeration.

unit operations and an explanation for the most important design decisions is given in supplement, and a detailed list of all the used data on compositions and temperatures is given in Appendix B:

The utility streams complete the input required to construct the component balances. The component balance diagrams for crude oil extraction, oil refining, and droplet construction are depicted in Fig. 3 and Fig. 4, respectively.

An overview of the electricity usage for all process equipment is listed in Table 4. The total electrical consumption is 373 MJ, which is much higher than the 74 MJ used in oleosome extraction. The largest expenses are in the extruder, DT and homogenisation. As power consumption for these operations depends on unknown parameters such as the generated viscosity field and the interfacial tension (Maskan & Altan, 2016) the individual values might be deviating, but the total consumption per tonne of capsicum seeds (255 MJ) compares well with the overall value for other oilseeds (230 MJ) (Özilgen & Sorgüven, 2011). The total electricity consumption for producing 5 tonnes of emulsion product is 459.6 MJ.

4.4. *Exergy flow of conventional and oleosomes process*

Process steam, heated air, and electricity are generated by combusting natural gas in a boiler, furnace, and steam turbine (Boom, 2022). In this, the chemical exergy inside the natural gas is lost as methane is oxidized into CO_2 and water, and the total amount of natural gas

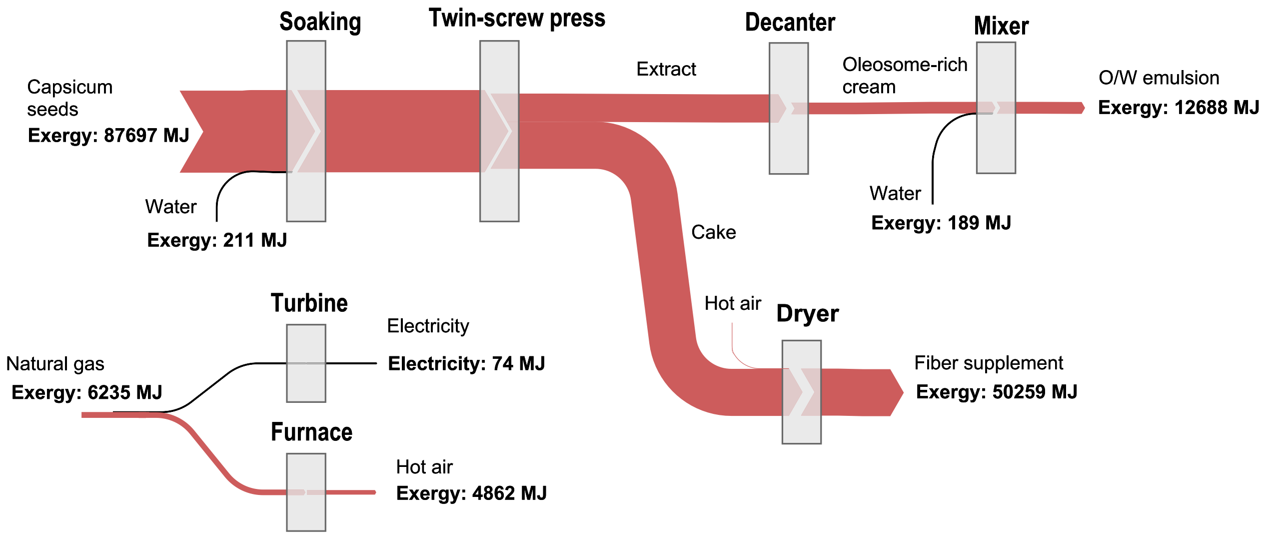

Fig. 5. Grassman diagram for O/W emulsion production from capsicum seed oleosomes.

