Valorization of tomato industrial by-products in Campania region for sustainable recovery of components and energy

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Valorization of tomato industrial by-products in Campania region for sustainable recovery of components and energy

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List of pubblications

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Outline

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Abstract of thesis

Italy is the 2nd country in the world for tomato transformation after the USA, due to 5 Mt of processed fresh fruits every year. The Campania Region, due to its long-standing experience, is the main and biggest production pool for the transformation of tomatoes in Europe; it is reported that companies, operating in this region, process almost half of the Italian tomatoes for industry, namely 2.2 Mt of fruits transformed every year.

The transformation of tomatoes leads to a huge production of residues, namely peels, and seeds that together form the so-called tomato pomace. These residues can represent even the 10% in weight of the processed tomato, with high moisture content in the range of 70-90 % by weight. Considering these data, it is estimated that 64 kt of tomato by-products are produced every year in Campania. However, their generation concentrates in only two months, according to the seasonality of the tomato supply chain.

Tomato pomace is composed of a mixture of pulp, skin, and seeds, carrying an enormous content of high-value compounds such as carotenoids in the extractive, pectin and cutin (mainly in the peels), and glycerides (mainly in the seeds). These by-products are classifiable as lignocellulosic biomass. Unfortunately, these residues are disposed of without any income for the tomato transformation companies, that is as animal feed or in the worst case sent to landfills, thus wasting high-value compounds, and contributing to earth pollution. In principle, tomato processing by-products could be exploited through thermochemical, biological, and chemical conversion to obtain biogenic fuels and then electricity and heat. Anyway, it is undoubtedly convenient to extract and recover, before conversion, the high-value compounds present in the pomace. A literature study carried out revealed 3 main components of interest: i. Lycopene, which is the most abundant carotenoid in peels and is well known to be the most powerful antioxidant; ii. cutin, which can be used as starting material for biopolymers; iii. pectin, which is another building block of the cuticle of fruits and can be used in food processing. As a side work, a careful study on funded European projects regarding the management of tomato wastes was carried out, assessing and reporting on their scientific and technical results. Moreover, the interconnection among them was highlighted by focusing on the

contribution that they gave to the European know-how, the management of these by-products and the progress they reached in waste minimization and valorization. Finally, the industrial and environmental outcomes of these projects have been reported by highlighting issues and problems that are still to be overcome

Considering this background, this work focused on the valorization of tomato by-products of Campania industries for the recovery of both added-value compounds and energy by making recourse to the "biorefinery cascade approach", namely a set of integrated unit operations that, while extracting the most valuable components from biomass first, leads to sustainable co-production of energy, fuel, and high-value chemical compounds, with minimal generation of waste. The first outcome of this work was a brief block diagram for a multi-product biorefinery based on tomato by-products. In the first instance, a brief economic evaluation was carried out to demonstrate the importance that tomato residues could have in the Campania economy and to estimate the added value that every year is wasted.

The multi-product biorefinery scheme was divided into operating blocks, like tomato pomace separation, lycopene extraction, biodiesel production and so on. For each operating block, two alternatives were selected from literature, one typical and commercially available, and the other one less studied and 'green'. Then, each alternative was studied, modelled, and optimized to check the techno-economic feasibility. Microsoft Excel ® and when possible, Aspen Plus ® were used to evaluate the mass and energy balances of the different operative blocks. Economic indexes, such as gross profit and return of investment, were used to assess the economic feasibility of each biorefinery section and to compare different alternatives. In general, results show that valorizing tomato by-products with a cascade approach are technically feasible; moreover, economic sustainability is always guaranteed, both for the commercial and the 'green' alternatives.

Finally, the Life Cycle Assessment was carried out to quantitatively assess the environmental impacts of two alternative biorefinery schemes, one based on the conventional techniques and another one on the 'green' alternatives. Then, two different scenarios were modelled for comparing the current situation, namely how tomato pomace is disposed of, with the two developed biorefineries. LCA results show that both biorefineries perform better than the current scenario in all categories except for the ozone depletion and slightly ionizing radiation. Conventional biorefinery performs worse than the actual scenario also in cancer effects, climate change and marine eutrophication. In general, the average reduction is 15.4% for conventional biorefinery and 39.7% for alternative biorefinery. This result suggests that, from an environmental perspective, processing tomato pomace in an alternative biorefinery is better than the actual situation. Choosing a conventional strategy would be less effective, even if it is worth noticing that product output is higher in this case.

Contents

The introduction of this work mainly reports about the main information regarding the field of application in which this study is placed. It contains information about tomato processing, its by-products, and their management. In addition, the introduction provides the minimum background to fully appreciate the solutions for the valorization of tomato industry by-products that are proposed, studied, and analyzed in the rest of the text.

Chapter 1 is a brief review on the state of the art of all the available techniques for the valorization of tomato by-products, in term of both extraction of high value compounds and production of energy and fuel through conventional technologies.

Chapter 2 delivers general information about European projects regarding the valorization of tomato by-products, assessing and reporting scientific and technical results. Moreover, the interconnection is highlighted among them by focusing on the contribution they gave to the European know-how, the management of the by-products and the progress they reached on waste minimization and valorization. Finally, the industrial and environmental outcomes of these projects have been reported by highlighting issues and problems that are still to be overcome.

Chapter 3 reports about the new biorefinery model developed and studied in this work for the sustainable co-production of fuel and chemicals from tomato pomace, with minimal generation of waste. Moreover, a theoretical mass flow for the proposed biorefinery and a brief introduction of the methodology used for the study are presented.

Chapter 4 contains, the techno-economic assessment of the different sections or blocks of two biorefineries. One biorefinery is based on conventional techniques while the other one is based on alternative and more environmentally friendly methods.

In Chapter 5 the Life Cycle Assessment of two different approaches for the valorization of tomato by-products is reported. The two approaches were based on the same biorefinery model shown in the previous chapter. Furthermore, the interpretation of results and sensitivity analysis are presented.

The final chapter contains the conclusions.

Introduction

Tomatoes (*Lycopersicon esculentum*) are one of the major vegetables and are second only to potatoes in terms of world production. On a global scale, the annual production of fresh tomatoes amounts to approximately 180 million tons, with China accounting for 32% of the total, followed by the European Union, India, the United States and Turkey as the major producers; Italy is one of the first producers among European nations (FAO, 2019). While most tomatoes are sold fresh, about a third of harvesting is processed for traditional products like canned tomatoes, juice, paste or puree, sauces, and ketchup, which makes tomatoes the world's leading vegetable for processing. Tomato processing yields a huge amount of the so-called tomato pomace, which represents 2-10 % of the whole fresh tomato (Ventura, Pieltain and Castanon, 2009; Gustavsson, Cederberg and Sonesson, 2011). In general, tomato pomace is a mixture of tomato cuticles (or peels), seeds and small amounts of pulp that remain after processing (Ventura, Pieltain and Castanon, 2009). It is often used to produce feed for pets and livestock (Ruiz Celma, Cuadros and López-Rodríguez, 2012) as a source of dietary fiber, as well as B vitamins, Lycopene and to a lesser extent vitamin A. In California (which accounts for 95% of US production) most of the pomace goes to dairies and is added to cattle feed, whilst in the Midwest, the majority ends up in landfills. Another possibility is the direct return to agriculture as soil amendment (Zanón, Font and Jordá, 2011). In Italy, the pomace is given for free to farmers as fodder or sent to landfill; in this latter case disposal of tomato, pomace implies an added cost of two hundred euros per ton for the producing companies. The above-mentioned destinations may be limited by the presence of toxic compounds for animals or the high moisture content (60-80 %wt.) leading to fast spoiling and pollution hazard. Tomato pomace is rich in nutrients and could be used as a potential source of fiber, protein, antioxidants, or fat. Table 1 reports the distribution of tomato parts constituting pomace and the organic macro-components, according to literature.

Table 1 *Main composition of tomato pomace on a dry basis.*

Pomace fraction	Content (% w/w)	Components	References
Pulp	0-15	Cellulose, hemicellulose, lignin	(Al-Wandawi, Abdul-Rahman and Al-Shaikhly, 1985; Liadakis et al., 1995; Benítez et al., 2018; P A Silva et al., 2019)
Peels	30-60	Cutin, pectin, hemicellulose, cellulose, extractives	
Seeds	35-55	Hemicellulose, cellulose, lignin, lipids	

The 2021 tomato processing campaign in Italy closed with a production of just over six million tons of processed product, up 17% compared to 2020. A result that brings Italy to be the second producer country in the world after the United States and well before China. This was reported by ANICAV, the National Association of industrial canned food vegetables, analyzing the two national production basins. In the Central and Southern Italy basin, 2.96 million tons of tomatoes have been processed (+22.3% over 2020), while in the North the tons are 3.09 million (+12.8% over 2020). ANICAV reports that in 2021, about 2.5 million tons of tomatoes were processed in Campania. Therefore, Campania is the largest production basin for processed tomatoes, both in terms of the number of processing companies (out of 120 companies operating in Italy, 70 are Campania companies), mainly concentrated in the provinces of Naples and Salerno, where the main groups of the agro-industrial sector are present not only at a national level but also at an EU level, and in terms of turnover, indeed about 1.5 billion euros out of a national turnover of 3.1 billion (ANICAV, no date).

Tomato is a versatile vegetable from which a variety of processed products are produced. Main processed products are juice, sauce, paste, ketchup, soup, and canned tomatoes. Figure 1 shows an overview of the processing of the most common tomato products (Heuzè et al., 2015).

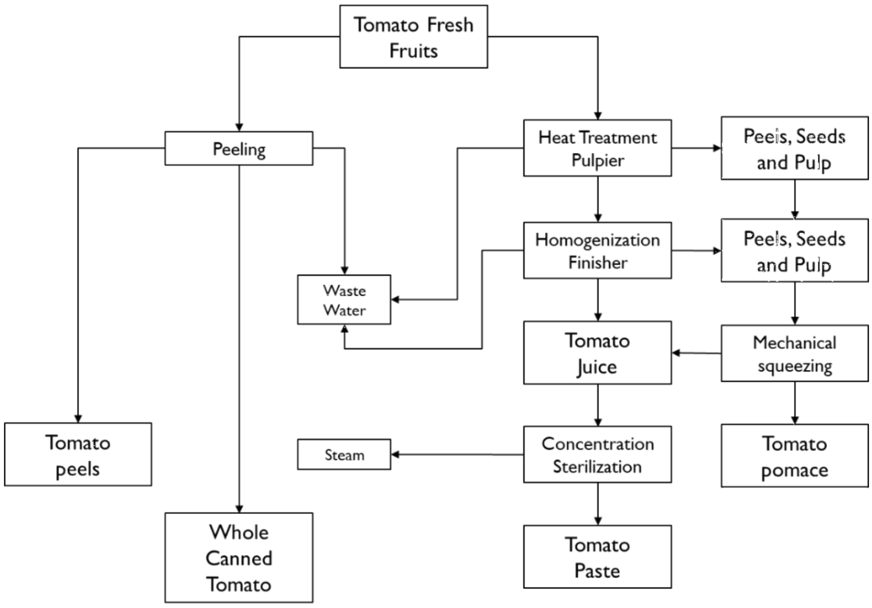


Figure 1 *Tomato processing simplified flow sheet*

Therefore, regardless of processing technique and products, tomato transformation leads to co-production of a mixture of tomato peels and seeds, which are usually underused even if their amount (2-10% of fresh fruit) and their composition. A recent study (Benítez et al., 2018) reported that plant cutin is the main component of the peel fraction of tomato pomace; it is a non-toxic, biodegradable, waterproof, UV-blocking, amorphous, insoluble and infusible bio-polyester made of esterified C_{16} and C_{18} hydroxy acids (Benítez et al., 2018). Moreover, Del Valle et al. (Del Valle, Cámara and Torija, 2006) reported that tomato pomace is a source of natural pectin (8% wt. on a dry basis), a thickening agent in the food industry. Knoblich et al. (Knoblich, Anderson and Latshaw, 2005) analyzed the tomato peel composition and their use as a source of carotenoids, natural pigments, and hydrophobic compounds with health-beneficial properties. Their results, reported in Table 2, showed that lycopene is the most abundant carotenoid in tomato processing by-products.

Table 2 *Carotenoid content of tomato peels (Knoblich, Anderson and Latshaw, 2005)*

Carotenoid	**Lycopene**	**Lutein**	**Zeaxanthin**	**β-Carotene**	**cis- β-Carotene**
Content (mg/100 g)	734	14.5	3.7	29.3	11.7

Tomato seeds are a specific by-product in the case of de-seeded canned tomatoes production. Typically, they are separated from the residual tomato pomace as well as from peels by floatation. The vegetable oil contained in seeds (i.e., 20-25% wt. according to Lazos et al. (Lazos, Tsaknis and Lalas, 1998)) can be recovered, for example by crushing in expellers. Tomato oil is brown with a strong smell and is considered suitable for dressing salads (Lazos, Tsaknis and Lalas, 1998). It contains saturated fatty acids up to 14-18% wt. and unsaturated fatty acids up to 76-80% wt. (Lazos, Tsaknis and Lalas, 1998). Its average composition is reported in Table 3.

Table 3 *Tomato seeds oil composition (Lazos, Tsaknis and Lalas, 1998)*

Fatty acids	Stearic acid	Oleic acid	Linoleic acid	Linolenic acid	Others
Content (% wt.)	20	25	50	2-3	2-3

Very recently. It was reported that with its high vitamin E, beta carotene and phytosterol content, tomato seed oil could penetrate the epidermis to nourish, soften and hydrate the skin and that it could help to treat dry and brittle hair, with high concentrations of vitamin A and Vitamin B complexes (Szabo et al., 2021).

Because a considerable number of high-value compounds are contained in tomato pomace, a feasible strategy for thorough exploitation of these residues is needed. Moreover, being tomato processing by-products classifiable as lignocellulosic biomass, they could be exploited through thermochemical, biological, and chemical conversion to obtain biogenic fuels, and then electricity and heat. For example, Mangut et al. (Mangut et al., 2006) reported that peels and seeds as tomato processing residues have low sulfur and ash contents, whereas their volatile matter and LHV (lower heating value) are significantly high after drying, which make them an interesting source for thermal energy production (Mangut et al., 2006). Moreover, the high content of fatty acids makes tomato seed oil a good candidate for the production of biodiesel (Giuffrè et al., 2016)

In 2020, Xue et al. (Xue et al., 2021) reported a comprehensive study on the waste and by-products generation and disposal of tomato processing in Europe, with the insight of the Italian situation. They report that the tomato supply chain covers six stages: production, postharvest handling, and storage, harvesting, distribution, retailing and household consumption. Each stage causes product loss, and in Italy, tomato processing is the stage with the highest waste production. In particular, they report that the tomato supply chain waste 30 tons of products for 100 tons of harvested tomato and that peels and seeds, produced by tomato transformation, account for around 62 % of all the wasted biomass, Figure 2.

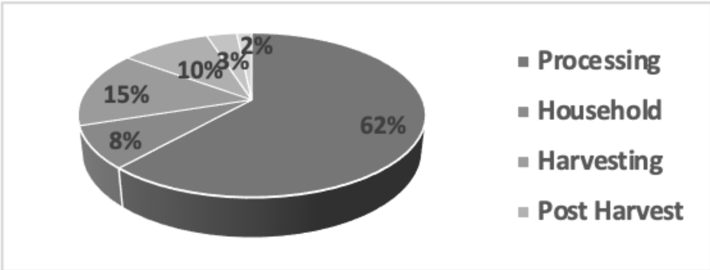


Figure 2 *Distribution of tomato waste in distinct stages*

Therefore, waste at the processing stage is the main loss in the tomato supply chain. Moreover, Xue et al. report the actual disposal of the tomato waste at different stages in Italy. Their study reveals that the tomato waste produced at the production, postharvest handling and storage, and processing stages mostly went for composting with a share of about 75%, followed by anaerobic digestion (18%), and just a small amount goes to incineration (4%) and landfill (3%), Figure 3 (Xue et al., 2021).

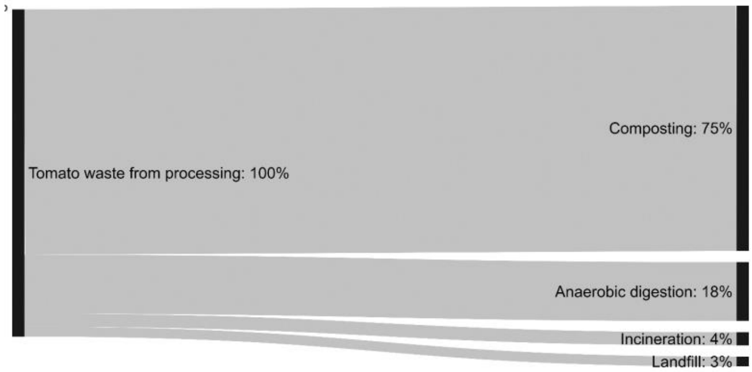


Figure 3 *Tomato waste from processing management*

Tomato pomace and skins are high-moisture products: often more than 80% moisture and it can be up to 98% (NRC, 1983). They spoil very quickly, in less than 2 days in some cases (Caluya, 2000). Unless they can be fed immediately to livestock, they must be preserved either by drying or by ensiling, to ensure their correct valorization and exploitation. Many drying methods are commonly used for fruits and vegetables, such as spray drying, hot air drying, drum drying, freeze-drying, and microwave-vacuum drying. Drying process help in extending the shelf life of fruits and their by-products by reducing water activity. Hot air-drying offers dehydrated products that can have an extended shelf-life of a year and removes most of the free water from the product by evaporation but unfortunately with a drastically reduced quality from that of the original foodstuff (Fellows, 2000; Askari, Emam-Djomeh and Mousavi, 2009; Famurewa and Raji, 2011). Generally, the color deterioration in hot air-dried materials is the most pronounced with a remarkable decrease in lightness and increase in yellowness values, meaning the loss or the oxidation of valuable compounds (Goula et al., 2006; Chen and Martynenko, 2013). Anyway, hot-air drying is the most used technique for drying vegetables, due to its relatively low cost and established technology (Cappelli and Vannucchi, 1998), though the quality of these dried products is poor because evaporation of water at elevated temperature causes chemical, physical and biological changes in food (Lewicki, 2006). Drum drying has the best efficiency in terms of the high rate of production and low labor requirements (Heldman, 2003). Freeze-drying is a gentle dehydration technique, representing the ideal process to produce high-value products because the product is kept almost intact. Anyway, the freeze-drying method is still relatively expensive, and time-consuming with complex units and operations (Cappelli and Vannucchi, 1998). As freeze-drying, vacuum drying is an important dehydration method usually used for high value and heat-sensitive fruits and vegetables (Drying of Fruits and Vegetables by Multi-line Vacuum Dryer, 2018). Drying in a microwave field is another dehydration technique offering the opportunity to reduce the drying time and improve the quality of a dehydrated product (Pierri, 2018). Silage is fermented, high-moisture stored fodder which can be fed to cattle, sheep, and other such ruminants (cud-chewing animals) or used as a biofuel feedstock for anaerobic digesters. It is fermented and stored in a process called ensilage or ensiling, and is usually made from grass crops, including maize, sorghum, or other cereals, using the entire green plant (not just the grain). Silage is made by one or more of the following methods: placing cut green vegetation in a silo or pit; piling the vegetation in a large heap and compressing it down to purge as much oxygen as possible, then covering it with a plastic sheet; or by wrapping large round bales tightly in plastic film (Murdoch, 1961). Tomato processing by-products should not be ensiled alone. Their water content generates large quantities of effluents and pH does not decrease sufficiently for good preservation (Galló et al., 2017). Consequently, it is recommended that a dry material such as straw be added to absorb part of the juice (Barroso et al., 2005).

1. Tomato by-products valorization: state of art

The industrial processing of tomatoes leads to substantial amounts of residues, typically known as tomato pomace or by-products, which can represent as much as 10% of the weight of fresh tomatoes. At present, these residues are either used as feedstock for composting and anaerobic digestion or, in the worst case, disposed of in landfills. This represents a significant waste because tomato pomace contains high-value compounds like lycopene, a powerful antioxidant, cutin, which can be used as a starting material for biopolymers, and pectin, a gelling agent. This chapter presents an overview of technologies that valorize tomato by-products by recovering added-value compounds as well as generating fuel for energy production. These technologies include operations for extraction, separation, and exploitation of lycopene, cutin and pectin, as well as the processes for conversion of the solid residues to fuels. Data collected from the review has been used to develop a biorefinery scheme, reported in Chapter 3, with the related mass flow balance, for a scenario involving the tomato supply chain of Regione Campania in Italy, using tomato by-products as feedstock.

1.1. Lycopene properties and extraction

Lycopene (from the neo-Latin Lycopersicum, the tomato species) is a bright red carotenoid found in tomatoes and other red fruits, and vegetables (red carrots, watermelons, gấc, and papayas) and photosynthetic algae. Due to the strong color and its solubility in organic matters, lycopene is useful as a food coloring (registered as E160d) and is approved for use in the USA by the US Food and Drug Administration since 2005 and in Europe by the European Food Safety Authority (EFSA) since 2008. Lycopene has also been studied for its potential health effects. Promising data from epidemiological as well as cell culture and animal, studies suggest that the consumption of lycopene-containing foods may improve human health. To this end, several advanced drug delivery systems have been developed, to enhance the in vivo delivery of lycopene (Kaur, Sandal and Dhillon, 2017; Caseiro et al., 2020). In recent years, tomato peels have been proposed as a low-cost source of lycopene, compared to fresh tomatoes or Blakeslea trispora, a fungus of the division of Zygomycota, industrially used due to its ability to produce carotenoids (Martínez-Cámara et al., 2018; Górecka et al., 2020). As for the extraction of carotenoids from other plant materials, solvent extraction and supercritical CO_2 extraction are the most studied and optimized techniques for lycopene extraction from tomato residues (Fritsch et al., 2017). In general, numerous variables can influence the yield of lycopene extraction, but the solvent type is widely considered to be the most important (Kaur et al., 2008). Organic solvents and their mixtures are the most investigated due to their affinity with lycopene (Pandya, 2017; Briones-Labarca, Giovagnoli-Vicuña and Cañas-Sarazúa, 2019; Zuorro, 2020). The EU allows a small number of solvents when lycopene is used within the food industry (including propanol, hexane, acetone, ethanol, methanol and ethyl acetate) and a maximum solvent residue of 50 mg per kg of lycopene (Commission Directive 2011/3/EU, 2011). The most promising environment-friendly alternative to traditional solvents is limonene, the major component in the essential oil of citrus fruit peels (Shakir and Salih, 2015) and typically used in the food industry as an additive (Kim et al., 2013; Ravichandran et al., 2018). Limonene, obtained from orange peels, has been also tested for lycopene extraction with results comparable to conventional organic solvents (Chemat-Djenni et al., 2010). Solvent extraction has usually low yields due to the complex structure of the cell walls where the lycopene is trapped; moreover, degradation of the carotenoids can occur due to high temperature and long extraction time, reducing the lycopene extract quality. To overcome this problem, several techniques have been proposed in the literature, including: sonication-assisted extraction (Yilmaz, Kumcuoglu and Tavman, 2017; Rahimi and Mikani, 2019), microwave-assisted extraction (Ho et al., 2015), enzyme-assisted extraction (Ranveer, Patil and Sahoo, 2013; Catalkaya and Kahveci,

2019) and Naviglio extraction (Naviglio et al., 2008). The commercial alternative to solvent extraction is supercritical fluid extraction (SFE) with CO_2 being the most common working fluid. Studies on the extraction of lycopene by the means of SFE show that increasing the density of CO_2 with a co-solvent (hexane or ethanol), leads to higher solubilization of the carotenoids in the fluid and, thus to an improved extraction (Cadoni et al., 1999; Baysal, Ersus and Starmans, 2000). However, recent works demonstrated that the supercritical extraction of lycopene without the use of co-solvent can reach high yields when operational parameters are optimized (Pellicanò et al., 2020). The main advantages of SFE are the high target specificity, the short extraction times, the use of a non-toxic solvent and a reduced environmental impact (Wang and Weller, 2006). On the other hand, a disadvantage is SFE's higher operating costs, since high pressures must be applied to maintain the fluid in a supercritical state, compared to the less energy demanding operational conditions of solvent extraction. The results together with the experimental conditions of the most recent works on the extraction of lycopene from tomato peels are reported in Table 4.