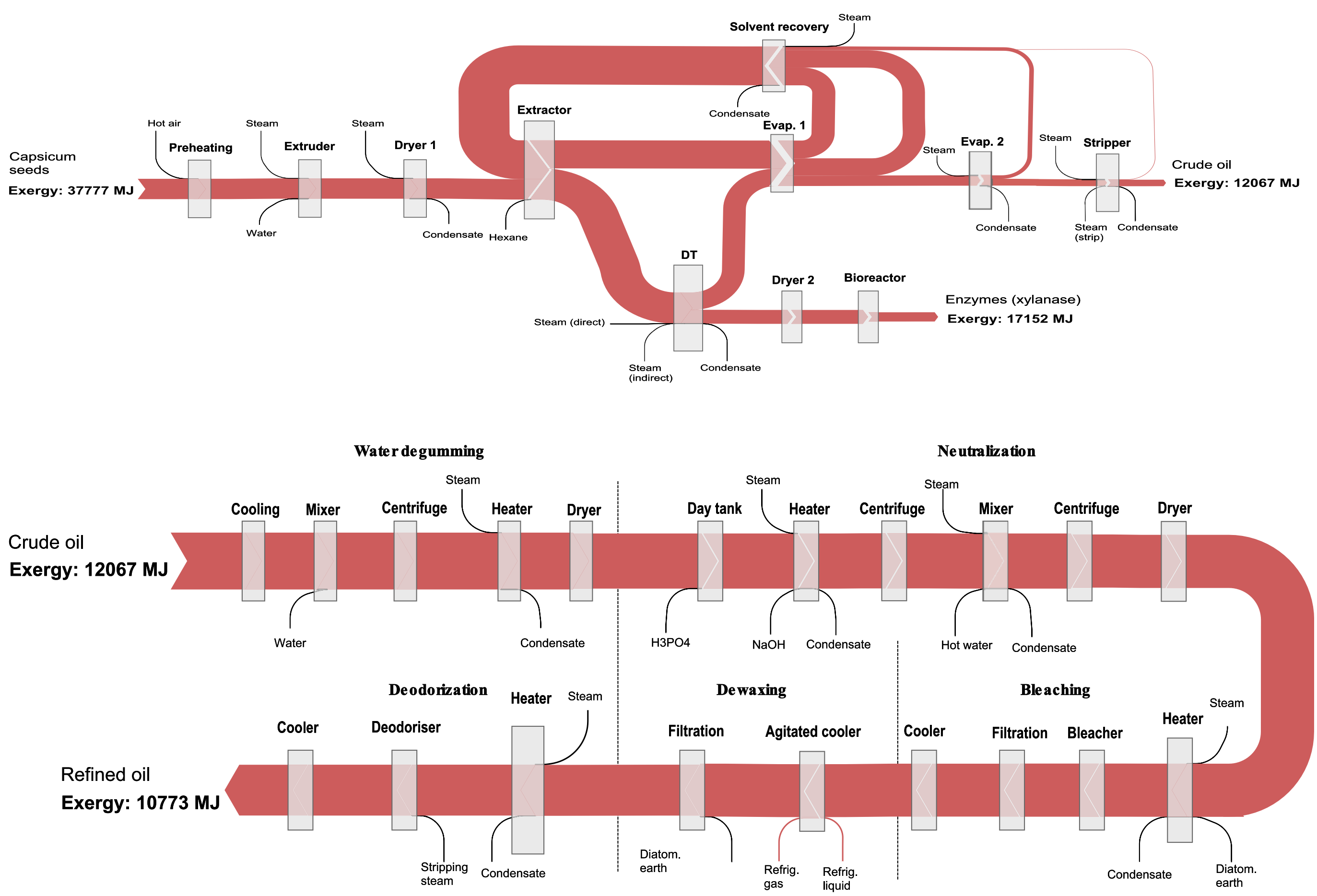

Fig. 6. A) Grassman diagram for crude oil extraction from capsicum seeds. B) Grassman diagram for oil refining. The natural gas use is summarised in figure 13. Diagrams use different scales.

required follows from the combustion efficiencies of the respective equipment. A detailed description of the natural gas consumption and neglected energies is presented in the supplementary.