Table 4 *Main experimental results for lycopene extraction from tomato pomace*

Technology	**Experimental conditions**	**Extraction solvents**	**Yield of extraction [on 100 g of dry peels]**	**Reference**
Solvent extraction	40°C for 5h and 1:30 feed to solvent ratio	50% acetone, 50% ethyl acetate	52.7 mg	(Pandya, 2017)
	40°C for 30 min and 1:30 feed to solvent ratio	30.6% hexane, 32.8% ethanol 36.6% acetone	272 mg	(Zuorro, 2020)
	RT and 1:1 feed to solvent ratio	d-Limonene	39 mg	(Chemat-Djenni et al., 2010)
	50°C for 30 min and 1:80 feed to solvent ratio	Ethyl acetate	135 mg	(Calvo et al, 2007)
Ultrasound-assisted extraction	70 W for 10 min and 1:20 feed to solvent ratio	Sunflower oil	91 mg	(Rahimi and Mikani, 2019)
Microwave-assisted extraction	400 W for 1 min and 1:20 feed to solvent ratio	Ethyl acetate	13.6 mg	(Ho et al., 2015)
Supercritical fluid extraction	80 min with a pressure of 550 bar at 60°C and 2ml/min of solvent flow	CO_2	37 mg	(Pellicanò et al., 2020)

The extraction processes, mentioned above, produce a fat-soluble extract that contains a high concentration of lycopene and all the hydrophobic compounds that were included in the pomace; lipophilic extract accounts for around 5% of tomato peels on dry weight (Brachi et al., 2016a). It is already available on the market and can be sold as produced or incorporated in products such as tablets, capsules, soft gels, powders, and drinks (Nagarajan et al., 2017).

1.2. Cutin extraction and application

Cutin is the polymeric building block of the plant cuticle. It represents around 40% wt. of the dry peels and consists of esterified fatty acids (Heredia, 2003; Domínguez, Heredia-Guerrero and Heredia, 2015). Cutin is mainly composed of a mixture of C_{16} and C_{18} fatty acids (Domínguez, Heredia-Guerrero and Heredia, 2011). These long-chain fatty acids (called cutin acids) represent innovative building-block chemicals for the synthesis of novel bio-resins and lacquers suitable as an internal protective coating for metal food packaging. However, these natural compounds are not currently available commercially (Cifarelli et al., 2019). Tomato pomace and tomato peels have been proposed as a renewable source of this biopolymer, due to their high content in cutin and their availability. Cifarelli et al., in 2019, reported three efficient, easy and environmentally safe procedures that could be commercialized for the extraction of cutin acids from tomato peels without the use of organic solvents, these include: i) alkaline hydrolysis of the tomato peel, ii) acid-free selective precipitation of cutin and iii) hydrogen peroxide-assisted hydrolysis (Cifarelli et al., 2019). Notably, those authors noticed that the products were different depending on the method used in terms of appearance, solubility, degree of observed crosslinking and molecular weight. They also noted that cutin obtained through alkaline hydrolysis resulted in the best raw material for bio-resin preparation (Cifarelli et al., 2019). Manrich et al., in 2017, proposed a hydrophobic edible film consisting of tomato cutin and pectin (Manrich et al., 2017), obtained using extraction of cutin using the procedure proposed by Cigognini et al. in 2015 (Cicognini et al., 2015). The procedure consisted in immersing dried peels in a solution of NaOH and then autoclaving at 121 °C. The liquid phase was collected by filtration and then acidified to precipitate cutin, which was recovered by centrifugation, washed, and freeze-dried with a yield of 25% of dried tomato peels. Pure cutin did not lead to free-standing film and, therefore, pectin was added as a ligand to produce water-resistant tomato cutin-based films (Manrich et al., 2017). Benitez et al., in 2018, proposed the production of a cutin-based polyester by melt-polycondensation without catalyst, after cutin extraction and depolymerization (Benítez et al., 2018). Even if cutin-based resins still must be optimized, they are promising alternatives to commercial polymers used as a coating for food packaging and represent a viable way to re-use industrial tomato by-products.

1.3. Pectin extraction and application

Pectin is a well-known, naturally occurring biopolymer that is finding increasing applications in the pharmaceutical and biotechnology industry. It has been successfully used for many years in the food and beverage industry as a thickening medium, a gelling agent, and a colloidal stabilizer (European Commission, 2012). Moreover, pectin has several unique properties that have enabled it to be used as a matrix for the entrapment and delivery of a variety of drugs, proteins, and cells (Sriamornsak, 2003).

Although pectin is found in most plant tissues, the number of sources that may be used for the commercial manufacture of pectins is extremely limited. At present, commercial pectin is exclusively derived from citrus peels or apple pomace as by-products from juice manufacturing. The process involves extracting pectin by treating the pomace with hot dilute mineral acid; the pectin is then recovered by precipitation with alcohol (May, 1990; Yapo et al., 2007). The main drawback of this process is represented by mineral acids, which are toxic and generate environmentally problematic effluents (Yapo, 2009). A potential alternative to mineral acids is represented by citric acid, which, has been tested for pectin extraction with comparable results (Pereira et al., 2016; Cho et al., 2019).In 2019, Adiletta et al. extracted and studied pectin contained in sugar beet processing residues (Adiletta et al., 2020). They proposed for the first time the valorization of sugar beet pulp to value-added chemicals and fuels by coupling the eco-friendly isolation of pectins via citric acid extraction with the upgrading of the residual pectin-free solid as biofuel through torrefaction. In 2006, for the first time, Del Valle et al. reported that tomato peels contain pectin in significant quantities (Del Valle, Cámara and Torija, 2006). In 2016, Grassino et al. developed a method to produce pectin from tomato peels; in their experiments, pectin was extracted from dried tomato peels using ammonium oxalate and oxalic acid as extracting solvents, in two steps. According to their results, it can be concluded that tomato peels are a suitable source of pectin that can be used to produce corrosion inhibitors and a valuable additive in the food industry (Grassino et al., 2016). In 2017, Alancay et al. optimized the pectin extraction from tomato processing waste by using a mineral acid, i.e. HCl, thus obtaining a maximum yield of 280 g/kg of tomato pomace (Alancay et al., 2017). The main results from pectin extraction experiments starting from different biomasses are reported in Table 5.

Table 5 *Main experimental results for pectin extraction from various sources*

Source of pectin	Extraction acid	Yield of extraction	Reference
Sugar beet pulp (dried)	Sulfuric acid	16%	(Yapo et al., 2007)
Yellow passion fruit by-product (dried)	Lemon juice concentrate	10%	(Yapo, 2009)
Pomegranate peels (dried)	Citric acid	8%	(Pereira et al., 2016)
Sugar beet pulp (dried)	Citric acid	25%	(Adiletta et al., 2020)
Apple peels (dried)	Tartaric acid	7%	(Cho et al., 2019)
Tomato peels(dried)	Ammonium oxalate and oxalic acid	32%	(Grassino et al., 2016)
Tomato pomace (dried)	Hydrochloric acid	28%	(Alancay et al., 2017)

1.4. Residues to energy

Residual biomasses can be an added cost for manufacturing companies because of the disposal processes. These residues streams are therefore consistent and could have two prevailing valorizations: the use as raw material for feeding livestock (Ruiz Celma, Cuadros and López-Rodríguez, 2012) and the direct return in agriculture as soil amendment (Zanón, Font and Jordá, 2011). These applications are limited by the presence of toxic compounds for animals and the high moisture content in the residues leading to fast spoiling. Therefore, further use of tomato pomace is represented by its energetic application, which environmental benefits have been highlighted by many authors (Mangut et al., 2006). Indeed, Mangut et al., in 2006, reported that peels and seeds biomass residues from the tomato processing industry have low sulfur, and ash contents and high volatile content and LHV, which make them an interesting source of thermal energy production (Mangut et al., 2006). Furthermore, tomato residues can be taken into consideration for the recovery of biogas by controlled anaerobic digestion of residues (Oleszek et al., 2016) or the production of ethanol by fermentation (Kheiralla et al., 2018). Recent works focused on the production of methanol by transesterification of tomato seed oil (Giuffrè et al., 2016). Then, as with other lignocellulosic biomass, tomato residues could be used to produce energy through thermochemical, biochemical, and chemical conversion, leading to several types of energy or fuel as shown in Figure 4.

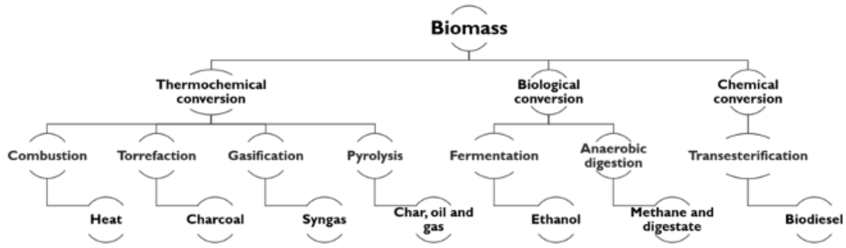


Figure 4 *Biomass-to-energy pathways*

1.4.1. Characterization, torrefaction and pelletization

In 2006, Mangut et al. provided ultimate analysis, proximate analysis, and LHV of tomato pomace, after drying, with a residual moisture content of around 10% wt. (Mangut et al., 2006). Their results show that the amount of sulfur is lower compared with that found in conventional fossil fuels. This outcome is interesting from environmental and technical standpoints because sulfur is well-known to generate important atmospheric pollutants and negatively affect process plant components upon combustion. Mangut and coworkers also stated that with an LHV value of around 20 MJ/kg, tomato by-products (peels, seeds and pulp) represent an interesting energy source with a high potential for heat and electricity production (Mangut et al., 2006). In 2013, Rossini et al. focused on the characterization of the tomato manufacturing residues finalized to the energy recovery. In their study, they reported the physical-chemical properties of tomato by-products and highlighted that nitrogen and chlorine content is considerable, especially in the seeds, this is undesirable in the combustion system due to corrosion of plant components as well as serious environmental problems. To this end, they suggested using tomato peels for combustion or torrefaction, while seeds for the production of vegetable oil (Rossini et al., 2013). In 2016, Brachi et al. carried out a comprehensive study on the torrefaction of dried tomato peels in a fluidized bed of inert particles, which included the identification of key performance parameters and the development of an experimental procedure to determine their values (Brachi et al., 2016b). Their results indicate that tomato peels are a suitable candidate for the torrefaction treatment. The authors also observed that higher temperatures and longer holding times (with a more marked effect of the torrefaction temperature) led to an increase in the calorific value of the torrefied tomato peels, in comparison with untreated peels. For instance, when pomace is thermally treated for 30 min at 285°C the calorific value is increased by a factor of 1.2 for the torrefied biomass, with a 40% reduction in the O/C elemental ratio and an improved hydrophobicity. These positive effects of the torrefaction treatment occurred while maintaining the mass yield (between ∼75% and ∼94%) and energy yield at satisfactory levels. The authors also demonstrated that the fixed bed torrefaction does not ensure a consistent quality of the torrefied solid product and, consequently, a reliable determination of the key process performance parameters (Brachi et al., 2016b). In 2012, Ruiz Celma et al. investigated the feasibility of pelletizing tomato by-products for use as solid fuels (Ruiz Celma, Cuadros and López-Rodríguez, 2012). They produced fuel pellets by forcing the feed product through 6 mm diameter nozzles in a matrix pattern, after the previous milling and air-drying process, conducted at 45 °C drying air temperature and 1.3 m/s drying air velocity. Their pellets had an LHV of 18 MJ/kg, which is comparable to that estimated by Mangut et al. (Mangut et al., 2006) and to that of commercial wood pellets (Telmo and Lousada, 2011).

1.4.2. Chemical conversion of tomato seed oil

The use of vegetable oil to produce biodiesel, a renewable source of energy, has multiple advantages: first, a reduction in the dependency on fossil fuels for energy production as well as a reduction of vegetal wastes; second, an increase of the economic value of crops and vegetable oils; and third, a reduction of carbon emissions. In 2016, Giuffrè et al. firstly suggested that tomato seeds could be used for biodiesel production (Giuffrè et al., 2016). The possibility of extracting oil from tomato seeds was already considered in the early 20th century. Seeds are obtained from pomace by sedimentation and pressed or extracted with solvent to produce oil, which can be refined using alkalis and then clarified with fuller's earth. The resulting oil is pale yellow and considered suitable for dressing salads. They reported that the physicochemical properties of tomato seed oil are comparable with those of rapeseed oil, which is currently used for biodiesel production in Europe. In 2017, the same research group reported a method to synthesize biodiesel from tomato seed oil (Giuffrè et al., 2017). The transformation of vegetable oil into biodiesel occurs via transesterification in a chemical reactor, in which the oil is mixed with alcohol in the presence of a catalyst and heated. The most common alcohol used for transesterification is methanol, with potassium hydroxide being the typical catalyst. Glycerin is produced as a by-product. This study showed that the resulting biodiesel can meet European regulations. In particular, the biodiesel with the best yield and composition was obtained at trans-esterification conditions with a temperature of 55 °C, a reaction time of 1 h, an oil/methanol ratio of 1/6 and a catalyst concentration of 1% wt. in oil.

1.5. Tomato processing residues composting

Compost is organic matter that has been decomposed in a process called composting. This process recycles various organic materials otherwise regarded as waste products and produces a soil conditioner (the compost). The composting process is determined by several factors, such as raw material composition, temperature, humidity, ventilation, pH value, and turning. Achieving a C/N ratio of 20-30 is recommended for digested materials (Fritsch et al., 2017). During composting, part of organic matter is degraded and cured, therefore, there is usually a weight loss of around 40% on a dry basis and 50% on a wet basis (Jolanun et al., 2005). Tomato residues usually contain a high nitrogen concentration. Therefore, they should be co-composted with dry and carbon-rich bulking agents to adjust the C/N ratio and humidity up to 40–60%. For example, Kulcu, in 2014 (Kulcu, 2014), reported a study on the composting of tomato residues, wheat straw, and separated dairy manure, in which he investigated the optimum mixture ratio. According to his results, the optimum mixture ratio for composting the experimental materials was found to be 60% tomato waste, 10% wheat straw, and 30% separated manures (Kulcu, 2014). He claimed that the end-product can be utilized as fertilizer. Previous studies have frequently demonstrated that compost from tomato wastes has adequate organic matter, nitrogen, phosphorous and potassium contents for plant growth. It has been also reported that long-term applications of these composts improve the nitrogen status of the soil over years (Tits et al., 2014). Recently, Olam, an agricultural firm active in 16 major commodities and 65 countries, started making up to 15,000 tons of compost from tomato skins and seeds produced by two canneries in California (GO Compost-Making up to 15,000 tons of compost from tomato skins and seeds, 2018), while National Industrial Symbiosis Programme (NISP) is helping agri-food industries to create a network for composting agro-industrial waste (‘National Industrial Symbiosis Programme (NISP) – Winner of a British Expertise Global Environmental Impact Award 2009 | Sustainability West Midlands’, 2010).

2. An overview of the R&D EU-funded projects

In the last years, the European Commission has been funding projects regarding the valorization of food wastes. Tomato by-products received great attention especially in Spain, Italy, Greece, and Portugal due to high volumes and high concentration of valuable compounds. Among forty funded projects about the management of tomato wastes in general, 14 projects are strictly connected to the valorization and exploitation of the tomato residues/by-products after processing and are of great interest for their scientific, technical, and economical outcomes. They received an overall budget of around 37 M€ over 35 years, involving 20 European and 4 non-European countries, with project coordinators located in Germany, Netherlands, and Italy in most of the cases. This chapter delivers general information about these projects, assessing and reporting scientific and technical results. Moreover, the interconnection is highlighted among them by focusing on the contribution they gave to the European expertise, the management of the by-products and the progress they reached in waste minimization and valorization. Finally, the industrial and environmental outcomes of these projects have been reported by highlighting issues and problems that are still to be overcome.

2.1. Funded projects

The Community Research and Development Information Service (CORDIS | European Commission, no date), namely the European Commission's primary source of results from the projects funded by the EU's framework programs for research and innovation, was used to gather all information such as project factsheets, participants, reports, deliverables and links to open-access publications about tomato by-products valorization. In the first instance, from research in this database, it came up that on 352 funded projects including the keyword "TOMATO" only 10% take into consideration wastes or by-products produced by harvesting, transformation, and use of this vegetable. In particular, the research on CORDIS with "TOMATO" and "WASTE" as keywords gives forty projects as a result. Other searches with other keywords were conducted with less significant results: for example, "TOMATO" and "VALORIZATION" give 9 projects as a result, or "TOMATO" and "RESIDUE" return 23 projects as a result. As it is possible to see from Figure 5 the number of funded projects in this field of application had a strong increase in the last five years, probably due to the growing interest, shown by academia and industries, in waste reduction, valorization of materials so far considered as undesirable by-products, and exploitation of the high-value compounds contained in these waste streams.

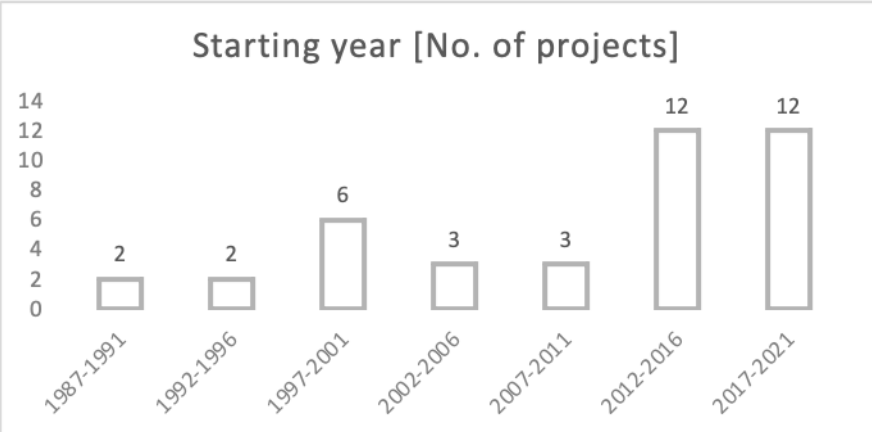


Figure 5 *Distribution during last years of funded research projects on tomato waste*

Then, these forty projects were deeply studied, ad it was possible to divide them into 8 categories regarding the topic:

- Production of bioplastic from tomato residues
- Extraction of high-value compounds from residues
- Production of food additives from residues
- Production of biogas from residues

- Biorefining of residues
- Harvesting optimization
- Shelf life of processed tomato
- Other (not included in the previous categories)

Figure 6 reports a bar chart of the number of projects per field of application.

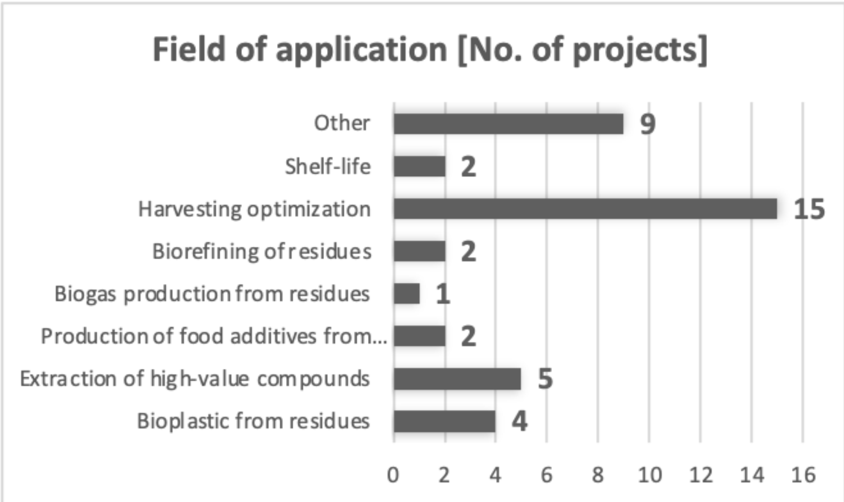


Figure 6 *Number of projects per field of application*

Among these, only fourteen projects are strictly connected to the valorization and exploitation of the tomato residues/by-products after transformation processes. In Table 6, the main information is reported about these projects of interest, sorted by topic.

Table 6 *Main information about funded European projects on valorization and exploitation of tomato wastes.*

Acronym	Start	Duration [months]	Budget [M€]	Leader	Partners
Bioplastic production					
BIOCOPAC	2011	33	1	SSICA (Italy)	10
BIOPROTO	2014	24	0.2	IIT (Italy)	-
ECOFUNCO	2019	33	5.6	CNISTM (Italy)	17
TOMAPAINT	2020	24	3	TOMAPAINT SRL	-
Extraction of high-value compounds					
QLK1-CT-2000-41137	2000	12	0.03	Conservas Vegetales De Extremadura (Spain)	1
QLK1-CT-2000-40942	2000	12	0.03	Hac Le Poole (Netherlands)	1
TOM	2003	24	0.9	Catchmabs (Netherlands)	8
BIOACTIVE-NET	2006	24	0.6	Hochschule Bremerhaven (Germany)	7
LYCOSOL	2019	6	0.07	Biocapsol (Turkey)	-
Production of food additives					
QLK1-CT-2001-42093	2001	12	0.03	ChiPro (Germany)	1
PRO-ENRICH	2018	36	3.3	Teknologisk Institut (Denmark)	15
Biogas production					
AVI*940005	1995	30	0.1	Universität Stuttgart (Germany)	2
Biorefining					
REFRESH	2015	48	9.4	Wageningen University (Netherland)	26
AGRIMAX	2016	48	15.5	Iris Technology (Spain)	29

The information reported in Table 6 was analyzed and summarized in Figure 7 to synthetically show the distribution of budget and participants among the considered application categories.

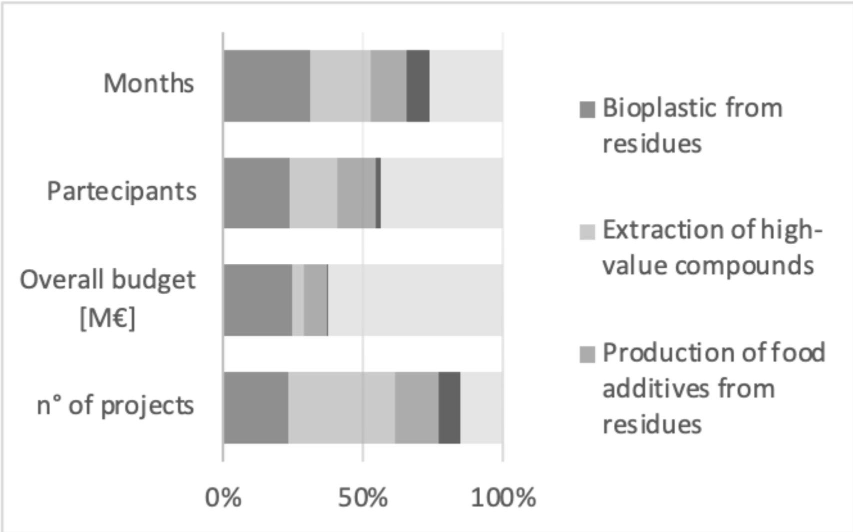


Figure 7 *Distribution of budget and participants among the considered application categories*

The overall budget is around 40 M€ involving 20 European and 4 non-European countries, with project coordinators located in Germany, the Netherlands, and Italy in most cases. It is worth notice that the field of biorefining, the one in which this thesis is involved, even if it is not the one with the highest number of the funded project, exhibits the highest budget and is the one with more partners involved. It is so probably because, even if the application of the biorefinery concept to tomato residual by-products is quite new, the European Commission believes that research in this field could strongly increase the EU technological level. In the next paragraph, the outcome of these projects will be reported and briefly discussed.

2.1.1. Early projects

Projects funded before 2001 lack results reports, for different reporting policies of the European Commission. Anyway, the project QLK1-CT-2000-41137 had likely as an outcome a patent EP1676888B1 entitled «Method of obtaining lycopene from tomato skins and seeds» (GARCÍA, 2012), assigned to Conservas Vegetales de Extremadura SA, which was the coordinator of the project. The patent refers to a process for obtaining lycopene from tomato skins and seeds. The carotenoid is obtained after a series of steps of dehydration, seed separation, pelletization, extraction, distillation, and crystallization. The extraction solvent is hexane and the purity of the lycopene obtained is between 65% and 85%, depending on the raw material.

2.1.2. TOM

The title of the project was "Development of new food additives extracted from the solid residue of the tomato processing industry for the application in functional foods". Partners of the TOM project had developed and optimized an extraction process whereby lycopene is extracted in tomato seed oil from tomato plant processing residue. This can then be used in functional food products and cosmetics. The carried-out process involves the use of supercritical carbon dioxide (CO_2) (Development of new food additives extracted from the solid residue of the tomato processing industry for application in functional foods | TOM Project | FP5, no date). The yield in tomato seed oil is 3-6%. The lycopene yield depends on raw material and ranges between 15-180 ppm, which is very low considering the extraction yield nowadays.

2.1.3. BIOACTIVE-NET

The title of the project was "Cultivation and processing of tomato, olive, and grape are the main agricultural businesses in the South European countries. Production of tomato paste, olive oil, and grape" and the main objectives of the project were:

- Create a broad information platform for dissemination of research results and state of art regarding the extraction of bioactive compounds from tomato, olive, and grape processing residues as well as their application facilities in the food and cosmetic industry
- Implement dissemination workshops in the South European countries aimed at transferring expertise and evaluating economic feasibilities of the extraction
- Strengthen the European market on natural ingredients

Remarkable was the study on the best available technologies (BATs) to separate vitamins, antioxidants, essential oils, and other valuable compounds from the processing residues. In «Guida pratica sui COMPOSTI BIOATTIVI ottenibili dai SOTTOPRODOTTI della TRASFORMAZIONE DEL POMODORO» they reported the main technologies available for: residues drying, lycopene extraction and lycopene purification. Moreover, an economic assessment that compares solvent and supercritical extraction for this compound was reported (Guida pratica sui COMPOSTI BIOATTIVI ottenibili dai SOTTOPRODOTTI della TRASFORMAZIONE DEL POMODORO - PDF Free Download, no date). The report clearly shows from an economic and technological point of view that supercritical CO_2 is rarely favorable, while solvent extraction is profitable only when a high amount of tomato by-products is processed.

2.1.4. LYCOSOL

The title of this 2019 project is “Feasibility Analysis on the Extraction of Lycopene from Tomato Peel through Organic Synthesis”. LycoSOL project proposes an environmentally friendly solution based on natural ingredients. The method involves extracting and processing healthy ingredients from the waste from food processing. The project aims to develop the process of extraction and encapsulation from plant waste, targeting production from tomato peels. No results reports or scientific papers are already disseminated.

2.1.5. PRO-ENRICH

The title of this 2018 project is “Development of novel functional proteins and bioactive ingredients from rapeseed, olive, tomato and citrus fruit side streams for applications in food, cosmetics, pet food”. Pro-Enrich will optimize existing biomass fractionation technologies and validate novel extraction approaches beyond the current state of the art (from TRL2 through to TRL 4/5) to isolate and purify proteins, polyphenols, and dietary fibers and pigments. The products being targeted are food ingredients, pet food, cosmetics, and adhesives. These will be developed through an iterative process of feedstock mapping, laboratory process development, functionality/performance testing of samples by industry and pilot upscaling. Rapeseed, olives husks, tomato seeds and citrus waste will be studied in the project. So far, a review paper on waste composition and edible protein extraction for the selected feedstock was published (Baker and Charlton, 2020) and a first pilot plant for protein production from rapeseed was started (Pro-Enrich project, no date).

2.1.6. BIOCOPAC

The title of the project is “Development of bio-based coating from tomato processing wastes intended for metal packaging”. BIOCOPAC initiative looked at tomato by-products to satisfy some of these needs. The goal was to develop a natural lacquer liner for tins that are made from the cutin raw material contained in discarded tomato skins. The coating was aimed to be applied to internal and external surfaces of food tins to ensure consumer health and safety. The next step was to develop the bio resin and the lacquer. Scientists developed two different formulas to produce the lacquer, one specifically designed for tinplate and a generic one for all types of metal can. BIOCOPAC produced canned goods using these lacquers, demonstrating that the lacquer performs as well as current products. An interesting outcome of the project is a Life Cycle Assessment (LCA) conducted using the SimaPro software, version 7.1. The analyses compared the LCA of a conventional epoxy-based lacquer to a bio-lacquer, tomato cutin based, obtained from tomato processing waste. The results showed clear environmental benefits of the "Bio-lacquer". The benefit of the cutin lacquer lies in the saving of natural resources and the recovery of part of the skins. This can lead to lower consumption of fossil fuels and lower CO_2 emissions.

BIOCOPAC project merged with the BIOCOPAC+ project, funded under LIFE+ Environment Policy and Governance project application (Grant Agreement No. LIFE13 ENV/IT/000590). The project was started on the 1st of June 2014 and lasted for 36 months. The project was industry-driven and focused on demonstration activities aimed to prove the technical feasibility and effectiveness of the cutin extraction and production systems currently developed at a laboratory scale. Its outcomes were a prototype pilot plant for cutin extraction, installed at Azienda Agricola Virginio CHIESA (IT) and a cutin-based lacquer production site in SALCHI (IT) plant ('Biocopac Plus: Sustainable bio-based coating from tomato processing by-products for food metal packaging', no date).

2.1.7. BIOPROTO

The project title is "Bioplastic production from tomato peel residues". The team investigated the possibility of creating a bioplastic film from discarded tomato skins. The idea proved feasible, yielding scalable and biodegradable options for food packaging. Results yielded a new set of films and coatings taken from the lipid portion of plant cuticles, reported in Figure 8. The outcome also represented a potentially scalable and cheap process for the manufacture of bioplastics intended for use in food packaging. BIOPROTO's new plastic was biodegradable, with minimal environmental impact (Bioplastic production from tomato peel residues | BIOPROTO Project | FP7 | CORDIS | European Commission, no date).

Figure 8 *Photographs of bioplastic made by tomato cuticle during the BIOPROTO project*

2.1.8. ECOFUNCO

The tile project is "ECO sustainable multi-FUNctional biobased COatings with enhanced performance and end of life options". The overall objective of project ECOFUNCO (ECOAT | Bio-Based Industries - Public-Private Partnership, no date) is to select, extract and functionalize molecules (proteins, polysaccharides, cutin) from highly available, low valorized biomass such as tomato, legumes, sunflower etc. for the development of new bio-based coating materials to be applied on two different substrates (cellulosic and plastic-based), with improved performances compared to currently available products and at the same time with the more sustainable end of life options. The products to be developed in the project are in particular:

- Antimicrobial-antioxidant coatings based on chitin nanofibrils, and/or chitosan, functionalized MC, for cellulose tissues (personal care), paper and cardboard (packaging for fresh products like pasta, tableware), woven and nonwoven (sanitary), plastic substrates (bio-polyesters) for active packaging
- Cutin-based formulations for water repellent coatings (paper cups, service paper etc.), water vapor barrier (packaging) and protective properties (non-food packaging)
- Protein-based barrier adhesive for multilayer food packaging (bio polyesters based), with sustainable end-of-life options (composting, recyclability).

2.1.9. REFRESH

The title of the project is “Resource Efficient Food and dRink for the Entire Supply cHain”. The overall aim of the REFRESH project is to significantly contribute toward the objective of reducing food waste across the EU by 30% by 2025 and maximizing the value from unavoidable food waste and packaging materials. The project aims to gather information about the main and most present food waste in the European countries, find the known way to exploit these by-products, and create a simplified tool to help the decision-maker to valorize at best these side streams, both in terms of economic feasibility and environmental impact. Tomato by-products are one of the considered waste streams. The project outcomes are 6 scientific publications regarding food waste, from their management to their reduction, a website and a software tool (REFRESH Home | REFRESH, no date). One of the main outcomes of the REFRESH project is a deliverable with the TOP20 waste streams in Europe, carefully reporting their current management and the reason for selection. Tomato by-products are in the list.

Another main outcome is FORKLIFT, a spreadsheet learning tool that indicates life cycle greenhouse gas emissions and costs for using selected food side flows. It allows users to interpret the results regarding the effects of intervention with the additional effect of making it possible to compare the results with alternative products available on the market (FORKLIFT: Assessing climate impacts and costs of using food side streams | REFRESH, no date). For tomato pomace conventional solutions for its exploitation were selected and modelled in the FORKLIFT® tool, allowing for evaluation via

LCA and LCC, cost and CO_2 emission for different scenarios of valorization, and to easily compare them as a support to decision making. Figure 9 shows the interface of the tool. In the analysis of tomato pomace, the following valorization routes are considered:

- Lycopene production
- Preparation of fodder
- Anaerobic digestion
- Land spread

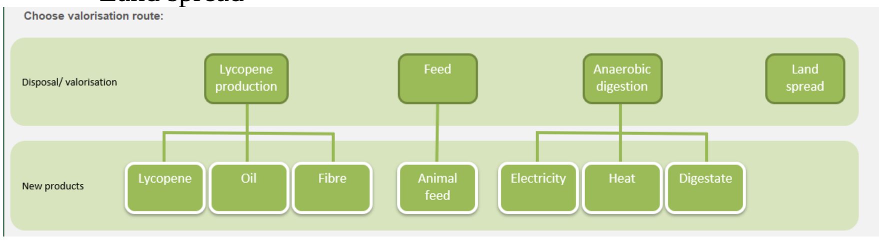


Figure 9 *Valorization routes available on the FORKLIFT spreadsheet*

For example, with this spreadsheet is possible to compare lycopene production cost and emission with carotenoid production from microalgae (Figure 10).

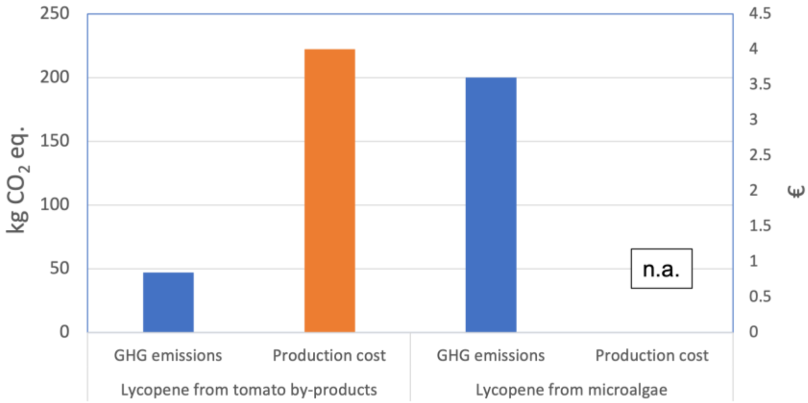


Figure 10 *FORKLIFT output for lycopene production*

2.1.10. AGRIMAX

The project title is “Agri and food waste valorization co-ops based on flexible multi-feedstocks biorefinery processing technologies for new high added value applications. The goal of the project was to extract the significant amounts of valuable compounds contained in food industry wastes, AgriMax combined affordable and flexible processing technologies for the valorization of side streams from the horticultural culture and food processing industry to be used in a cooperative approach by local stakeholders. The project merged previous knowledge and outcome of other European projects, such as cutin extraction and exploitation studied in the BIOCOPAC project. LCA and LCC studied the best approach to minimize the environmental impact of the new value chains. Moreover, a pilot multi-feedstock bio-refinery process was set up at two demonstration sites in Spain and Italy. Currently, the Italian pilot plant is valorizing the tomato by-products, producing cutin bioplastic, a small amount of lycopene and compost. The pilot plant flowsheet is reported in Figure 11.

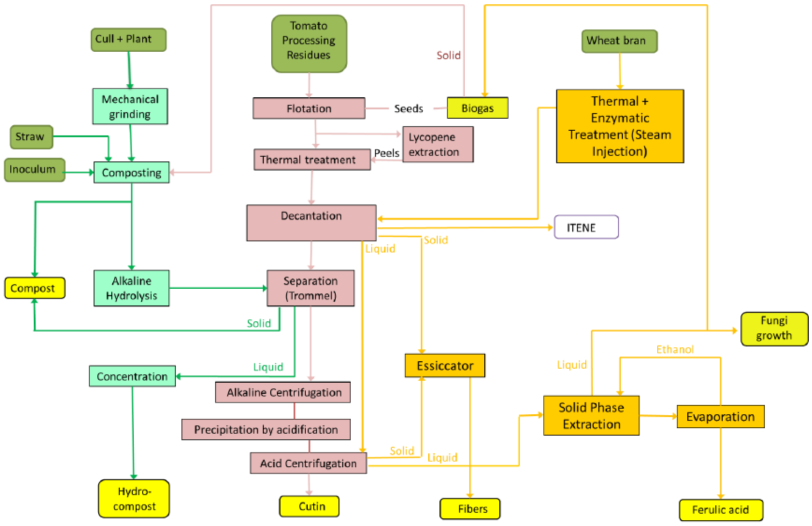


Figure 11 *Flowsheet of Italian pilot plant located in the factory of Azienda Agricola Virginio Chiesa, Canneto Sull'Oglio (MN), Italy*

2.2. Discussion and conclusion

In conclusion, 11% of funded European projects having tomato as a topic are dealing with tomato wastes and by-products. Forty projects were found when searching CORDIS with "tomato" and "waste" as keywords; 14 regard by-products valorization, categorizable in the following topics: production of bioplastic or biofilm, extraction of high-value compounds, preparation of food additives or fodder, biogas production via fermentation and biorefining of tomato by-products. The overall budget, that European Commission furnished to the participants, has been around 40 M€ for about 35 years: These projects involved 130 participants coming from all over the world. Extraction of compounds is the topic of most projects, but biorefining received the highest budget. Projects on the extraction had as an outcome the optimization of commercial techniques, leading to patents, moreover, some studies showed that supercritical CO_2 is never economically feasible for lycopene extraction. PRO-ENRICH is the only project about food additives that were recently found, to start a pilot plant for protein production from different waste streams, including tomato pomace. In the last years, bioplastic production from tomato by-products received great attention and funding, leading a pilot plant in Italy to produce metal packaging cover with a biofilm obtained from tomato peels. Recent projects (AGRIMAX and REFRESH) aim to best exploit food waste, making recourse to a biorefining approach. Main problems remain in the tomato by-products valorization: the high economic or environmental cost of lycopene extraction, absence of a 'green' alternative for cutin extraction, and absence of similar biomass to overcome the seasonality issue related to tomato pomace. Moreover, a lack of data, studies, and projects on energy recovery from tomato by-products was evidenced by the present survey.

3. A multi-product biorefinery approach

The previous chapters demonstrate the substantial value of tomato by-products and the availability of techniques for their valorization. Considering this, a new biorefinery model was developed for the sustainable co-production of fuel and chemicals from tomato pomace, with minimal generation of waste. The model follows the biorefinery cascade approach (Keegan et al., 2013) and is sketched as a block diagram in Figure 12. Notably, the model only includes the main unit operations that are associated with each product. The model assumes that tomato pomace is only composed of peels and seeds. These components are separated and sent to different exploitation pathways. On the one hand, seeds are sent to an extraction unit with the resulting oil collected and purified. The oil is then sent to a transesterification section to produce biodiesel that meets European regulations via catalytic reaction in methanol media. On the other hand, peels undergo several process steps in series for their complete exploitation. First, lycopene-containing lipophilic extract is extracted using organic solvents; the lipophilic extract is collected, purified, and used for preparing tablets that are sold as a dietary supplement. Second, pectin is separated by acid-assisted extraction, collected by ethanol precipitation, and washed to meet the appropriate purity for use in the food industry. Third, cutin is extracted from the solid residue, via hydrolysis; a cutin-based polyester is then produced via melt-polycondensation. The final solid residue, composed of seed residues and spent peels is dried, sent to a pelletizer and then torrefied to produce pellets with LHV of around 18 MJ/kg.

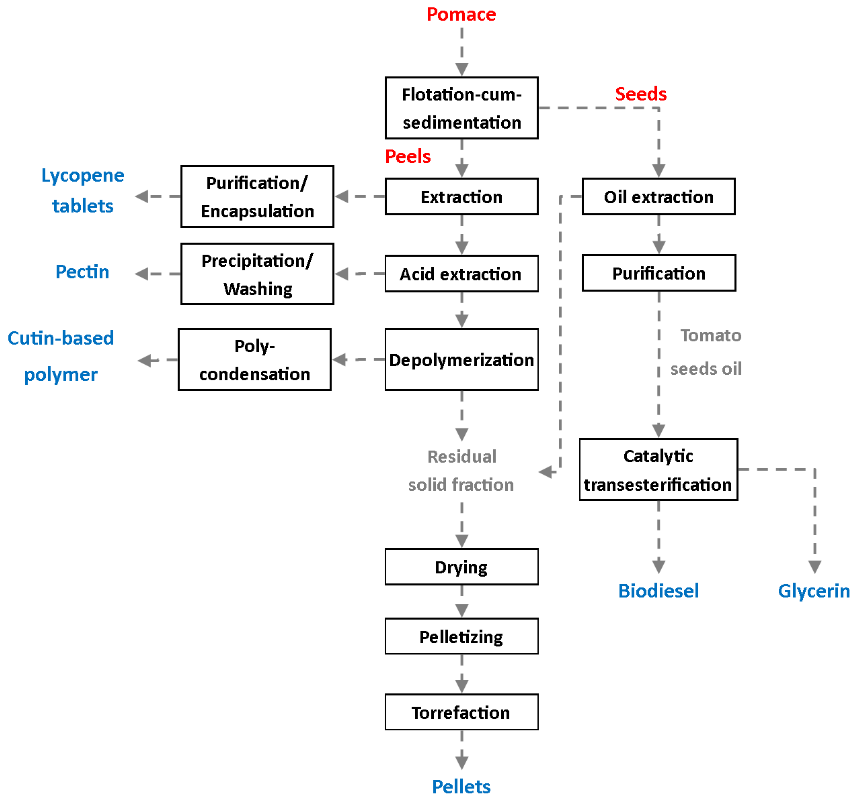


Figure 12 *Biorefinery model for full exploitation of tomato processing by-products (feedstocks are reported in red font, process units in black, intermediate materials in grey and biorefinery products in blue)*

3.1. Theoretical mass flow for biorefinery

A general mass balance of the biorefinery model was carried out using data from the literature, as reported in previous sections, including feedstock characteristics and process yields. The main literature data used for the preliminary balance are reported in Table 7.

Table 7 *Literature data for lycopene, cutin and pectin and for pellets and biodiesel production from tomato by-products*

	[%w/w]	References
Content of tomato peels in by-products	40-60	(Benitez et al. 2018, P A Silva et al., 2019)
Moisture content in by-products	65-80	(Benitez et al. 2018, Brachi et al., 2016)
Lycopene-containing lipophilic extract mass fraction on dry basis in peels	5.2-10	(Knoblich, Anderson and Latshaw, 2005, Brachi et al., 2016)
Cutin yield on dry basis	25-28	(Kulcu, 2014, Manrich et al., 2017, Benitez et al. 2018)
Pectin yield on dry basis	28-32	(Alancay et al., 2017, Grassino et al. 2016)
Tomato oil in seed fraction on dry basis	25-30	(Giuffrè et al., 2017, Lazos, Tsaknis and Lalas, 1998).
Mass yield for pelletization	92-96	(Brachi et al. 2016b)

The mass balance shows that from 100 t of tomato pomace on a wet basis, it is possible to extract 0.6 t of lycopene-based lipophilic extract, 3 t of cutin and 3.7 of pectin from tomato peels, whilst producing 3.9 t of biodiesel and 0.4 t of glycerin from tomato seed oil and methanol. In addition, it is possible to send 88.3 t of biomass to thermal treatment (drying, torrefaction and pelletizing), producing 17.5 t of pellets and generating 71.2 t of emissions composed mainly of removed water and torgas (i.e., gases produced during torrefaction). The results obtained from the mass balance are shown in the Sankey diagram in Figure 13.