The final exergy loss for the oleosome route is presented in Fig. 5, and the loss for the conventional route is in Fig. 6 and Fig. 7. To avoid having too many streams and numbers, electricities are summarised as one single stream coming out of the turbines, rather than separate electricity flows going to all the respective unit operations. The same applies to the makeup water. Also, the smaller exergy values for streams are not visualised. For all diagrams, black arrows were used to visualise minimally sized streams.

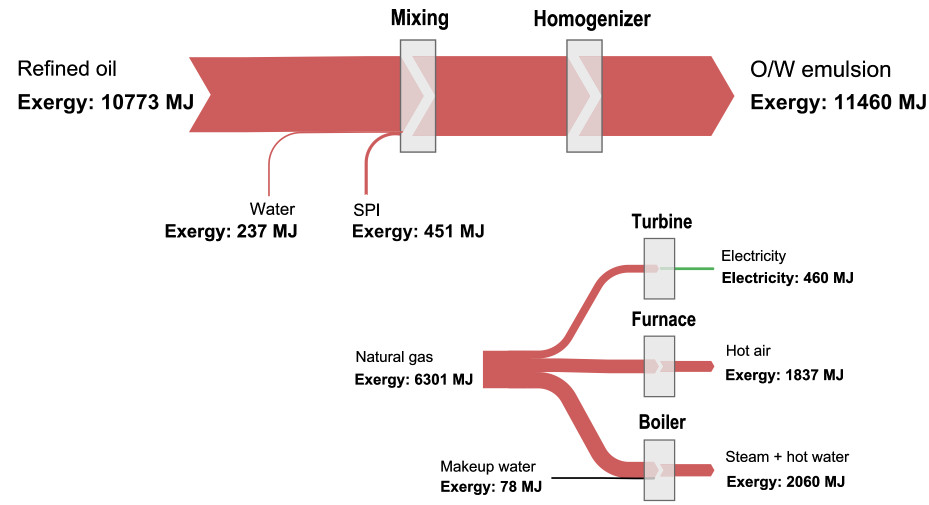

Fig. 7. A) Grassman diagram for emulsion construction. B) Grassman diagram for combined utility use crude oil extraction, oil refining and emulsion construction. Diagrams used different scales.

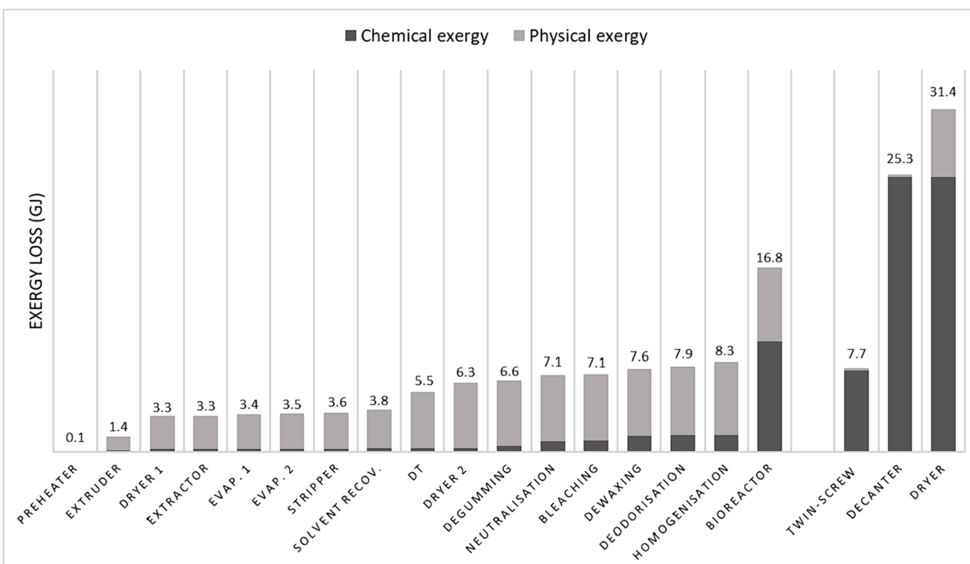

Fig. 8. Accumulative exergy loss for A) the conventional process and B) the oleosome extraction.