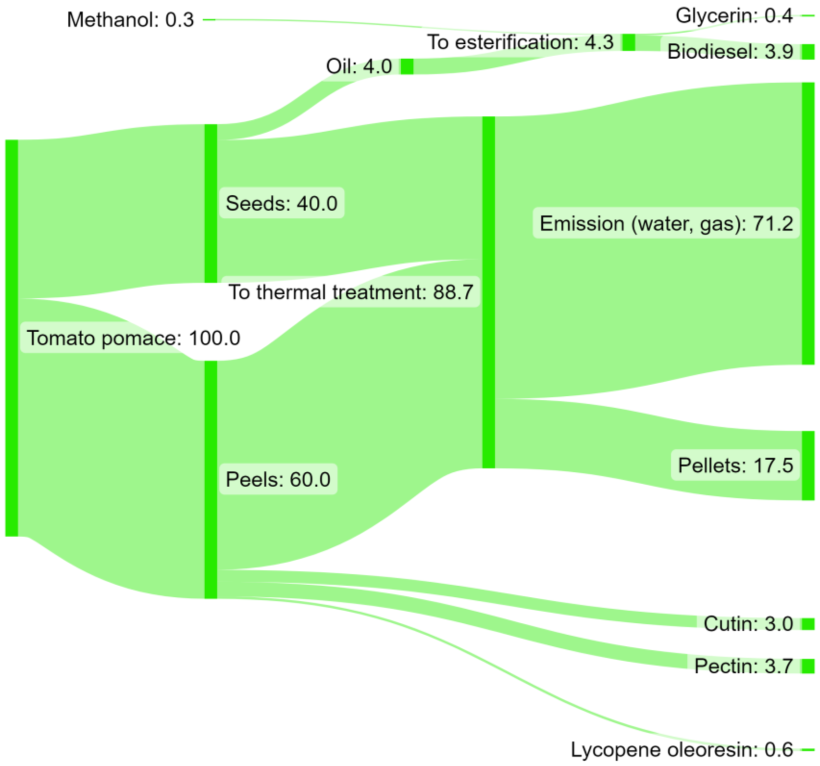


Figure 13 *Mass balance for tomato by-products in tons*

Finally, Table 8 shows an application of the biorefinery model to the Campania region in Southern Italy, which processes nearly half of all Italian tomatoes; this corresponds to about 2.2 Mt of fresh fruits transformed every year, as reported before, and leads, therefore, to a yearly availability of tomato by-products of around 110 kt. The table illustrates the potential production capacity of a biorefinery plant based in the Campania region. Such a plant could produce up to 3.9 kt of pectin, which covers about 10% of the European demand (Pagliaro et al., 2016) and 0.41 kt of glycerin, that is 3% of the amount of glycerin, natural and synthetic, produced in Campania in 2019 (ISTAT, no date). Concerning the fuel and energy sector, a Campania-based biorefinery plant could contribute with 20 kt of pellets, i.e., 16% of all wood pellets consumption in Campania in the last 5 years (ISTAT, no date), and with 4800 m^3 of biodiesel, i.e., a volume that is 3 times the Italian demand of recent years (Italy: biodiesel consumption 2005-2018, no date). Moreover, such a plant could supply all Italian population with lycopene tablets during cold months, ensuring the required daily intake of 10 mg of lycopene when fresh tomatoes are not available (Story et al., 2010).

Table 8 *Production flow of biorefinery products with tomato pomace as feedstock (base case: 2.2 Mt/y of processed tomatoes in Campania)*

Product	Amount (unit/year)	Application	Commercial alternatives
Tablet containing 10 mg of lycopene	6.6 10^9 pills	Dietary supplement for lycopene intake provides antioxidant properties that help cells fight damaging free radicals in the body	Pills containing lycopene extracted from fruits
Pectin	3.9 kt	In the food and beverage industry as a thickening agent, a gelling agent, and a colloidal stabilizer	Pectin extracted from citrus peels
Cutin based polymer	3.1 kt	In the food packaging field	Polyester
Biodiesel	4.8 10^3 m^3	In pure form or blended with petroleum diesel at any concentration in most injection pump diesel engines	Biodiesel from vegetable oil
Glycerin	0.41 kt	It is also widely used as a sweetener in the food industry and as a humectant in pharmaceutical formulations	Generally obtained from plant and animal sources
Pellets	20 kt	Energy source with a high potential for heat and electricity production	Wood pellets

This preliminary analysis confirmed that tomato by-products can be turned from a puzzling issue into a useful resource for the Campania in the frame of a circular economy approach.

3.2. Methodology of the study

After the development of the biorefinery cascade model, each section was studied, analyzed, simulated, and optimized when possible. After the study of the state of art reported in the previous chapter, for each biorefinery product or intermediate material, two alternative techniques were selected: a conventional one (more studied and well established) and an alternative one (greener and promising). The next chapter reports the techno-economic analysis of each operative unit for either one of the two contrasting techniques selected. The analysis, with the mass and energy balances, and all related and side calculations, were initially set up in Microsoft Excel ® worksheets. Then, when possible, to benefit from a more powerful software, they have progressively switched to implementation in AspenPlus® flowsheets.

It is worth noticing that the final biorefinery model was not the one reported in Figure 12; indeed, during the preliminary study, it was found that cutin and pectin are never extracted together from biomass. It is possible to extract the carotenoids and then pectin as reported by Jayeseree et al. (Jayesree et al., 2021) for carrot peel waste. In addition, Sengar et al. (Sengar et al., 2020) report that, to improve the color and quality of pectin extracted from tomato peels, a pretreatment which extracts the lycopene is recommended. On the other hand, cutin can be produced together with lycopene from tomato peels as obtained in the Agrimax European project (see Chapter 2). Therefore, to choose which extraction sequence to exploit (lycopene-pectin, cutin-lycopene), the market value of the commercial alternatives was considered. In particular, pectin, from orange peels, has a market value of 35 €/kg, therefore a biorefinery based on tomato pomace could have a revenue of 1.29 € per each ton of pomace from selling the produced pectin: On the other hand, polyester, that is the benchmark for cutin, has a market value of 7 €/kg, therefore, the revenue coming from selling cutin would be 0.21€ per each ton of exploited pomace, as reported in Table 9.

Table 9 *Market value of pectin and cutin*

Commercial alternative	Market Value [€/kg]	Added Value [€/100 ton of pomace]
Pectin from orange peels	35	129
Polyester	7	21

Therefore, the final biorefinery scheme on which the tecno-economic analysis was carried out is reported in the Figure 14.

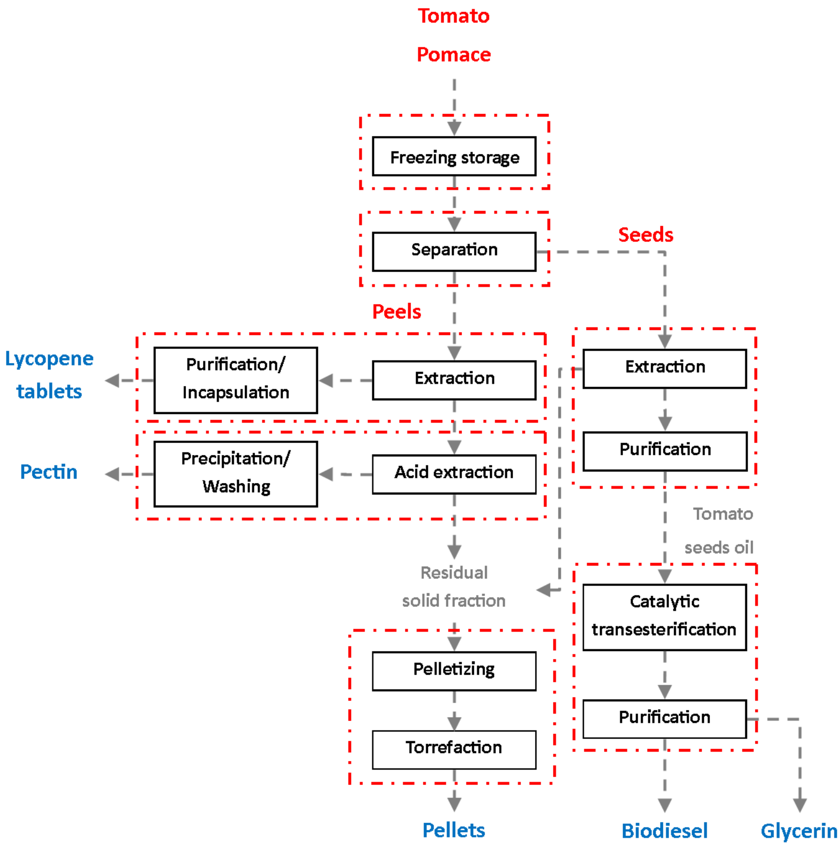


Figure 14 *Final biorefinery scheme with highlighted sections*

Figure 14 reports in red the biorefinery feedstock, in grey the flows of intermediate materials and in blue the biorefinery products. Red dotted lines highlight the biorefinery sections that were studied separately in terms of mass and energy balances, namely:

- Storage
- Separation of peels and seeds
- Lycopene extraction and encapsulation
- Pectin production
- Tomato seed oil extraction
- Biodiesel production by transesterification
- Torrefaction of solid residues

For each block, two different technologic approaches were studied and compered; one based on conventional techniques and materials with higher technology readiness level (TRL) and one based on alternative techniques and materials, considered more environmentally friendly but with lower technologic readiness level: Table 10 reports the considered technologies for each block and their TRL.

Table 10 *Technologies considered in the study and their TRL*

Block	Conventional biorefinery	Alternative biorefinery	TRL
Storage	Freezing storage		9
Pomace separation	Floatation-cum-sedimentation		7
		Air separation	4
Lycopene extraction	Extraction with ethyl acetate		8
		Extraction with limonene	3
Pectin production	Extraction with HCl		4
		Extraction with citric acid	1
Seed oil extraction	Extraction with hexane		8
		Expeller pressing	8
Biodiesel production	Transesterification with KOH		7
		Transesterification with eggshells	4
Pellets production	Torrefaction and pelletizing		4

4. Techno-Economic assessment of the biorefineries blocks

In this chapter, the techno-economic assessment for two different alternatives of the different sections of the biorefinery is reported. The Techno-economic assessment (abbreviated TEA) is a method of analyzing the economic performance of an industrial process, product, or service. It typically uses software modeling to estimate capital cost, operating cost, and revenue based on technical and financial input parameters. It can be used for studying new technologies or optimizing existing ones. It combines elements of process design, process modeling, equipment sizing, capital cost estimation, and operating cost estimation, by using an integrated process and cost model (Green and Perry, 2008; Seider et al., 2008; Turton, Bailie and Whiting, 2012). In this thesis work, this task addressing TEA is composed of five main steps:

- Process design: the system is defined in the form of a process flow diagram (PFD) or block diagram, showing major equipment and material streams.
- Process modeling: it uses engineering and material balance calculations to simply characterize the system to the best. The results are summarized in the form of a material balance table or stream table.
- Equipment sizing: it estimates sizing parameters for each piece of equipment and utility requirements (i.e., electrical power, fuel, cooling water, etc.)
- Operating cost estimation: it includes raw materials, waste treatment, and disposal, and utilities. Raw material and waste treatment costs are estimated by applying prices to raw material and waste flow rates from the process model. Similarly, utility costs are estimated by applying prices to the utility rates from equipment sizing.
- Economic indicator evaluation: gross profit is calculated by subtracting cost of manufacturing (operating cost) from the net revenue (the earnings from selling main products, and even by-products).

The price of main utilities considered in the analysis are reported in Table 11.

Table 11 *Price of main utilities*

Utility	Cost
Electricity	0.129 €/kWh
Methane (for heating)	4 €/m3
Cooling	0.013 €/MJ
Wastewater treatment	187 €//t

Considering that this assessment can be categorized as “Study Estimate”, utilizing a list of roughly size major equipment found in the process, and that the average TRL of the studied process and technology involved in the biorefinery model is quite low, the accuracy level can be considered of Class 4 ranging from 35 to 40% (Turton, Bailie and Whiting, 2012).

As a basis for calculations, 4032 t/y, namely 720 kg/h of tomato by-products are considered, considering a plant working 350 days in a year for 16 hours per day. This is the amount of tomato pomace contained in tomato by-products (TB) produced by 5 medium-size companies during a two-month working season, located in Campania in a small area with a diameter of 10 km.

4.1. Preservation and storage

Biorefineries are integrated process plants producing several chemical products to better exploit all the components of a biomass feedstock. One of the main limitations hindering the development of biorefineries is the uncertainty of a continuous supply of biomass feedstock during the year and during the whole plant lifetime. Moreover, due to the high moisture content, tomato by-products spoil very quickly in less than 2 days in some cases (Caluya, 2000). Unless they can be used immediately, they must be preserved. Freezing is simple and keeps food more like fresh produce than other preservation methods (Food Freezing Guide — Publications, no date). In particular, it is reported that at a temperature of -15°C, vegetables can be preserved for as long as 20 months (Greek Cold Storage & Logistics Association, no date). For this reason, it was considered that tomato by-products undergo a blast freezing to reach the desired temperature in a short time and then are preserved by freezing before entering the biorefineries, in 23 m3 rectangular cellar (60% full, 2.5 m height) as reported in Figure 15.

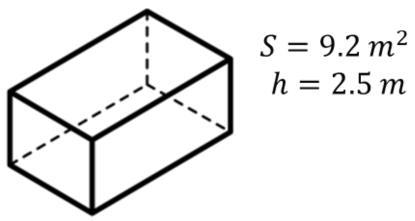


Figure 15 *Sketch of a freezing cabinet for tomato by-products storage*

To ensure a feedstock of 720 kg/h of TB entering the biorefinery constantly, it was considered from July to September (during the tomato processing operation) the cellars are filled at a rate of 33.2 t/d, while 11.5 t/d go to the biorefinery process (to ensure that the produced by-products are stored the same day they are produced, and the biorefinery is fed at a constant rate). During the rest of the year, while no tomato is processed, the cellars are emptied at a rate of 11.5 t/d to feed the biorefinery. The mass balance is reported in the Figure 16.

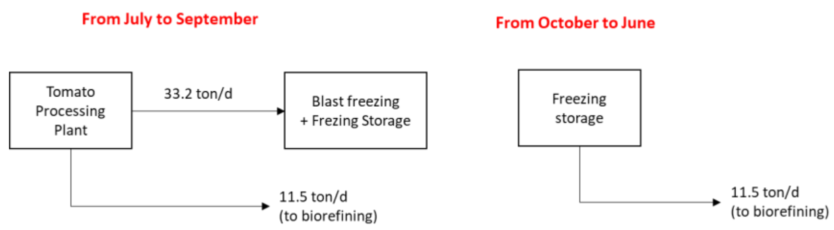


Figure 16 *Mass balance for storage unit*

Then, the needed number of cellars, the operative ones during the year and the allocated surface, the energy demand and the cost of the operation were evaluated, considering the following information reported in the literature:

Table 12 *Specific energy for blast freezing and freezing storage*

Storage temperature	-15 °C	(Greek Cold Storage & Logistics Association, no date)
Specific energy for blast freezing	0.133 kWh/kg (yearly)	(Swain, no date)
Specific energy for freezing storage	5.1 kWh/kg (yearly)	(Kendall and Payton, no date)
Cost of electricity	0.05 €/kWh	(Italy: household electricity prices 2020, no date)

With assumption, it was found that:

- The maximum number of working cellars is 534 in September
- An allocated surface of around 5000 m^2 is needed
- 3300 MJ/t of tomato by-products are needed to ensure their preservation
- The total operative cost is around 0.37 M€ for one year of operation

4.2. Separation between peels and seeds

As reported in the biorefinery scheme, the effective recovery and utilization of pomace require the separation of the peel and seeds as the basic step. At present, two different methods were proposed to achieve a reasonably clean separation of peel and seeds. Previous reports showed that tomato seeds could be separated from peels by a sedimentation system using water (Sogi, Bawa and Garg, 2000; Kaur et al., 2005) and then dried before use. Most recent studies have recommended the separation of dried pomace by sieves based on the difference in the particle sizes of peel and seeds, in contrast to the separation of wet pomace using water (Shao et al., 2013). In 2015, Shao et al. proved the feasibility of air separation of tomato pomace using a laboratory-scale fluidized-bed dryer (Shao et al., 2015). We developed two different flowsheets for the implementation in an industrial plant of the technologies mentioned above, considering the process scheme and process yield reported by the authors both for floatation-cum-sedimentation (Kaur et al., 2005) and air separation (Shao et al., 2013), to verify the technical feasibility of tomato pomace separation at industrial scale. With this intent a mass flow of tomato pomace of 720 kg/h was considered, that is the amount of tomato pomace produced by 5 medium transformation companies settled in Campania. This data was estimated after several interviews with plant engineers of local industries. Moreover, the tomato pomace stream was considered composed of 60 %wt. of peels and 40 %wt. of seeds (P A Silva et al., 2019), with peels containing 80 %wt. of moisture (Brachi et al., 2016a) while seeds containing 60 %wt. of moisture (Nassari et al., 2014). Finally, the drying temperature was taken in the range of 60-70 °C to avoid or minimize lycopene degradation, as reported in the literature (Demiray, Tulek and Yilmaz, 2013; Mendelová et al., 2013).

4.2.1. Process parameters and flowsheeting

According to Kaur et al. (Kaur et al., 2005), the wet tomato pomace readily available after tomato transformation is directly sent to a floatation-cum-sedimentation, in which pomace is mixed with a water flow and separated in its component by gravity. They report a schematic diagram of the pilot-scale floatation-cum-sedimentation system, shown in Figure 17. It consisted of one mixing tank (T1) having an impeller with three paddles for mixing pomace and water, three settling tanks (T2-T4), three trays to collect seeds, skin, and fibrous residues, one water collection tank (T5) and one recirculation pump (RP).

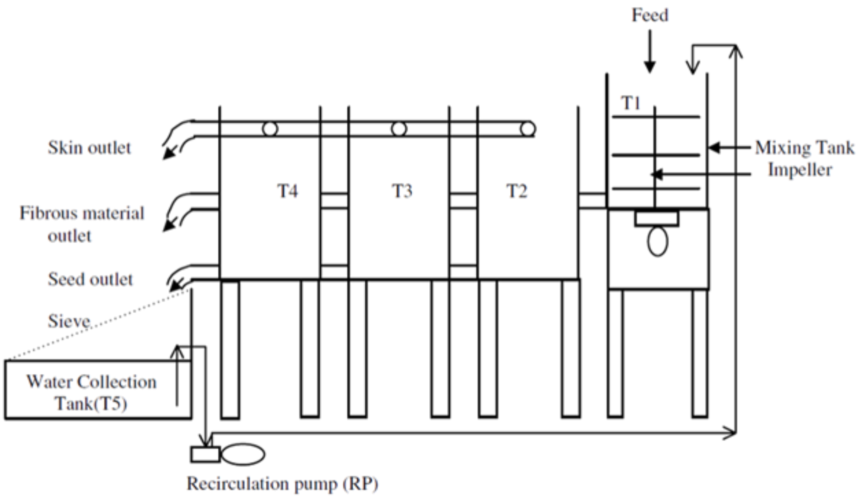


Figure 17 *Schematic diagram of flotation-cum-sedimentation system for peel and seed separation from tomato pomace (Kaur et al., 2005)*

They report the purity of outlet streams at different water flows. In particular, in our study, we considered the best result of Kaur's study in terms of purity of separation outlet streams, namely seeds and peels, considering neglectable the pulp amount (Benítez et al., 2018) and outlet streams were dried to a moisture content of 8 % after separation. an IKE conveyor mesh belt large food dehydrator for automatic continuous drying was considered (Best Customized Conveyor Mesh Belt Large Food Dehydrator | Ike Food Dehydrator, no date). Their results are reported in Table 13:

Table 13 *Purity of outlet streams of floatation-cum-sedimentation system*

Productivity of single unit [kg/h]	Water Demand [t/h]	Number of sedimentation units	Purity of peels at the outlet	Purity of seeds at the outlet
360	42.6	2	0.987	0.932

For the tomato pomace floatation-cum-sedimentation system, then, a flowsheet was developed and mass flows, energy demand to obtain separation and operative cost were evaluated. As shown in Figure 18, the flowsheet contains three operating blocks, one for the separation of tomato pomace into its component and two for drying of seeds and peels streams. Moreover, it shows the energy needed (E_n) for the steps, including the energy for conveying materials to different blocks and the energy for operating the recirculation pump for auxiliary water and the auxiliary mass flows like the water needed for separation, the air flows needed for drying and the water removed from wet materials.

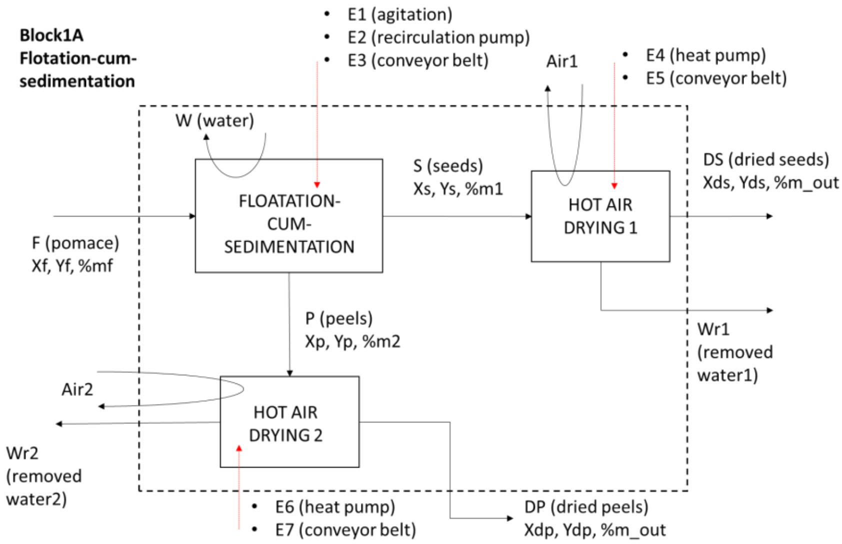


Figure 18 *Flowsheet for floatation-cum-sedimentation system of tomato pomace*

Regarding air separation, according to Shao et al. (Shao et al., 2015), tomato pomace was dried to a moisture content of 8.0% wt. For this step, an IKE conveyor mesh belt large food dehydrator for automatic continuous drying was considered (Best Customized Conveyor Mesh Belt Large Food Dehydrator | Ike Food Dehydrator, no date). Because the dried pomace contained large lumps by peel and seed particles adhering together, they were broken into peel and seed particles to make them float in the air stream and subsequently separate by the difference in their terminal velocities. A Vibra-Blender Model III by Vibra Screw inc. was considered to break up the lumps of peel and seeds (Continuous Blenders | Continuous Blender | Vibra Screw Incorporated, no date). Then a fluidized-bed dryer (model FC2K rice huller, Yamamoto Co. (Yamamoto CO., LTD. Yamamoto impeller type husker, no date)) was used to study the air separation of tomato pomace with different velocities.

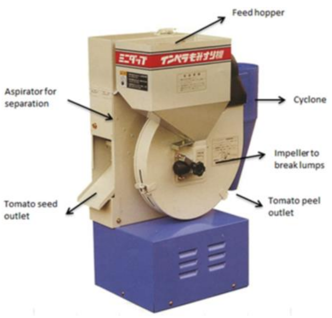


Figure 19 *Yamamoto Impeller Type Husker*

In particular, the best result of Shao's investigations in terms of purity of separation of outlet streams was considered in this study and reported in Table 14.

Table 14 *Purity of outlet streams of the air separation system*

Productivity of single unit [kg/h]	Number of air separator units	Purity of peels at the outlet	Purity of seed at the outlet
40	6	0.839	0.851

For the tomato pomace air-separation system, then, a flowsheet was developed, and mass flows, and energy demand to obtain separation and operative cost were evaluated. As shown in Figure 20, the flowsheet contains three main operating units, one for drying, one for blending and one for the final separation of seeds and peels. Moreover, it shows the energy needed (En) for the steps, including the energy for conveying materials to different blocks and the auxiliary mass, flows like the water removed from tomato pomace and the air flows needed for drying and air separation.

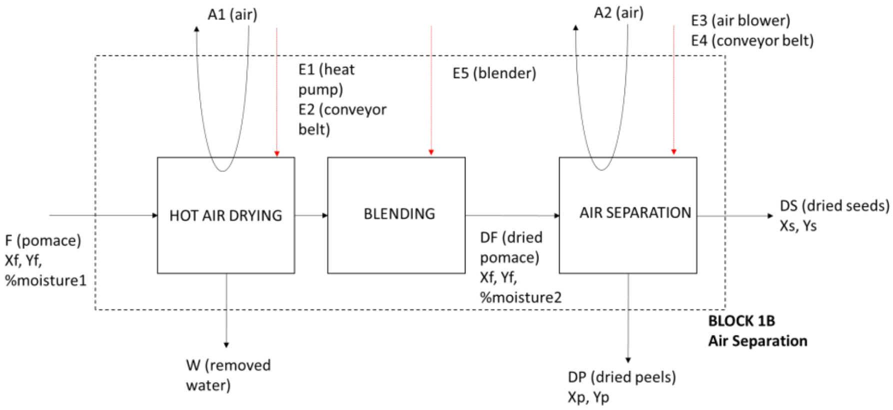


Figure 20 *Flowsheet for air separation system of tomato pomace*

4.2.2. Energy Demand evaluation

To evaluate the energy demand or the needed power for the systems mentioned above, different equations and laws reported in the literature were used or commercially available equipment was considered:

- Agitation system: the system for separation with sedimentation was considered as an agitated tank with 3 Rushton impellers, usually used for food process. Therefore, the volume of the tank was considered 1 m3 has reported in the patent US901195B2 (Bhushan et al., 2015), while the power required to rotate an impeller can be calculated using the following equations (Paul, Kresta and Atiemo-Obeng, 2003):

$$P = P_o \rho N^3 D^5 \quad [W] \quad \textit{Turbulent regime}$$
$$P = k_p \mu N^2 D^3 \quad [W] \quad \textit{Laminar regime}$$

  P_o is the (dimensionless) power number, which is a function of impeller geometry; ρ is the density of the fluid; N is the rotational speed, typically rotations per second; D is the diameter of the impeller; k_p is the laminar power constant, and μ is the viscosity of the fluid. In our case, the regime is turbulent due to a high Reynolds number, N is equal to 200 rpm, D is 0.28m (Bhushan et al., 2015) and P_o is 5 for Rushton impellers.
- Recirculation Pump: The pump used for recirculation of water was a centrifugal pump usually implemented to transport fluid. The energy usage in a pumping installation is determined by the flow required, the height lifted and the length and friction characteristics of the pipeline. The power required to drive a pump P is defined simply using SI units by:

$$P = \frac{\rho g H Q}{\eta} \quad [W]$$

  Where ρ is the density of the fluid, g is the standard acceleration of gravity, H is the energy head added to the flow [m], Q is the fluid flow rate, and η is the efficiency. In our case, the H is equal to 0.42 m (Bhushan et al., 2015), while the efficiency is considered 0.4 as evaluated with Thermexcel software (Calculation, pump, hydraulic, npsh, suction, fluid, water, net, no date).
- Conveyor belt: for modelling and brief design of conveyor belts needed in the separation system, technical specification provided by Rulmeca Group, the world's largest supplier of rollers/idlers, pulleys and motorized pulleys for heavy-duty belt conveyors for quarries and mining applications (Material handling rollers | Rulmeca Rollers, no date). The power needed for the handling of the solid streams was evaluated with:

$$P = \frac{F_u\, v}{100\, \eta} \quad [W]$$

Where F_u is the shear stress, v is the velocity of the belt and η is the efficiency. For our cases, η was considered as 0.86 while the velocity was 2.5 m/s, e.g., a standard value for volatile powders handling. For shear stress, the following equation provided by Rulmeca was used:

$$F_u = [L\, C_q\, C_t\, f(2\, q_b + q_g + q_{RU} + q_{RO}) \pm (q_g\, H)]0.981 \quad [daN]$$

Where L is the length of the belt, C_q and C_t are the coefficients of fixed and passive resistance, f is the internal friction factor, q_g, q_{RU} and q_{RO} are the weight of the belt, of the handled material, and the rotative part in kg/m and H is the height gain. Their values were evaluated by using tables and formulas provided by Rulmeca.

- Other equipments: for the other operations, a commercially available industrial machine was found, taking into consideration our mass flows, and checking their feasible application in our system. Yamamoto Impeller Type Husker was implemented for air separation of dried tomato pomace (60 kg/h capacity, 250 W power supply). A Vibra-Blender Model III by Vibra Screw inc. was implemented for dried tomato pomace blending (33.6 m3/h capacity, 1.9 kW power supply). IKE conveyor mesh belt large food dehydrator was considered for drying of the streams (40 kg/h dehumidification amount, 24 kW power supply). It is worth noticing that for double-checking the power needed by the continuous dehydrator, the energy of vaporization for removing the moisture inside the tomato pomace was evaluated by using DWSIM® software, a chemical process simulator, for easy and rapid simulation. NRTL was used as a method for the simulation.

4.2.3. Mass and energy balances

Considering the developed flowsheet for the floatation-cum-sedimentation system, the separation yield reported in Table 13, and literature data, the mass flows for all the involved streams were calculated by using simple mass balance, taking into account the two main components of tomato pomace, namely seeds and peels. The obtained results are reported in Table 15:

Table 15 *Mass flows for floatation-cum-sedimentation system*

Raw materials [kg/h]	
Tomato pomace	720
Water	42603
Air	196000
Emissions [kg/h]	
Wastewater	43104
Spent air	196000
Products flows [kg/h]	
Dried peels	91.7
Dried seeds	127.4

As reported in the table, when 720 kg/h are fed to the sedimentation system followed by the peels and seed drying, 91.7 kg/h of dried peels and 127.4 kg/h of dried seeds are produced with a small content of impurities. Moreover, 42.6 t/h of water and around 200 t/h of air are needed. Regarding the power demand for sedimentation, Figure 21 reports the allocation of power needed, in kW. Almost 340 kW is needed to obtain the desired separation yield and dried intermediate products. It is worth noticing that almost 99% of this power is due to drying operation. In terms of energy demand, this separation system needs 1700 MJ for each tonne of tomato pomace entering the system, 1680 MJ of thermal energy for heating streams and 20 MJ of electric energy for powering machines.

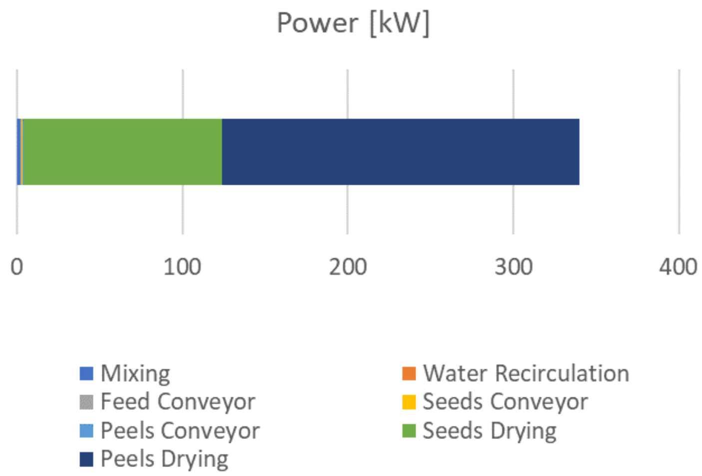


Figure 21 *Power allocation for floatation-cum-sedimentation system*

Considering the developed flowsheet for the air separation system, the separation yield reported in Table 14, and literature data, the mass flows for all the involved streams were calculated by using a simple mass balance. The obtained results are reported in Table 16.

Table 16 *Mass flows for air separation system*

Raw materials [kg/h]	
Tomato pomace	720
Air	182000
Emissions [kg/h]	
Wastewater	501
Spent air	182000
Products flows [kg/h]	
Dried peels	88.7
Dried seeds	130.4

As reported in the table, when 720 kg/h is fed to the air separation system preceded by the peels and seed drying and blending, 88.7 kg/h of dried peels and 130.4 kg/h of dried seeds are produced with a higher content of impurities compared to floatation-cum sedimentation. On the other hand, no auxiliary water is involved and around 182 t/h of air is needed. Regarding the power demand for sedimentation, Figure 22 reports the allocation of power needed, in kW. Almost 350 kW is needed to obtain the desired separation yield and dried intermediate products. It is worth noticing that almost 90% of this power is due to drying operation and 9% due to blending operation. In terms of energy demand, this separation system needs 1728 MJ for each tonne of tomato pomace entering the system, 1560 MJ of thermal energy for heating streams and 168 MJ of electric energy for powering machines.

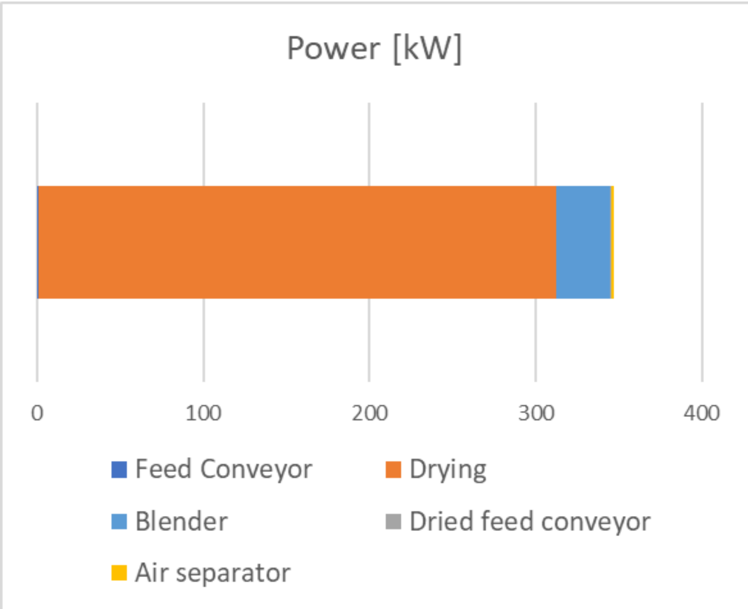


Figure 22 *Power allocation for air separation system*

4.2.4. Separation system comparison

In conclusion, an extensive literature study showed that there are only two available technologies for the industrial separation of tomato pomace in its two components, peels, and seeds. The first one is a continuous separation by floatation-cum-sedimentation in water media using gravity to obtain a separation, this method allows to obtain very high purity for the outlet streams at expense of a high amount of needed water (Kaur et al., 2005). The alternative is an air separation method using drying materials as feed and exploiting the differences in terminal velocity as the basis for separating mixtures (Shao et al., 2015). Then, these two alternatives were implemented in two flowsheets, to verify their industrial feasibility, evaluate the mass flows involved and compare them in terms of output yield and energy demand. Mass flows were evaluated by simply mass balance while to evaluate the energy demand or the needed power for the systems mentioned above, different equations and laws reported in the literature were used or commercially available equipment was considered. As reported before both technologies allow a good level of purity at outlet streams and energy demands are comparable. In Figure 23, a comparison between different process performance variables is reported for a separation plant based on either flotation-cum-sedimentation or air separation.

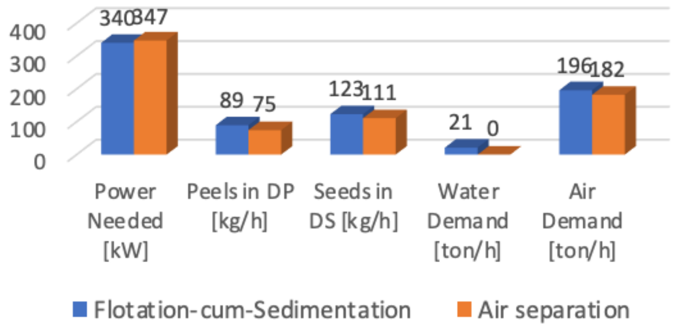


***Figure 23** Comparison between the two technological alternatives*

As shown in the figure, the sedimentation system allows higher peels and seeds output, due to higher separation efficiency, with lower energy demand. On the other hand, auxiliary streams have a higher mass flow rate. Meaning a higher environmental and economic burden for this type of operation. It is worth noticing that, even excluding from the analysis the power allocation for the drying step, the floatation-cum-sedimentation reveals itself as the best alternative due to the high energy demand for blending operation needed in the air separation system.

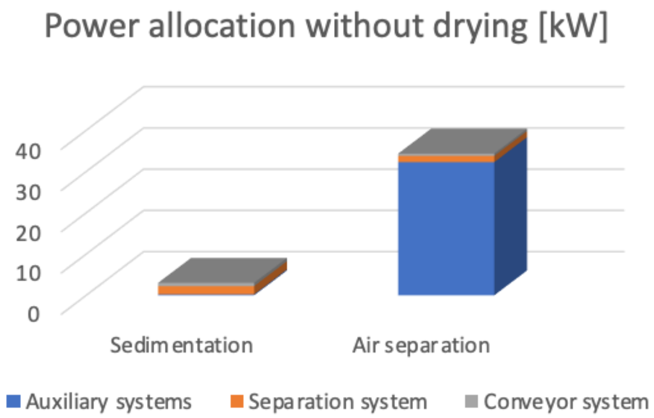


***Figure 24** Power allocation without drying*

Finally, considering that, in the first analysis, the costs for working the two splitting systems are: the cost of methane for heating, the cost of electricity and the cost for treating the water removed from the pomace, an operative cost comparison was carried out. Figure 25 shows that the operative cost during a year for separate peels and seeds by floatation is 1.15 M€ while for an air separation system is 1.11 M€. It is worth noticing that the total cost is mainly due to the drying operation (cost of heating and treatment of the removed water).

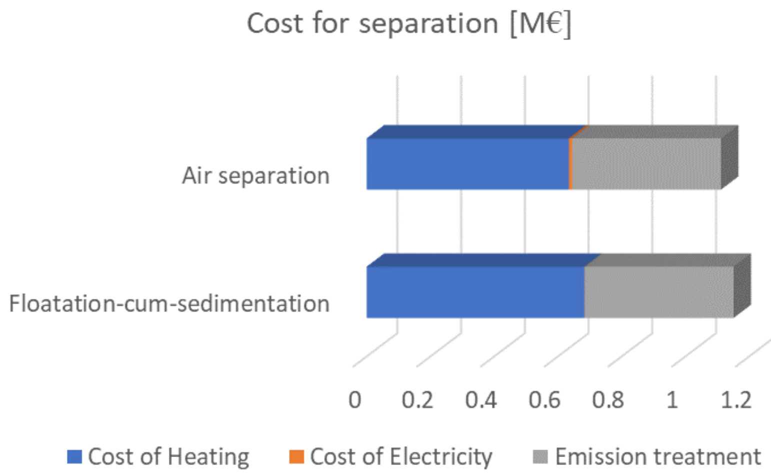


Figure 25 *Cost comparison for separation systems [M€]*

4.3. Lycopene extraction from tomato peels

As reported in Chapter 1 solvent extraction is the most used method for the recovery of carotenoids from plant materials, due to their hydrophobicity and limited solubility in water. The same is for the extraction of lycopene from tomato peels (Stajčić et al., 2015). Therefore, this paragraph reports on the conceptual development and optimization of a plant section producing tomato lipophilic extract containing lycopene (around 10 % wt.) to produce dietary supplement capsules with nutraceutical applications. The use of two different solvents is proposed: a conventional organic solvent and a “green” alternative. Namely, ethyl acetate, which is among the solvents with the best extraction performance, and limonene, which is a natural solvent coming from citrus by-products and the best eco-friendly alternative for carotenoid extraction. Therefore, two flowsheets are developed; the technical feasibility of the processes is discussed, and their gross profit is evaluated. The feedstock characteristics are dictated by the upstream processing in the proposed biorefinery reported in the previous paragraph. Therefore, the basis for the present calculations is provided by the output of the upstream floatation-cum-sedimentation section, i.e., the feed rate of dried peels (DP) is 91.7 kg/h, with a purity of 0.987 and a moisture content of 8% wt.

4.3.1. Process parameters and flowsheeting

According to Calvo et al. (Calvo, Dado and Santa-María, 2007) dried tomato skins were ground with a mill (0.05–0.250 mm particle size), and stored in a tank at a controlled temperature, then, ground peels were mixed with ethyl acetate with a liquid to solid mass ratio L/S = 80 and kept at the desired temperature (50 °C) in agitated condition for 30 minutes. The authors reported the following extraction yield:

Table 17 *Extraction yield and process parameters for lycopene extraction with ethyl acetate*

Temperature [°C]	Lipophilic extract [g/100g dried peels]	Lycopene content in lipophilic extract [%]	L/S
50	1.64	8.23	80

Solvent extraction is a batch process; for this reason, the extraction step is designed with 4 agitated vessels working in parallel. Each vessel has a volume of 4000 L, to keep the loading/unloading step and extraction step of the same duration, and undergoes 4 different operations alternatively: charging, extraction, discharging and washing. **Figure 26** shows the extraction setup.

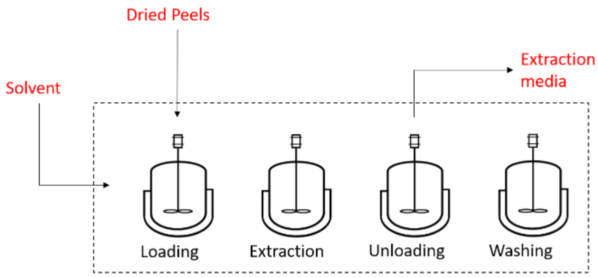


***Figure 26** Extraction vessels configuration*

After leaching, the extraction medium is mainly made of the solvent, in which lipophilic extract and the solid residue are dispersed. Then, the solid residue is removed by centrifugation, dried to remove the adsorbed solvent, and sent to another biorefinery block. The obtained liquid mixture is sent to a flash evaporator to remove the solvent and the residual water. Then, the solvent is filtrated to remove residual lipophilic extract, conveyed to a molecular sieve to remove water, condensed, cooled, and recycled to the extraction step. The lycopene-containing lipophilic extract recovered at the bottom of the flash is sent to a capsule filling machine and bottled up. An amount of 10 mg of lycopene, the recommended daily dose for an adult (Story et al., 2010), is considered in a capsule. Moreover, peanut oil, hydrogenated vegetable oil and soy lecithin are used as additives to improve the product workability and quality as reported in the patent USOO5897866A (Bombardelli et al., 1999).

***Table 18** Composition of a capsule containing lycopene lipophilic extract*

	Amount [mg]	Cost [€/kg]
Lycopene	10	
Peanut oil	151	2.49
Hydrogenated vegetable oil	80	0.86
Soy lecithin	1	77

During the process, three types of emission are produced: spent oil composed of residual lipophilic extract, residual water in the air and spent solvent coming from solid drying. The flowsheet for this process is reported in Figure 27, with the energy-demanding operation highlighted at the bottom.

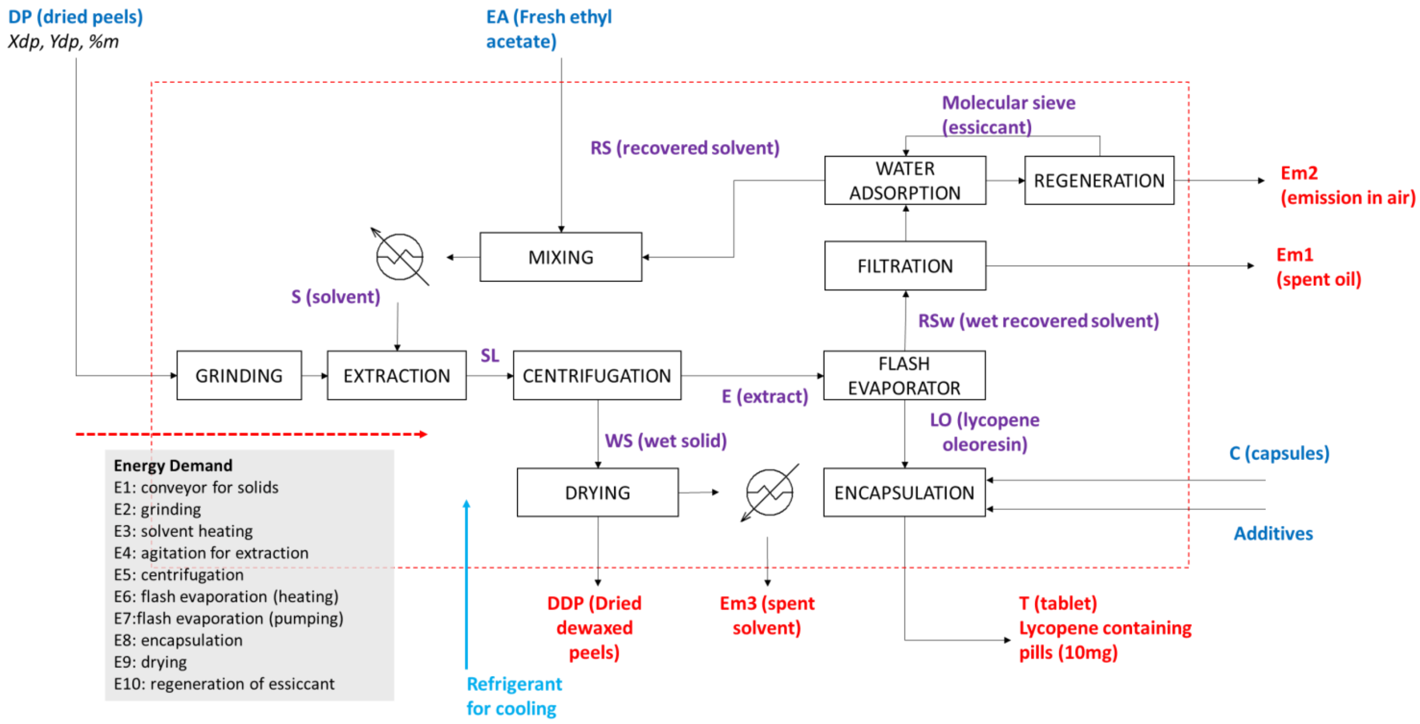


Figure 27 *Flowsheet for the extraction of lycopene-containing lipophilic extract with ethyl acetate and tablet encapsulation*

Regarding the extraction with limonene, Chemat-Djenny et al. reported that after grinding dried tomato peels are mixed with a solution of limonene and water (40 % wt. in limonene) at room temperature and kept in agitation for 30 minutes (Chemat-Djenni et al., 2010). With this condition, the authors reported the following extraction yield:

Table 19 *Extraction yield and process parameters for lycopene extraction with limonene*

Temperature [°C]	Lipophilic extract [g/100g dried peels]	Lycopene content in lipophilic extract [%]	L/S
25	0.39	10	6.25

Due to the lower L/S ratio for the extraction with limonene, the vessel size is much smaller in this case. Each vessel has a volume of 300 L. After the extraction, the process scheme for this case is quite similar, but it involves a squeezing step of the solid residue due to the higher evaporation temperature of the limonene-water solution and the direct recycling of the solvent solution after the lipophilic extract purification in the flash evaporator. For these reasons only spent oil and spent solvent emissions are produced. The flowsheet for this process is reported in Figure 28, with energy-demanding operations highlighted in the shaded area.