4.5. Evaluation of the exergy losses

The accumulated exergy loss for the complete process sequences is summarised in Fig. 8. In the diagram, the physical exergy includes the thermal and pressure exergy loss, as well as the exergy loss associated with producing the utilities: steam, hot water, heated air, and electricity. The total exergy destroyed for the production of 5000 kg (5 %) O/W emulsion via the conventional process is 16.8 GJ. The most important exergy loss is the 8.6 GJ of chemical loss that is lost in the bioreactor when meal biomass is converted into enzyme biomass. For the physical exergy, the most significant losses occur at the dryer 1, where 1.8 GJ is lost for reducing collet moisture, at the DT, where 1.7 GJ is lost in desolventising the meal, and at the extruder, where 1.2 GJ is lost for processing the seed material.

The total exergy loss for the oleosome process is 31.4 GJ, about twice the value of the conventional route. The result can be fully described by the chemical losses associated with the material residue that is lost in the twin-screw press, 7.7 GJ, and the material lost by disposing of the serum and the pellet fraction, 17.6 GJ. Additionally, a significant amount of exergy is lost in drying the cake to the required moisture content for application as a fiber supplement, 6.1 GJ.

Although this seems like a disappointing result, a closer interpretation of the results shows many silver linings for the oleosome route. The main argument is that the current analysis is done between a basic process, unoptimized and based on lab-scale data, competing against an industrial process that has been optimised for years. The effects of more realistic process optimisations are discussed below.

4.5.1. Scenario A: Extraction using twin-screw press and without having losses

The current mass balance for the twin-screw press is based on lab-scale twin-screw press, where 9.12 % of the incoming material is lost as machine residue, containing 11.2 % of the total lipids entering the process in Table 3. If an industrial twin-screw press is used, the machine residue may be removed completely. Assuming that the compositions and extract-to-cake ratio remain unchanged, the total oil in the extract weight increases by 10.0 %, lowering the required amount of seeds processed, hence the utility uses, and removing the chemical exergy losses associated with the machine residue. The total exergy loss would now be 23.5 GJ, compared to 31.4 GJ.

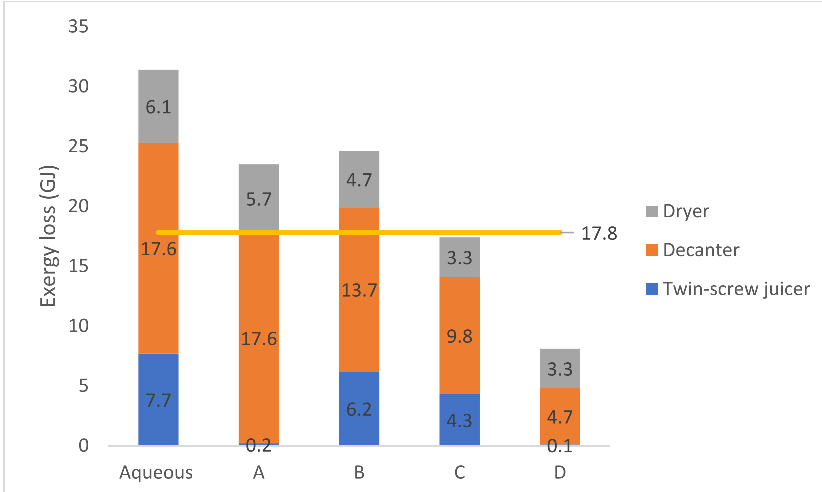

Fig. 9. Effect of process optimisations on exergy loss. Scenario A) No press residue. Scenario B) Centrifuge oil yield of 70%. Scenario C) Second press cycle for the cake, corresponding to twin-screw oil yield of 90%. Scenario D) All process optimisations combined.