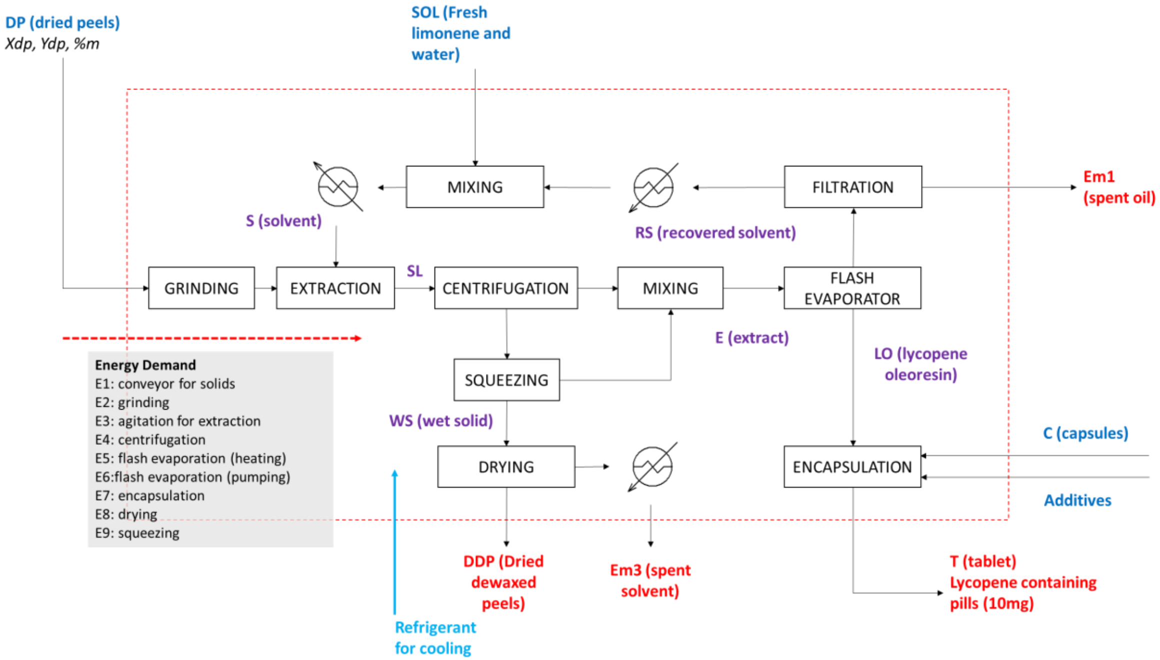


Figure 28 *Flowsheet for the extraction of lycopene-containing lipophilic extract with limonene and tablet encapsulation*

4.3.2. *Energy demand evaluation*

As reported in the previous section, energy demand or the needed power was evaluated with different equations and laws reported in literature or commercially available equipment technical datasheet; moreover, Aspen Plus was used to estimate energy demand for flash operation:

- Grinding: for the size reduction of the tomato peels, the energy consumption of two-stage fine grinding of Douglas-fir wood was considered as reported by Wang et al. (Wang et al., 2018). They report that to reduce the size of woody biomass to a median size diameter of 0.229 mm a specific energy consumption of 0.25 kWh/kg is required.
- Centrifugation: for the separation of the spent peels from the extraction media a Flottweg centrifugal decanter Model C2E-4 was considered (Figure 29). In the rotating bowl of the decanter the solid particles, which are heavier than the liquid, move towards the periphery of the drum for the effect of the centrifugal force and form a sediment layer on the inner wall of the decanter drum.

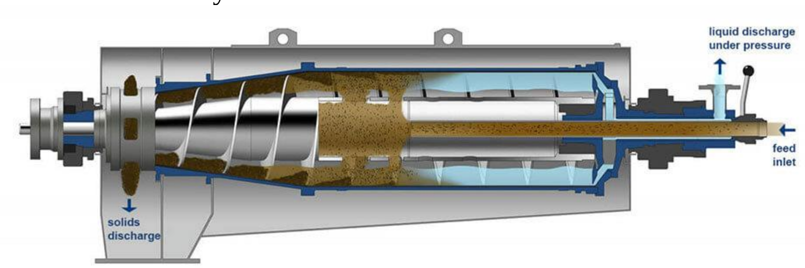


Figure 29 *Sketch of a centrifugal decanter for sludges*

In particular, the technical datasheet reports that for a feed inlet of 1-10 m^3/h, 5.5-7.5 kW are needed for the drum drive motor, while 2.2 kW are needed for the auger drive motor (Tecnologia di separazione meccanica | Separazione solido-liquido per il vostro successo, no date).

- Encapsulation: a liquid capsule filling sealing machine From Upmack® Model LCFS 300 was considered (**Figure 30**). It is a fully automatic machine that fills and seals up to 18,000 capsules per hour with oily liquid, solution, mixed suspensions or paste formulations, with a power demand of 9 kW (‘Liquid Capsule Filling Sealing Machine’, no date).

***Figure 30** LCFS 300 from Upmack®*

- Regeneration of the desiccant: when lycopene-containing lipophilic extract is extracted with ethyl acetate, the recycled solvent is purified from water by a molecular sieve from Supelco®. Technical datasheet reports, that the heat of regeneration is 4200 kJ/kg of adsorbed water.
- Other equipment: for the other operations, such as conveyor machines, drying and agitation the same methodology as reported for the separation section was used. For the heating of the materials, Aspen Plus ® calculations were used. The flash evaporation unit was modelled and optimized in Aspen Plus® and the results are reported in the following paragraph.

4.3.2.3. Flash evaporator optimization and heat evaluation

Among all the unit operations involved in this section, the most important and energy-consuming is solvent recollection/lipophilic extract purification, due to technology and purification issues. Indeed, the organic solvent removal is a hard task because of the high evaporation temperature of the solvent, as ethyl acetate boils at 77°C, while the binary mixture limonene-water boils at 117°C. On the other hand, lycopene-containing lipophilic extract cannot undergo high-temperature processing, due to its easy degradation. Moreover, as stated by the European Commission rules the solvent amount in the final lipophilic extract cannot be higher than 50 mg/kg of lipophilic extract (Commission Directive 2011/3/EU, 2011). For this reason, the evaporation process has to be carried out in vacuum conditions (Rath and Olempska-Beer, 2009), which are generally more energy-consuming than atmospheric ones. With this background, the flash evaporation for extraction with ethyl acetate was first modelled and then optimized by using AspenPlus ® software. The optimization was carried out with the Sensitivity tool of the software, while NRTL was used as the base method. For the calculation, the feed stream was considered the reaction media coming out of the extraction and centrifugation steps. The lipophilic extract composition (triglycerides) was considered as the one reported by Rath and Olempska-Beer (Rath and Olempska-Beer, 2009), with the lycopene amount as reported by Calvo et al. (Calvo, Dado and Santa-María, 2007). They appear as a table in Figure 31.

	Units	REACOUT
Phase:		Liquid
Component Mole Flow		
WATER	KMOL/HR	0.405212
ETHYL-01	KMOL/HR	74.989
TRILI-01	KMOL/HR	0.000599271
GLYCE-01	KMOL/HR	2.80427e-05
TRIOL-01	KMOL/HR	3.83986e-05
TRILI-02	KMOL/HR	6.87007e-05
TRIPA-01	KMOL/HR	0.000252683
ALL-T-01	KMOL/HR	7.12917e-05
Mole Flow	KMOL/HR	75.3952
Mass Flow	KG/HR	6615.19
Volume Flow	L/MIN	127.353

Figure 31 *Composition of the stream entering the flash evaporator*

This liquid stream (REACOUT) comes from the centrifugation section and is composed of the solvent (SOL) and the extractives, i.e., the residual water in the peels (WATER), the lycopene (LYCOPENE) and the oily fraction (OILFRAC). It enters the flash evaporator and two different streams come out, i.e., a liquid stream rich in lipophilic extract (OLEORES) and a gaseous stream rich in the organic solvent and water (SPENTSOL). The OLEORES stream is brought to ambient pressure by a pump (B5), while the SPENTSOL stream reaches ambient pressure thanks to a cooler that turns it into a liquid stream (B10) to be pumped (B11). This configuration was implemented in AspenPlus ® and reported in Figure 32.

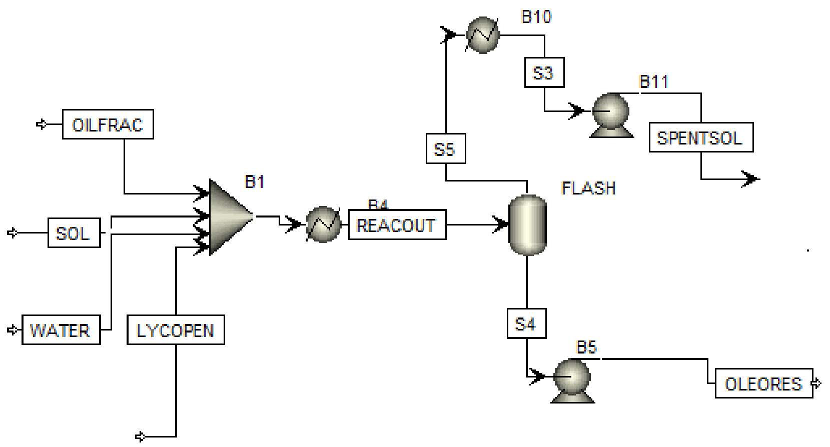


Figure 32 *Flowsheet of the flash evaporator in AspenPlus ®*

The Flash evaporator is optimized by a Sensitivity in which pressure and temperature are studied. Pressure ranges between 0.05 mbar and 1 mbar while the temperature is between 30°C and 70°C. The optimized parameters were the amount of ethyl acetate in OLEORES (<50 mg/kg) and the lycopene recovery factor (>0.9995). The outcome of the sensitivity is reported in Figure 33 where the feasibility areas are in light and dark green.

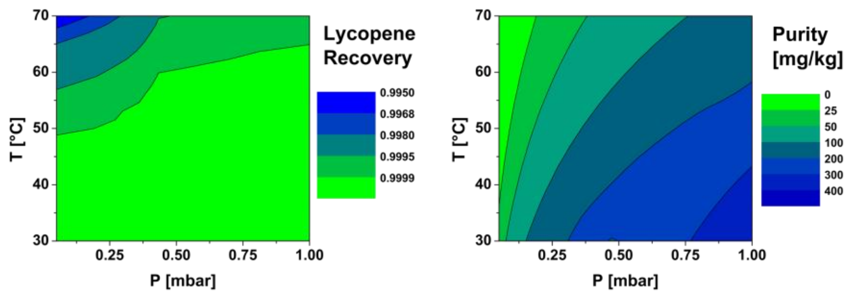


Figure 33 *Feasibility areas of flash evaporator regarding the two design constraints*

Then, the feasibility zones for these two parameters were plotted together to find the operating zone where both constraints are satisfied. The result is reported in Figure 34, where the red crosses represent the points in which the lycopene recovery is higher than 0.9995, while the blue dots represent the points in which the solvent content in the lipophilic extract is lower than 50 mg/kg.

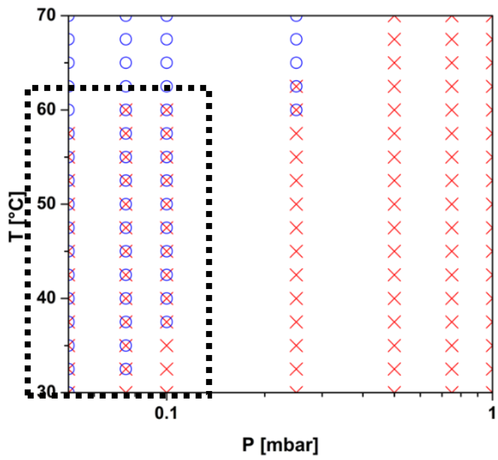


Figure 34 *Operating points for flash evaporator*

The black dotted line highlights the operating range, namely P comprised between 0.05 and 0.1 mbar and T in the range 37.5-57.5°C. Then, in the operating range, another sensitivity was carried out to optimize the total net duty of the separation: heat duty at the flash and net work at the pumps. The pump efficiency was taken at 0.9. The result of the second sensitivity is reported in Figure 35.

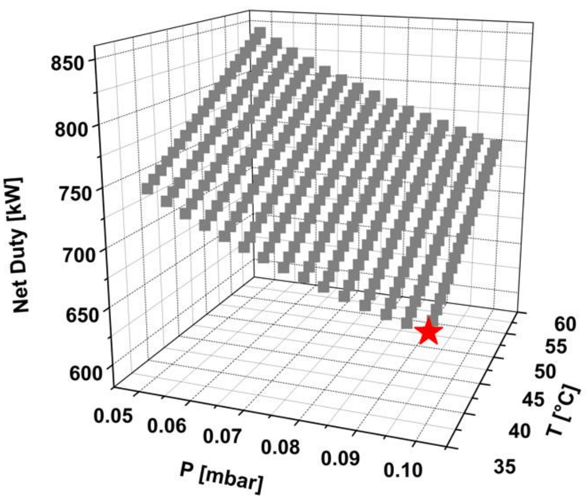


Figure 35 *Net duty optimization for the flash operation*

As shown in the figure, the optimum operating condition for flash evaporation, i.e., the one that satisfies the constraints and minimizes the duty (red star), is given by P = 0.1 mbar and T = 37.5°C, with a total duty of 656.84 kW. The same methodology was used to optimize the separation of the extracted lipophilic extract from the solvent mixture limonene-water, for the alternative extraction scheme. The optimization results for both schemes are reported in the Table 20.

Table 20 *Optimized parameters for solvent removal in the lycopene extraction process*

	Ethyl acetate removal	Limonene-water removal
Pressure at flash [mbar]	0.1	0.05
Flash temperature [°c]	37.5	52.5
Flash operation total duty [kw]	656.84	237.94

As reported in the table, the removal of limonene-water solution requires heavier conditions due to the higher boiling point, but the total duty is lower due to the lower L/S ratio. After the solvent removal, Aspen Plus software was also used to evaluate the heat duty for recycled solvent and feedstock heating. For this operation, the tomato peels were considered as cellulose (CELLU-01), which is the only component in the Aspen database that could be used to represent biomass. The biomass flow (PEELS), the required fresh solvent (FRSOLV) and the recycled solvent (SPENTSOL) were sent to a heater to reach the required temperature for the extraction step. Figure 36 shows the implementation in Aspen of this operation.

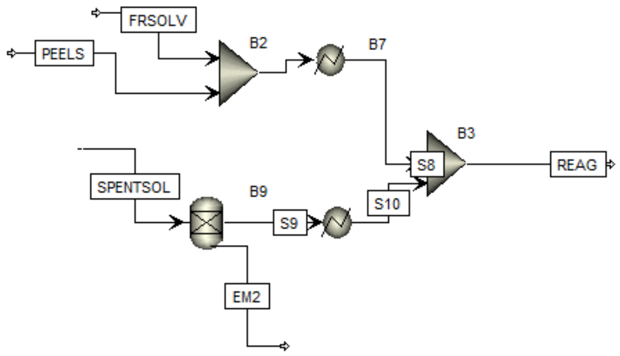


Figure 36 *Solvent and feedstock heating section in Aspen Plus*

The heat duty obtained for the extraction with ethyl acetate and limonene-water solution is reported in Table 21.

Table 21 *Solvent and regent heat duty in the lycopene extraction process*

	Ethyl acetate removal	Limonene-water removal
Solvent and reagent heating [kW]	398.43	46.78

These results were used in the evaluation of the mass balances and energy balances for the two alternative methods for the extraction of lycopene from tomato peels reported in the next paragraph.

4.3.3. Mass and energy balances

Considering the developed flowsheet for the lycopene extraction with ethyl acetate, the separation yield reported in Table 17, and literature data, the mass flows for all the involved streams were calculated by using simple mass balances, implemented in an MS EXCEL spreadsheet. The obtained results are reported in Table 22:

Table 22 *Mass balance for lycopene-containing lipophilic extract extraction with ethyl acetate*

Raw materials [kg/h]	
Dried peels	91.7
Ethyl acetate	248.69
Capsules [pz/h]	12000
Peanut oil	1.81
Hydrogenated vegetable oil	0.96
Soy lecithin	0.01
Molecular sieve [kg]	466.08
Emissions [kg/h]	
Em1 (spent lipophilic extract)	0.054
Em2 (water to air)	7.29
Em3 (spent solvent)	248.69
Em4 (spent sieve)	0.89
Products flows [kg/h]	
Lycopene-containing lipophilic extract	1.41
Lycopene tablets [pz/h]	12000
Dried dewaxed peels	82.90
Recycled stream [kg/h]	
Recycled ethyl acetate	6358.38

As reported in Table 22, when 91.7 kg/h of dried peels are fed to the extraction section, 248.69 kg/h of fresh ethyl acetate is needed. Regarding the molecular sieve, two parallel desiccant units are considered (for adsorbing/desorbing operations), therefore 466.08 kg of the molecular sieve is needed. This plant section produces 12000 lycopene containing capsules and 82.90 kg/h of dried dewaxed peels that can be used for pectin extraction.

Four different emissions or wastes to be treated are produced: 0.054 kg/h of spent lipophilic extract, 7.29 kg/h of water emitted in the air, 248.69 kg/h of spent solvent and 0.89 kg/h of spent molecular sieves. For the evaluation of the spent sieve, it was considered that the fresh desiccant is fed to the filter every month.

Regarding the energy demand of the extraction with ethyl acetate, the power allocation for the different unit operations is reported in Figure 37. The total power demand is 1134 kW, with heating as the most energy-demanding part, indeed 58% of the power demand is due the flash operation and 35% is due to solvent and peels heating. In terms of energy demand, this extraction system needs 0.340 MJ for each tablet produced by the plant, 0.327 MJ of thermal energy for heating streams and 0.013 MJ of electric energy for powering machines.

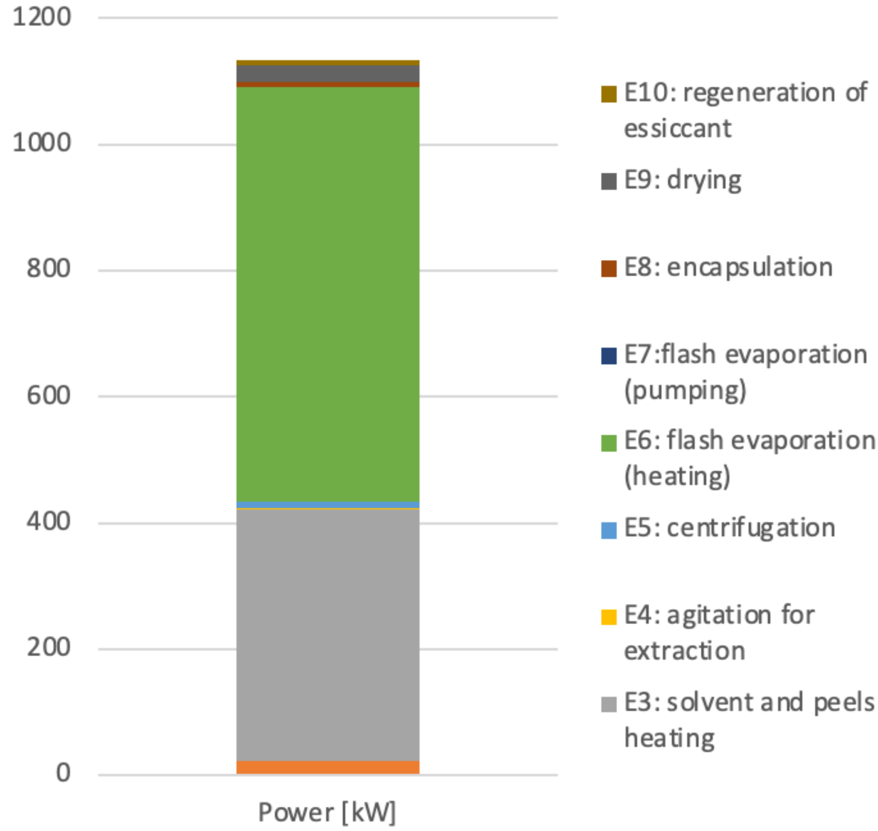


Figure 37 *Power allocation for lycopene extraction with ethyl acetate*

Regarding the extraction system with limonene-water solution, the obtained results, in terms of mass balance are reported in Table 23:

Table 23 *Mass balance for lycopene extraction with limonene-water solution*

Raw materials [kg/h]	
Dried peels	91.7
Limonene	19.26
Water	35.12
Capsules [pz/h]	3500
Peanut oil	0.53
Hydrogenated vegetable oil	0.28
Soy lecithin	0.0035
Emissions [kg/h]	
Em1 (spent lipophilic extract)	0.014
Em3 (spent solvent)	54.37
Products flows [kg/h]	
Lycopene-containing lipophilic extract	0.334
Lycopene tablets [pz/h]	3500
Dried dewaxed peels	84.02
Recycled streams [kg/h]	
Recycled limonene	173.3
Recycled water	316.09

As reported in Table 23, when 91.7 kg/h of dried peels are fed to the extraction section, 19.26 kg/h of limonene and 35.12 kg/h of water are needed. This plant section produces 3500 lycopene containing capsules and 84.02 kg/h of dried dewaxed peels that can be used for pectin extraction. Two different emissions or wastes to be treated are produced: 0.014 kg/h of spent lipophilic extract and 54.37 kg/h of spent solvent.

Regarding the energy demand of the extraction with the limonene-water solution, the power allocation for the different unit operations is reported in Figure 38. The total power demand is 337 kW, with flash evaporation as the most energy-demanding part (70% allocation). In terms of energy demand, this extraction system needs 0.347 MJ for each lycopene tablet produced by the plant, 0.292 MJ of thermal energy for heating streams and 0.055 MJ of electric energy for powering machines.

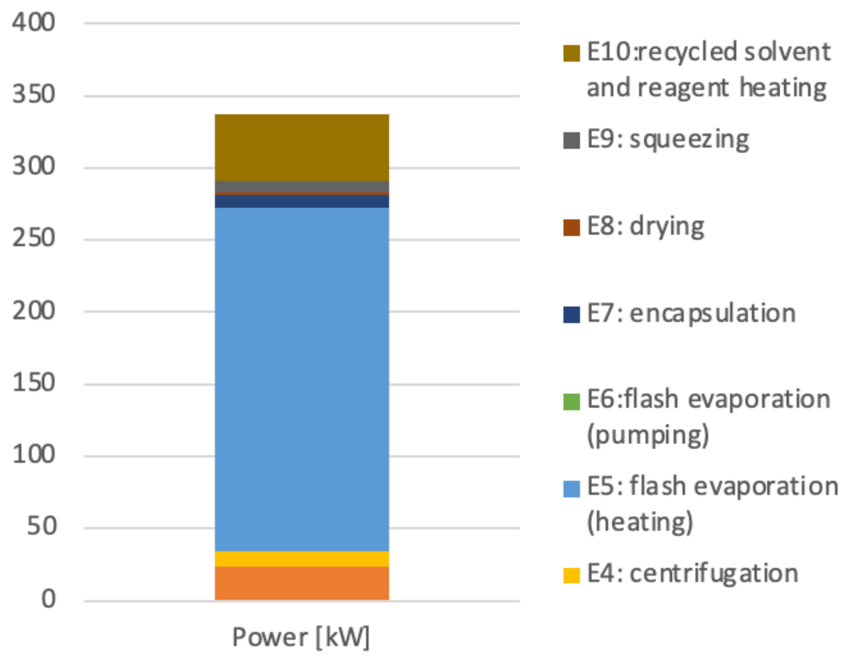


***Figure 38** Power allocation for lycopene extraction with limonene-water solution*

4.3.4. Lycopene extraction systems comparison

In conclusion, after an extensive literature review, solvent extraction for lycopene production from tomato peels was selected, due to its easiness and readiness. Among organic solvents allowed for carotenoids extraction two alternatives were chosen: ethyl acetate, which has the highest extraction yield and limonene which is the best eco-friendly alternative to commercially used solvent. Then, two different flowsheets were developed, considering all the issues connected to the solvent extraction, to verify their technical feasibility, evaluate the mass flows involved and compare them in terms of output yield and energy demand. Mass flows were evaluated by simple mass balances; vice versa, to evaluate the energy demand or the needed power for the systems mentioned above, different correlations and laws reported in the literature were used or commercially available equipment was considered. Both solvents allow good extraction yield, with a non-negligible difference in terms of output flows and power demand. When ethyl acetate is used as extractive solvent 12000 lycopene tablets per hour are produced, while only 3500 capsules per hour are produced when the limonene-water mixture is used as a solvent. On the other hand, a larger amount of waste streams is produced, and higher power demand is needed for the first scheme (1134 kW for ethyl acetate and 337 kW for limonene-water). Anyway, the specific energy demand to produce a single capsule is comparable: 0.340 MJ for the first alternative and 0.347 MJ for the eco-friendly one. Figure 39, a comparison between different process performance variables is reported for a lycopene extraction plant based on either ethyl acetate or limonene.

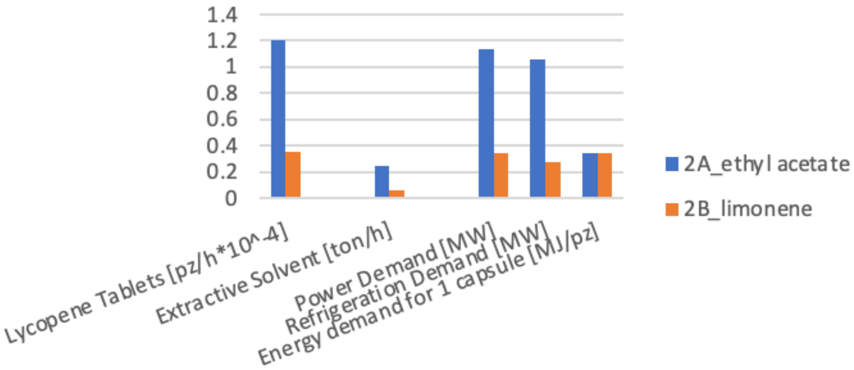


Figure 39 *Comparison between the two technological alternatives for lycopene extraction*

Finally, considering that, in a first analysis, the costs for working the two separation systems are those due to methane for heating, electricity, refrigeration, raw materials and waste stream treatment, an operating cost comparison was carried out.

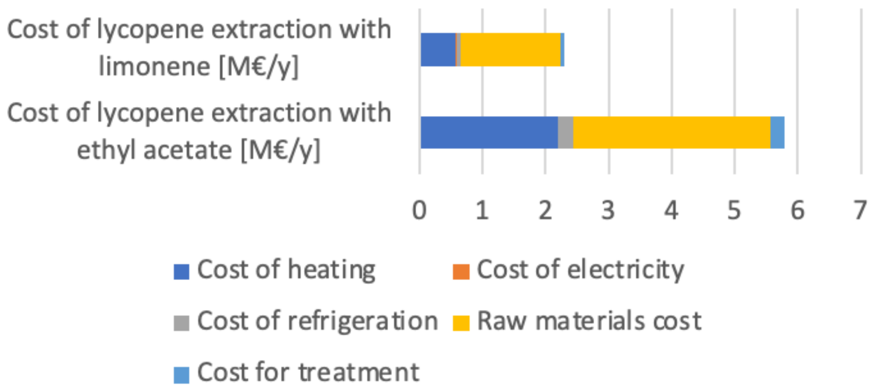


Figure 40 *Cost of lycopene extraction for the two alternatives*

Figure 40 shows that to obtain lycopene tablets by using ethyl acetate as the solvent, a total operating cost of 5.79 M€/y is predicted. This cost is mainly due to raw materials (54%) and reagent heating (38%). For the limonene extraction, the operating cost is 2.29 M€/y. Again, in this case, most of the cost is due to materials (69%) and heating (25%). Regarding the cost for a single produced tablet, it is 0.08 € for the first case and 0.11 €, making the scenario with ethyl acetate as solvent more economically convenient. Indeed, considering that boxes of 60 tablets are the final product of the plant, with an economic value of 36 €/box (as found as an average prize found on selling platform as Amazon® and Pharmacosmo®), the gross profit of the plant section is:

$$\text{Gross Profit} = \text{Revenue} - \text{Operative Cost}$$

Considering this equation, the gross profit for a plant that uses ethyl acetate as the extraction solvent is 39 M€/y, whereas it is almost 11 M€/y when the limonene-water solution is used as a solvent.

4.4. Pectin extraction from dewaxed and dried tomato peels

As reported in Chapter 1, pectin is commonly present in most plant tissues, commercial pectins are almost exclusively derived from the citrus peel or apple pomace, both by-products of juice production, due to higher quality standards, in terms of molecular weight and color, and the possibility to have sufficient quantity to run a cost-effective production operation (Marić et al., 2018; Ruano et al., 2019). The industrial process for pectin production is constituted of four main sections: an acid extraction in which the protopectin, contained in the raw material, is hydrolyzed and transformed into a water-soluble molecule; the purification of the extract, which is separated from the solid matrix by filtration step; the repeated washing/precipitation of pectin by alcohol, a final pectin purification by drying and grinding (Marić et al., 2018). The core of the process is therefore the extraction step that is conventionally carried out by treating the raw material in a reactor; batch operation under agitation is usually involved at the industrial level, but recent research demonstrated that a continuous reactor could reach the same pectin yield (Soemargono et al., 2016). The optimum temperature is usually in the range of 70-100°C (Marić et al., 2018), while the pressure is kept at atmospheric in almost all cases (Morris and Binhamad, 2020). The residence time of the process may change from one producer to another, but in general, it depends on the type of raw material (May, 1990). The extracting agent is usually a mineral acid, mainly hydrochloric acid, sulfuric acid, or phosphoric acid, at pH values ranging between 1-3. However, the main disadvantage of these mineral acids is their toxicity and the generation of environmentally harmful effluents (Yapo, 2009). Therefore, some organic acids, such as citric, tartaric, and maleic acid, have been tested for pectin extraction with results comparable to mineral ones (Yapo, 2009). Regarding alternative feedstocks, in 2006, Del Valle and coworkers were the first to report the presence of pectin in tomato peels (Del Valle, Cámara and Torija, 2006). Then, Grassino et al. (Grassino et al., 2016) developed a laboratory method to produce pectin from dried tomato peels, using ammonium oxalate and oxalic acid as extracting solvents. On another side, Alancay et al. (Alancay et al., 2017) optimized the pectin extraction from tomato processing waste by mineral acid extraction, i.e., with hydrochloric acid. According to their results, it can be concluded that tomato peels are a suitable source for pectin that can be used in the food and pharmaceutical industry, and the extraction yields are between 20-30% when starting from dried peels and adopting acid extraction. In addition, Sengar et al. report that to improve the color and quality of pectin extracted from tomato peels, a pretreatment that extracts the lycopene is recommended (Sengar et al., 2020). To the best of the authors' knowledge, no studies or research were carried out to investigate the scalability as well as the technical and economic feasibility of a process plant producing pectin from dewaxed tomato peels. Therefore, this work reports on the conceptual development and optimization of a plant section based on tomato peels as feedstock and producing pectin, after lycopene extraction, for the food industry. The use of two different acids was studied: a conventional mineral acid and a "green" alternative. Therefore, two alternative flowsheets are proposed, and in parallel, the technical feasibility and the economic indexes of the two processes are discussed and evaluated. Aspen Plus® was utilized for simulation and optimization of processes. As a basis for calculations, 465 t/y, namely 83 kg/h, of dried dewaxed tomato peels (DDP) are considered, considering a plant working 350 days in a year for 16 hours per day. This is the amount of treated TP produced by the plant section for lycopene extraction, which uses ethyl acetate as an extractive solvent.

4.4.1. Process parameters and flowsheeting

Two different scenarios for the extraction process were considered: the first one in which hydrochloric acid is used and the second one where the extraction is activated by citric acid obtained from waste lemons. The key parameters were inferred by experimental research on the extraction of pectin from citrus by-products, assuming a similar outcome for tomato peels. The conditions for the first scenario were gathered by the experimental research of Seggiani et al. (Seggiani et al., 2009). A reactor temperature of 70°C, a solid to liquid ratio of 1/17 and a 0.2M of HCl were considered; moreover, with a residence time of 1 h, an extraction yield of 26 g/100g of tomato peels was assumed (Seggiani et al., 2009). In the 2nd scenario, an extraction temperature of 90°C, a solid to liquid ratio of 1/4.3 and a pH of 1.5 were considered; moreover, with a residence time of 1.5 h, a reaction yield of 17g/100g of tomato peels was assumed (Casas-Orozco et al., 2015). Main parameters are summarized in Table 24.

Table 24 *Process parameter for pectin extraction with different acids*

	Acid	**S/L ratio**	**Residence time [h]**	**Temperature [°C]**	**Extraction yield [g/100 g of DDP]**
1st scenario	HCl	1/17	1	70	26
2nd scenario	Citric acid	1/4.3	1.5	90	17

Process flowsheeting was carried out to assess the technical feasibility of the production of pectin from tomato peels, considering the recycling of the auxiliary streams, namely the ethanol for washing and the extracting acid, and, hence, enabling the comparison of the two scenarios. The simulation was performed with Aspen Plus®. The method selected to describe a solution was NRTL (Non-Random Two Liquid Model), which correlates the activity coefficients of a compound with its molar fractions. This is the most used model in the chemical engineering field for the calculation of phase equilibria. The LEVOG-01 component is the one adopted to represent the pectin content. The brute formula of this compound is $(C_6H_{10}O_5)_n$, corresponding to the most representative building block of pectin. While DEXTR-1 ($C_6H_{12}O_6$) was used for representing the solid portion of the feed. The compounds' properties were imported in the simulation from APV88 PURE32, a primary component databank from Aspen Tech, allowing the process simulation in the absence of experimental data. Both schemes can be divided into 3 main sections (see Figure 41):

- Extraction: in this section, the dried and dewaxed tomato peels are mixed with water and acid, then the reaction mixture is brought to the selected condition and sent to the extraction reactor.
- Pectin purification: in this section, the reaction mixture is centrifuged to remove the spent solids, the extracted pectin is precipitated and washed with ethanol in a settling vessel, alcohol is removed by squeezing and successive drying, and the final pectin is grounded to the desired fine size
- Reagent recovery: in this section, the ethanol and the acid water solution are recovered by distillation and sent back to the extraction and purification stage.

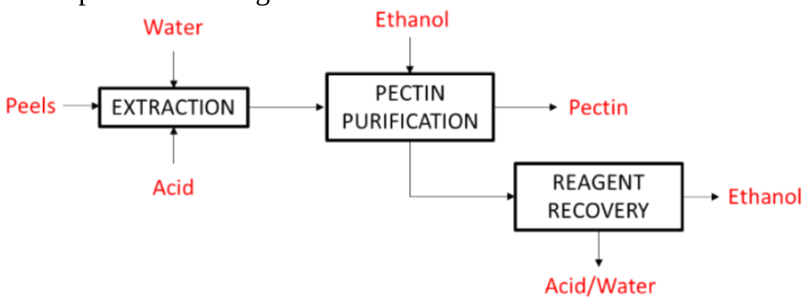


Figure 41 *Simplified block diagram for pectin production from tomato peels*

For the sake of clarity and readability, the two main flowsheets developed in Aspen Plus® software are reported in the Appendix but highlights of the main sections are shown and discussed in the following.

4.4.2. Mass and energy balances

Figure 42 shows the developed block diagram for the section in which extraction is carried out.

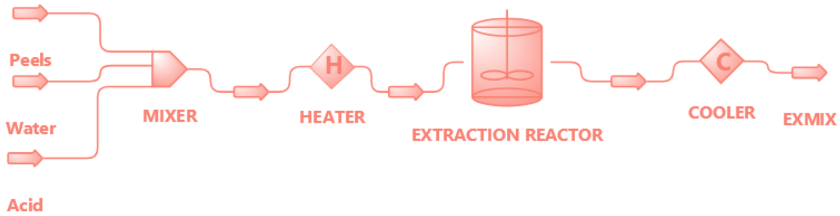


Figure 42 *Flowsheet for pectin extraction section*

In this section, 83 kg/h of tomato peels are mixed with 1400 kg/h of water and 10.3 kg/h of HCl in the first scenario. Vice versa, 249 kg/h of water and 107 kg/h of citric acids are used in the second one. The mixture is brought to reaction conditions and sent to the extraction reactor. The reactor cannot be designed by Aspen Plus®, due to a lack in the software of a unit block that can simulate solid-liquid extraction. Therefore, the reactor was designed by an EXCEL worksheet, considering the residence time equal to the reaction time reported in the literature (Seggiani et al., 2009; Casas-Orozco et al., 2015) and a loaded volume equal to 75% of the total reactor volume (Casas-Orozco et al., 2015). Under these conditions, the reactor geometry was evaluated and reported in Table 25:

Table 25 *Design for extraction reactor in the two scenarios*

	Volume [m3]	Height [m]	Diameter [m]	Impeller [No.]
1st scenario	2.12	0.55	1.1	3
2nd scenario	1	0.43	0.86	3

Due to the higher flows involved in the first scenario, the volume is bigger even if the residence time is smaller. After extraction, the mixture is cooled to ambient temperature and sent to the next section. EXMIX stream contains the extracted pectin dissolved in the acid mixture and the spent solid. The purification section was simulated in Aspen Plus® and the developed flowsheet is reported in Figure 43.

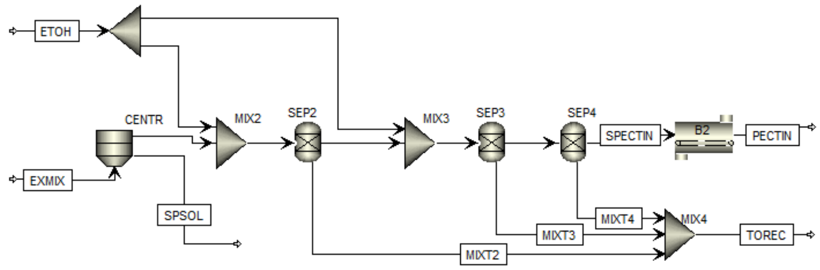


Figure 43 *Flowsheet for purification section in Aspen Plus® software*

In this section, the pectin is recovered from the extractor outlet and purified. In particular, the stream EXMIX is firstly centrifuged to remove the spent solid. In the simulation, the separation efficiency for CENTR was set to 1, as suggested by literature (Casas-Orozco et al., 2015). Then the liquid mixture containing pectin is mixed (MIX2 and MIX3) with two ethanol flows (86% wt.). In SEP2 and SEP3 blocks, in presence of ethanol, the pectin precipitates as a solid and is recollected at the bottom of the two settling vessels. The total mass flow of ethanol is 2890 kg/h for the first scenario and 846 kg/h for the second scenario. The lower amount of ethanol is due to the reduced aqueous mixture coming out from the extractor. SEP4 simulates a press unit in which the solid pectin is squeezed to remove a part of adsorbed ethanol. The split fraction for the SEP unit of this block was extrapolated from a process simulation for pectin production by orange peels (Casas-Orozco et al., 2015), as mentioned above. In B2 unit block residues of ethanol and water are removed from solid pectin by hot air drying to 98% wt. of purity (Casas-Orozco et al., 2015). In terms of mass flow, the plant productivity for pectin was 21.58 kg/h for the first scenario and 14.11 kg/h for the second one. For the energy demand of press and drying, commercial equipment suitable for this process yield was considered: Squeezing belt type filter press machine KZ1000 by Porvoo© and DW-series Belt Food Drying Machine by Food Drying Machine©. The PECTIN, MIXT2, MIXT3 and MIXT3 streams contain the spent ethanol with water and acid, therefore are collected in MIX4, and the TOREC output stream is sent to the recycling section. In the final section, the TOREC stream, containing ethanol, the extraction water, and the extracting acid, are separated by distillation to obtain the ethanol rich stream to be recycled to the purification section and an acid water stream to be recycled to the extraction section. The flowsheet section developed in Aspen Plus® is reported in Figure 44 while the operating conditions of the distillation tower for both scenarios are reported in Table 26.

Table 26 *Operating conditions of the distillation tower for reagents recovery*

	Temperature	**Pressure**	**Stage Number**	**Reflux ratio**	**Heat load at reboiler**
1st scenario	25 °C	1 bar	10	0.65	1.8 MW
2nd scenario	30 °C	1 bar	10	7	2 MW

The inlet temperature for the distillation is set as the TOREC temperature, that is around ambient temperature for both scenarios, and the pressure is set as atmospheric. The stage number (N) and reflux ratio (R) were optimized using a series of sensitivity analyses to have ethanol recovery in the RECETOH stream higher than 0.9975 and its purity around 86%wt, which is the concentration of ethanol solution used for washing steps. The heat load is high in both cases due to the massive flow rate of the TOREC stream.

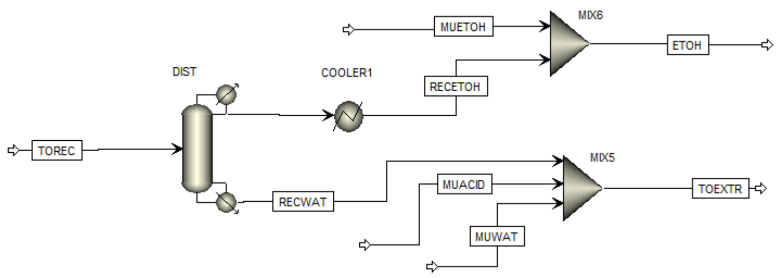


Figure 44 *Flowsheet of distillation section for recovering and recycling*

After the distillation, the two streams are mixed with a make-up of ethanol, acid, and water respectively to recycle the ETOH stream in the purification section and TOEXTR in the extraction section. The make-up flow rates were calculated by using the Calculator block of Aspen Plus®, which allows the evaluation of a variable stream (MUETOH, MUACID, MUWAT) depending on a fixed variable (RECTOH, RECWAT) to obtain the desired value of a third variable (ETOH, TOEXTR). The make-up flow rates of the fresh reagents for plant operation are reported in Table 27.

Table 27 Make-up flows for both scenarios

Make-up [kg/h]	**Ethanol**	**Water**	**Acid**
1st scenario	105	46	0.510
2nd scenario	3.25	8.2	3.3

Make-up streams compared to the operating flows are consistently lower, they are less than 5% for all reagents and both scenarios, meaning an optimal performance of the recycling section. Regarding the energy demand of pectin production in the first scenario, the power allocation for the different sections is reported in Figure 45. The total power demand is 2471 kW, with reagent recovery as the most energy-demanding section, with 83% allocation. In terms of energy demand, this extraction system needs 381 MJ for each kilogram of pectin produced by the plant, 311 MJ of thermal energy for heating streams and distillation and 70 MJ of electric energy for powering machines and pumps.

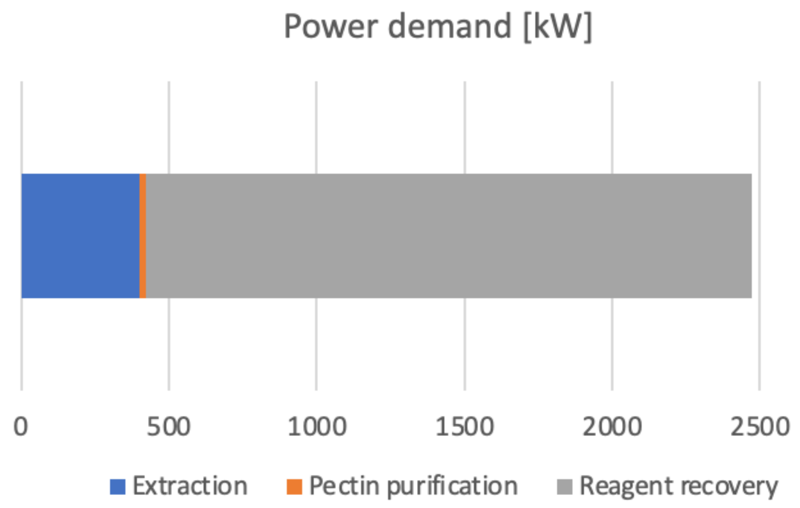


Figure 45 *Power allocation for pectin production with hydrochloric acid*

On the other hand, for the second scenario, the total power demand is 2051 kW, with reagent recovery almost the only energy-demanding part, with 99% allocation. In terms of energy demand, this extraction system needs 519 MJ for each kilogram of pectin produced by the plant, almost totally coming from the distillation. The power allocation for the different sections is reported in Figure 46.

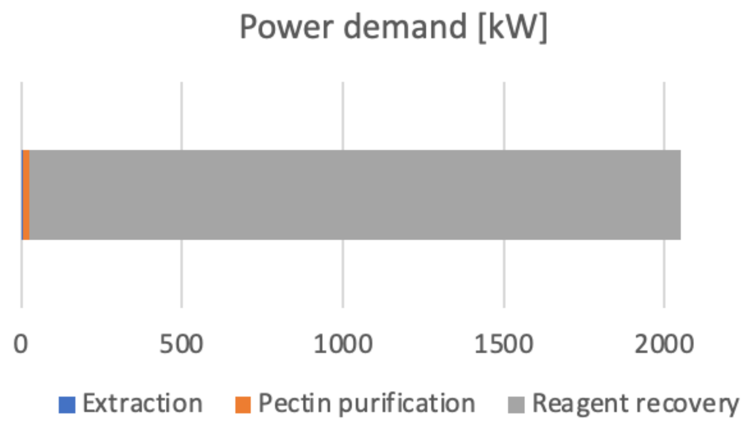


Figure 46 *Power allocation for pectin production with citric acid*

4.4.3. Pectin production system comparison

In conclusion, it was demonstrated the technical feasibility of the production of pectin from tomato skins by two alternatives: the first one uses hydrochloric acid and the second involves extraction with citric acid. AspenPlus® was used to implement the work and generate the results, except for the solid-liquid extraction reactor, for which the pectin yield was calculated using the MS Excel® spreadsheet. The developed process schemes were composed of a pectin extraction section, a purification unit, and a recovery system for solvent. Literature data provided the basis for materials description and acid-assisted extraction yield and conditions. Productivity of 22.58 kg/h of pectin for extraction with HCl, while in the case of citric acid the productivity was 14.11 kg/h. On the other hand, the first scenario requires a considerably higher amount of water for the preparation of the extractive media and ethanol for washing. The extractive acid amount is comparable for both scenarios, as reported in Table 28.