4.5.2. *Scenario B: Using a decanter to improve oleosome yield*

Additionally, the current method of collecting the cream layer using a vertical scoop inevitably results in a loss of oleosomes to the serum fraction. For an industrial decanter with a 30 % solids concentration in the feed, comparable to the oleosome extract, the oil yield may be expected to be at least 70 % (Zhu et al., 2020). As the centrifuge is able to isolate more of the incoming oleosomes into the cream, the amount of seeds processed to obtain the emulsion decreases by 21.5 %. Here, it is assumed that only more fat is isolated into the cream, the content of the remaining fractions stays the same. The total exergy loss would then reduce to 24.6 GJ.

4.5.3. *Scenario C: Pressing one more time for the cake*

Finally, the current oleosome yield from the extract obtained after one cycle of screw-pressing is 55.7 %, but can increase to 90 % if the fibrous cake is rehydrated (1:1) with pure water re-pressed through the twin-screw press (M. J. Romero-Guzmán et al., 2020, b). Assuming the composition of the second press cake is equal to the first, this would decrease the required seed amount by 45.5 %. If the lower fat-content in the cake does not affect its applicability as a fiber supplement, the total exergy loss would be reduced to 17.4 GJ. In this, it is taken into account that the electric consumption for the twin-screw press is doubled due to the second press cycle.

An overview of the described improvements is provided in Fig. 9. If the improvements are combined into one scenario the exergy loss to create 5 tonnes of emulsion totals to 8.1 GJ, which is an improvement of 8.7 GJ compared to the conventional route. The reduction in resource use is attributed to the fact that the increase in oleosome yield and reduction in material losses allows for a reduction in total seeds processed to obtain the same amount of emulsion. This not only lowers the chemical exergy losses associated with the solids wasted via the pellet and serum fraction, it also lowers the total utility use to 3.4 GJ, which is half the amount spent for the conventional route (6.7 GJ).

Next to these relatively simple improvements, a key optimisation point to further minimise resource loss is finding an effective way to the solids lost via the serum and pellet fraction. Drying the serum has been suggested but the high moisture content results in an energy-intense operation with a poor exergy performance (M. J. Romero-Guzmán et al., 2020, b). A potential alternative is provided by the brewing industry, where side stream proteins are solubilised in alkaline conditions using enzymatic treatment, followed by a separation using ultrafiltration (Treimo et al., 2008).

5. Conclusion

The potential of aqueous oleosome extraction as a means to valorise capsicum seed biomass was evaluated using an exergy loss comparison with the conventional technology. Component balances were constructed using compositional data from the lab-scale process for the oleosomes, and literature review for the conventional route. For the latter, a subsequent heat balance calculation allowed for a detailed estimation of the thermal utilities. The analysis is may be regarded as extensive in the sense that it includes the potential uses of side streams as well as the losses associated with steam, air and electricity production.

In the pre-optimised scenario, aqueous oleosome extraction obtained emulsions at an exergy loss twice that of conventional droplet construction, where the biggest losses were ascribed to the solids lost via the twin-screw press and the centrifuge. In a scenario where oleosome yield is increased to 90 % by reprocessing the fiber fraction, and both twin-screw press loss as well as centrifuge yields are improved to values that may be expected from industrial equipment, a stable oil-in-water emulsion is produced at only half the resource-use compared to conventional droplet construction. From this, it may be concluded that aqueous oleosome extraction has clear potential to valorise capsicum seed biomass, justifying further research to confirm whether industrial upscale is able to improve material efficiencies as expected.

CRediT authorship contribution statement

Mingzhao Han: Writing – original draft, Investigation, Formal analysis. **Stefan ten Voorde:** Writing – original draft, Methodology, Investigation, Data curation. **Xin Wen:** Supervision, Funding acquisition. **Yuanying Ni:** Supervision, Funding acquisition. **Remko M. Boom:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Constantinos V. Nikiforidis:** Writing – review & editing, Supervision, Methodology, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.biortech.2024.130571.

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