Table 28 *Raw materials for pectin production*

	1st scenario	**2nd scenario**
Extraction Acid [kg/h]	2.9	3.33
Water [kg/h]	46.7	7.64
Ethanol [kg/h]	118.6	3.24

Moreover, pectin production in the first scenario led to a higher amount of waste flows, composed of a mixture of ethanol, water, and residual acid: 164 kg/h of wastewater are produced in the first scenario and only 14.76 kg/h for the second. In terms of power demand, the two scenarios are comparable, due to the similar heat at reboiling for ethanol distillation, around 2000 kW: in the first case, this high heating demand is due to the high ethanol flow, while in the second scenario due to hard separation of ethanol-limonene-water solution. Anyway, in terms of total power demand, the system is comparable, same for cooling demand, with 2400 kW and 2000 kW, respectively of heat to be removed from the system (Figure 47)

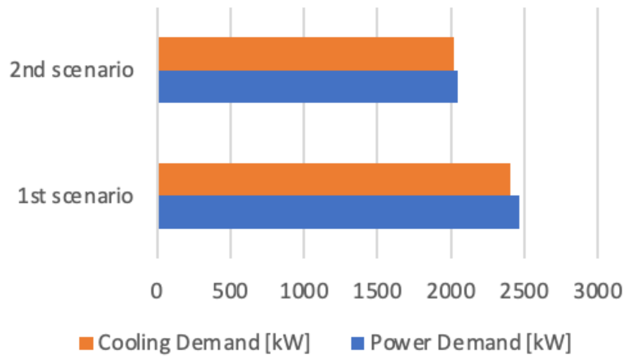


Figure 47 *Power and cooling demand for pectin production in different scenarios*

After the mass and energy balances, to assess the economic feasibility of the plant for pectin production, two categories of costs were considered: total capital cost for the construction and operating ones needed for the operations over time. The capital cost was evaluated as the sum of costs for unit equipment, the establishment of services, the production site and project design. Operating costs included raw materials, energy demand for operating equipment, labour and maintenance cost, patent cost and general expenses. The net profit of the plant was evaluated as the revenues coming from the selling of the produced pectin (food additive grade) minus the operating costs, considering taxes and depreciation. Therefore, indexes such as the return of investment (ROI) and the payback period (PBP) were calculated (Seider et al., 2008) with the following equations:

$$\mathrm{ROI} = \frac{\text{Net profit}}{\text{Total capital cost}}$$

$$\mathrm{BP} = \frac{\text{Total capital cost}}{\text{Net profit} - \text{Annual depreciation}}$$

For the calculation of Net Profit, ROI and PBP (reported in Table 29), the Energy and Economic Analyzer tool of Aspen Plus® were used. These tools allow the evaluation of capital and operative costs of the equipment involved in the process. For the equipment not included in Aspen Dataset, commercial options were selected and used to gather equipment cost and energy demand. Moreover, for the economic analysis, 4 workers, 5600 working hours per year and a tax index of 4% (Seider et al., 2008) were considered. Table 29 shows the economics for both scenarios.

Table 29 *Economic indexes for both scenarios*

	Net Profit [M€/y]	**Operative cost [M€/y]**	**ROI**	**PBP [y]**
1st scenario	0.81	1.22	0.26	2.5
2nd scenario	0.45	0.76	0.4	1.75

Although both scenarios lead to a positive Net Profit the second scenario, which represents a green alternative, has a higher ROI and lower PBP, meaning a better economic profitably; mostly due to the lower size of the plant caused by the smaller distillation tower. Anyway, it is worth noticing that both scenarios have ROI and PBP slightly better than standard chemical plants (0.15 ROI and 4y PBP), meaning that the production of pectin from tomato peels is both technical and economically feasible.

4.5. Tomato seed oil extraction

Extraction is the first step to separating the natural or essential oils from the raw materials. Extraction methods include solvent extraction, distillation, pressing and sublimation according to the extraction principle. Solvent extraction is the most widely used method. The properties of the extraction solvent, the particle size of the raw materials, the solvent-to-solid ratio, the extraction temperature and the extraction duration will affect the extraction efficiency (Zhang, Lin and Ye, 2018). The choice of solvent is crucial for the extraction of the desired substance. Selectivity, solubility, cost, and safety are the key parameters in the selection phase. Considering the law of similarity and intermixability (like dissolves like), solvents with a similar polarity to that of the solute are likely to perform better. Hexane is the universal solvent in the extraction of vegetable oil. In general, the finer the particle size, the higher the extraction yield. The efficiency will be improved by the small particle size due to the easier penetration of the solvents into the biomass. Too fine a particle size, however, will make the separation step much more complex. High temperatures increase solubility and diffusion. Too high temperatures, however, may cause solvents to be lost, leading to extracts with undesirable impurities and to the decomposition of thermolabile components. Extraction efficiency increases with increasing contact time. The increase in time will not affect the extraction once the solute has saturated the solvent. The greater the solvent-to-solid ratio is, the higher the extraction yield is. However, a solvent-to-solid ratio that is too high will require a long time for post-extraction concentration. The conventional solvent extraction methods use organic solvents and require a large volume of solvents and a long extraction time (Zhang, Lin and Ye, 2018). Greener extraction method such as expeller pressing has also been applied in natural products extraction and offers some advantages such as lower organic solvent consumption and shorter extraction time (Farr and Proctor, 2013). The possibility of extracting oil from tomato seeds was already set in the early 20th century. Seeds, which usually contain about 30 %wt. of oil (see Table 30), are obtained from pomace by sedimentation and pressed or extracted with solvent to produce oil (Lazos, Tsaknis and Lalas, 1998).

Table 30 Tomato seed average composition

	Content (%db.)
Oil	28.23
Proteins	31.62
Fibre	15.81
Sugars and starch	23.71

Tomato seed oil is brown with a strong odour. It contains saturated fatty acids up to 14-18 %, and unsaturated fatty acids up to 76-80. Table 31 shows its fatty acid composition (Lazos, Tsaknis and Lalas, 1998).

Table 31 *Composition of the main fatty acids in tomato seed oil*

Fatty acids	**Content (%) up to**
Stearic acid (C18:0)	20
Oleic acid (C18:1)	25
Linoleic acid (C18:2)	50
Linolenic acid (C18:3)	2-3

Since no studies for tomato seed oil extraction were found in the literature, two different concept flowsheets have been developed, considering the technologies mentioned above, and process schemes and yields reported in the literature for other biomasses (Tambunan et al., 2012; Elkhaleefa and Shigidi, 2015). This is aimed at verifying the technical feasibility of tomato pomace separation for the possible implementation in an industrial plant. As a basis for calculations a mass flow rate of tomato seeds of 127.4 kg/h was considered, that is the flow of dried tomato seeds obtained after pomace separation by sedimentation. The tomato seeds stream was considered composed of 97.50 %wt. of seeds and 2.5 % of impurities on a dry basis, and 8% of moisture on a wet basis.

4.5.1. Process parameters and flowsheeting

Two different scenarios for the oil extraction process were considered: the first one in which hexane is used as a solvent and the second one where the extraction is carried out by expeller pressing. The key parameters were inferred by experimental research on the extraction of vegetable oil from different seeds, assuming a similar outcome for tomato dried seeds (DS). The conditions for the first scenario were gathered from the experimental research of Elkhaleefa and Shigidi, on the optimization of solvent extraction with hexane of sesame oil (Elkhaleefa and Shigidi, 2015). After a preceding step of separation and drying, the dried seeds are milled to reduce the particle size and then mixed with hexane, with an S/L ratio of 0.2. The mixture is heated at 40°C and kept in agitation at this temperature for 30 min (Elkhaleefa and Shigidi, 2015). After the extraction, the solid residue is separated by filtration and dried. The liquid mixture containing the tomato seed oil is purified by flash evaporation, under vacuum at 0.5 bar and 60°C, to separate hexane. The removed hexane is recovered by condensation and sent back to the extraction section. A solvent loss of 0.8 kg for each tonne of processed tomato seeds is considered. The block diagram developed for this scenario is reported in Figure 48.

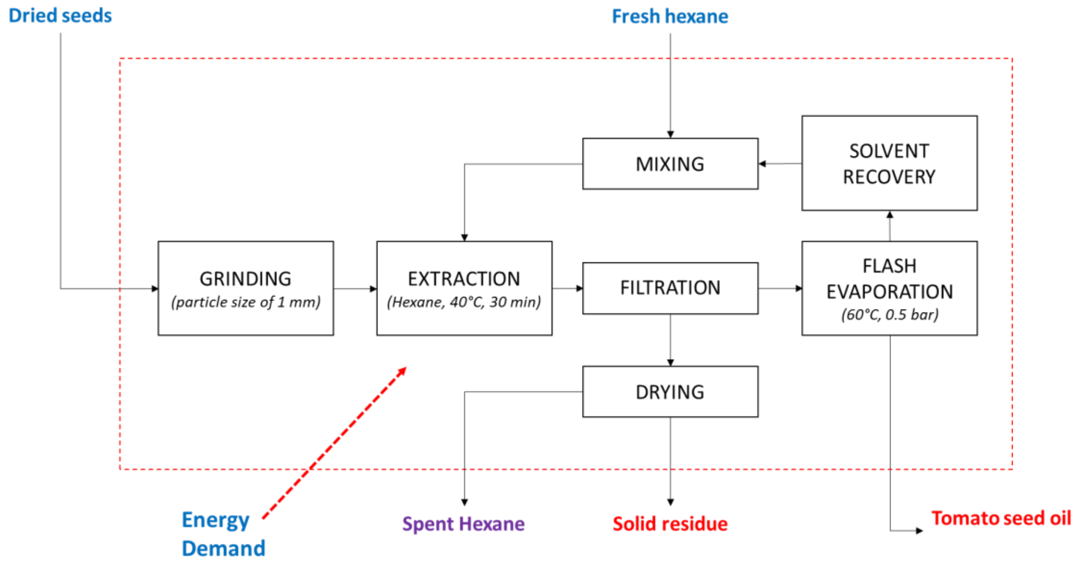


Figure 48 *Block diagram for solvent extraction of tomato seed oil*

In the 2nd scenario, gathered from the experimental research of Tambunan et al. (Tambunan et al., 2012), the dried seeds are crushed and sent directly to an industrial filter press machine, Goyum® oil press machine G MK-V (38 kW, 25 t/d). The obtained sludge is cooled to remove the heat generated by compression and then centrifuged by a Flottweg decanter C2E-4 (10.5 kW) to separate solid residues and tomato seed oil. The block diagram developed for this scenario is reported in Figure 49.

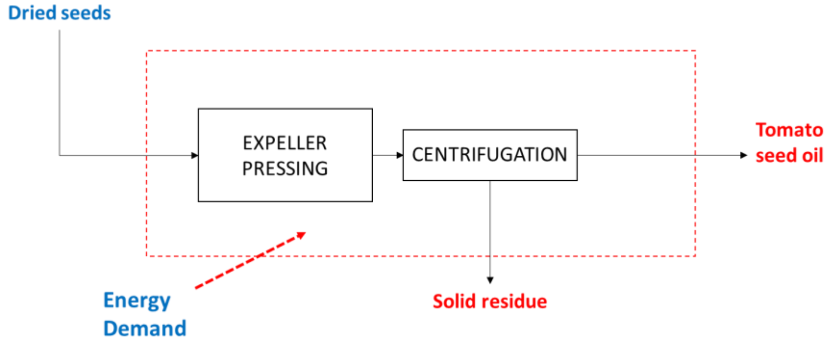


Figure 49 *Block diagram for extraction by expeller pressing of tomato seed oil*

The extraction yield of tomato seed oil considered for the two scenarios is reported in Table 32.

Table 32 *Process parameters and extraction yield for tomato seed oil extraction*

	Extraction method	S/L ratio	Temperature [°C]	Extraction yield [g/100 g of DS]
1st scenario	Solvent extraction	1/5	40	24.3
2nd scenario	Expeller pressing	-	Ambient	19.7

4.5.2. Mass and energy balances

Considering the developed flowsheets for the tomato seed oil extraction with hexane and by expeller pressing, the extraction yield reported in Table 32, and literature data, the mass flows for all the involved streams were calculated by implementing simple mass balances in MS EXCEL® spreadsheets. The obtained results are reported in Table 33:

Table 33 *Mass balance for tomato seed oil extraction in both scenarios*

		1st scenario	2nd scenario
Output	**Tomato seed oil [kg/h]**	27.740	22.580
	Solid residue [kg/h]	99.660	104.820
Raw materials	**Dried tomato seeds [kg/h]**	127.4	127.4
	Hexane make-up [kg/h]	0.091	

As reported in Table 33, when 127.4 kg/h of dried seeds are fed to the extraction section in1st scenario, 0.091 kg/h of fresh hexane is needed, and 27.74 kg/h of tomato seed oil is produced. On the other hand, in the 2nd scenario, the lower output of seed oil is produced, 22.58 kg/h, without using any solvent.

Regarding the energy demand of the 1st scenario, the total power demand, evaluated with the Aspen Plus® energy analyzer, is 146.8 kW, with machine operation as the most energy-demanding part, indeed 84 kW of the power demand is due to electricity consumption. In terms of energy demand, this extraction system needs 19 MJ for a kilogram of seed oil produced by the plant, 8.1 MJ of thermal energy for heating streams and 10.9 MJ of electric energy for powering machines. In the 2nd scenario, the power demand is remarkably lower, due to ambient temperature, indeed only 48.5 kW for electricity is needed. This extraction system requires 6.3 MJ of energy (electricity) per kilogram of tomato seed oil produced. Energy demand comparison between the two scenarios is reported in Figure 50

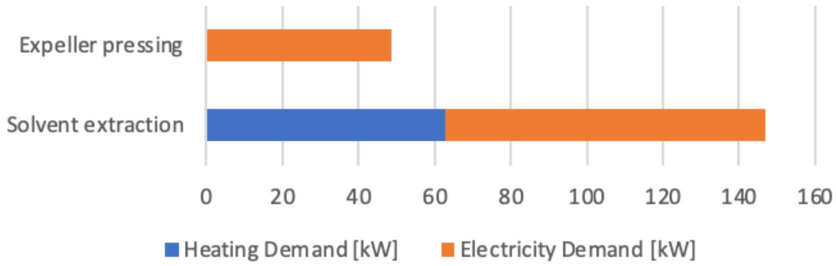


Figure 50 *Power demand for seed oil extraction*

Finally, the Aspen Plus® energy analyzer was also used to evaluate the refrigeration duty, for solvent recovery in 1st scenario and for cooling after extraction in 2nd scenario, and it was found 145 kW in the first scenario and 0.280 kW in the second one.

4.5.3. Oil extraction system comparison

In conclusion, a literature study showed that vegetable oil is typically extracted by solvent extraction with hexane while the most ‘greener’ alternative is expeller pressing. These two alternatives were implemented in two flowsheets, to verify their industrial feasibility, evaluate the mass flows involved for tomato seed oil extraction and compare them in terms of output yield and energy demand. The involved mass flows were evaluated by simple mass balances while, to evaluate the energy demand or the needed power for the systems mentioned above, an Aspen Plus energy analyzer was used or commercially available equipment was considered. The two technologies provide different oil output, even though to a limited extent: the production of oil is higher in the 1st scenario, but in the 2nd scenario the use of organic solvent is avoided. Moreover, the energy demand and the refrigeration duty are remarkably lower for the ‘green’ alternative. Finally, considering that, in the first analysis, the operating cost of the two separation systems are: the cost of methane for heating, the cost of electricity and the cost for treating the water removed from the pomace, a cost comparison was carried out. The continuous operating cost every year for solvent extraction is 1.55 M€/y while for expeller pressing is only 16 k€/y. It is worth noticing that most of the cost is due to the flash evaporator operation.

4.6. Biodiesel production from tomato seed oil

As reported in Chapter 1, the use of vegetable oil for biodiesel production can play an important role in developing a new eco-friendly system fostering the transition to renewable energy (Mishra and Goswami, 2018). Biodiesel is obtained as the result of a chemical reaction, namely alcoholysis or transesterification, between the triglycerides, contained in the starting oil, and alcohol. The transesterification of the triglycerides is usually carried out with a catalyst to reach a reasonable reaction rate (Mumtaz et al., 2017). From the catalytic transesterification process crude glycerol is obtained as a reaction byproduct containing 70-80% of glycerin, in addition to resulting amounts of water, catalyst, FFA and salts. A purification process of glycerin, up to 98%, enables its use in the most diverse areas, in particular in the pharmaceutical and food processing field (Monteiro et al., 2018). The reaction is performed at a temperature close to the boiling point of the alcohol and pressures slightly higher than atmospheric, ensuring that it takes place in a liquid phase. The alcohols typically used for the reaction are butanol, ethanol, and methanol. Methanol is often preferred due to the lowest cost, which is a significant feature because the reaction requires a high amount of alcohol to ensure a high yield, moreover, it avoids the formation of undesired emulsions and thus facilitates the separation of the reaction products (Meher, Vidya Sagar and Naik, 2006). Catalysts may be acid, basic or enzymatic. The catalyst amount can be adjusted to reach the desired conversion of the product, but generally, the optimum catalyst corresponds to concentration ranges between 0.5 and 1% wt. Base-catalyzed transesterification allows higher rates and, consequently, better performance. It is characterized by a less corrosive nature of the used reagents and fewer costs related to purchasing and transport, as well as subsequent disposal stage. The most studied and used alkaline catalysts are sodium and potassium hydroxides ($NaOH$ and KOH) (Mumtaz et al., 2017). On the other hand, a heterogeneous catalyst such as the alkaline one could lead to higher costs for the separation of the reaction media as they are partially miscible in reaction products. Homogeneous catalysts have been recently studied and tested as alternatives. These studies show that "eggshell" or "fish and chicken bones" can be used as starting materials for the production of catalysts for transesterification, leading to comparable biodiesel yield, easy separation steps, and a more sustainable process, by avoiding the burden of wasting these materials (Tan et al., 2019). Regarding the organic feedstock, edible oils, in particular soybean, palm and rapeseed oil are the mainly used vegetable oil for this process, guaranteeing high biodiesel yields with the use of alkaline catalysts, thanks to their low Free Fatty Acid (FFA) content. However, the disadvantage of these raw materials is the high cost and the competition that is created between oils intended for human consumption and those subtracted from them to produce biodiesel (Gupta, Agarwal and

Dalai, 2016). For these reasons many efforts have been made by researchers and industries to find alternative oils, coming from waste streams, while ensuring reasonable yields with mild reaction conditions (Bhuiya et al., 2016). A valid example is provided by the WCO (waste cooking oil) or spent cooking oil, which is not intended for human consumption and is advantageous for its low cost (compared to virgin vegetable oil). Moreover, the use of this kind of feedstock prevents its landfilling or, even worse, its incorrect disposal, by avoiding unwanted noxious emissions (Bhuiya et al., 2016). Recently tomato seed oil (TSO) was proposed as an alternative feedstock to produce biodiesel, due to its characteristics and easiness of extraction from tomato peels. Moreover, it was demonstrated that the physicochemical properties of tomato seed oil are within the standard for rapeseed oil currently used for biodiesel production in Europe (Giuffrè et al., 2016) and it was shown that the esterification of tomato seed oil could lead to the production of biodiesel that meets European legislation (Giuffrè et al., 2017). To the best of the authors' knowledge, no studies or research were carried out to investigate the scalability and the technical and economic feasibility of a process plant producing biodiesel and glycerol from tomato seed oil as feedstock. Therefore, this section reports on the conceptual development and optimization of a plant producing biodiesel and glycerin with pharmaceutical grade. The use of two different catalysts is proposed: a conventional heterogeneous catalyst and a "green" alternative. Therefore, two flowsheets are developed; the technical feasibility of the processes is discussed; the EROI index assessing the energetic feasibility is evaluated. The Aspen Plus® software was smartly employed to carry out simulation and optimization of processes. As a basis for calculations, the amount of tomato seed oil (TSO) to be processed is 27.74 kg/h, that is the tomato seed oil produced by solvent extraction, as reported in the previous paragraph. The composition of the oil was considered as the one reported by Giuffrè and Capocasale (Giuffrè and Capocasale, 2016), with trilinolein as the main component, moisture content as low as 0.5%wt and a free fatty acid content lower than 2%.

4.6.1. Process parameters and flowsheeting

Two different scenarios for the transesterification reaction were considered: the first in which the reaction is catalysed by potassium hydroxide (KOH) homogeneously and the second in which the reaction is catalysed in a heterogeneous way by calcium oxide (CaO), this latter being obtained by wasted eggshells. The conditions for the first scenario were gathered by the experimental research of Giuffrè et al. (Giuffrè et al., 2017). In particular, a reactor temperature of 55°C, a methanol/oil ratio of 6 and KOH content of 1% on a weight basis was considered; moreover, with a residence time of 1 h, a reaction yield of 96.2% was assumed (Giuffrè et al., 2017). Regarding the second scenario, the key parameters were inferred by two experimental works on the transesterification of vegetable oils (Kouzu et al., 2009; Fayyazi et al., 2018). In particular, a reactor temperature of 60°C, a methanol/oil ratio of 6.03 and a CaO content of 0.2% on a weight basis was considered; moreover, with a residence time of 2 h, a reaction yield of 96.5% was assumed (Kouzu et al., 2009; Fayyazi et al., 2018). Main process parameters for biodiesel production with different catalyst are reported in Table 34.

Table 34 *Process parameters for biodiesel production with different catalyst*

	1st scenario	**2nd scenario**
Catalyst	KOH	Eggshells
Catalyst content [% wt.]	1	0.2
Methanol/0il ratio	6	6.03
Residence time [h]	1	2
Temperature [°C]	55	60
Reaction yield	96.8	96.5

Process flowsheeting was carried out to assess the technical feasibility of biodiesel production, with a quality that meets European standard, and glycerin, with pharmaceutical grade, from tomato seed oil, hence, allowing the comparison of the scenarios. The simulation was performed with Aspen Plus®. The method selected to describe the liquid phase was NRTL (Non-Random Two Liquid Model), because it allows a good simulation of the interaction between components, even if they have high polarities like methanol and glycerin. For the tomato seed oil, trilinolein, included in the Biodiesel database of Aspen Plus® was used as a representative component. With this background, the two scenarios for biodiesel production were implemented in Aspen Plus®. Both schemes can be divided into 5 main sections (see Figure 51):

- Transesterification reaction: in this section, the feedstocks are sent to the reactor, the reaction conditions are set, and the tomato seed oil is converted to biodiesel and glycerine.
- Washing: water is used to enable phase separation, to obtain a biodiesel-rich and a glycerine-rich phase
- Biodiesel purification: in this section, the biodiesel is purified from minor substances through distillation under vacuum and a sedimentation step
- Catalyst recovery: the homogeneous catalyst (KOH) is neutralized with an acid and recovered as salt, while the heterogeneous catalyst (CaO) is separated by centrifugation and recycled to the reactor

- Glycerin purification: glycerine purity is brought up to 98% via a series of distillation steps removing residual methanol and water. The methanol is recovered and sent back to the reaction section.

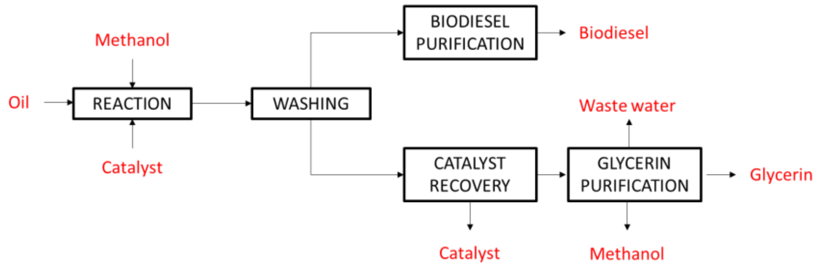


Figure 51 *Simplified block diagram for biodiesel production from tomato seed oil*

For the sake of clarity and readability, the two main flowsheets developed in Aspen Plus® are reported in the Appendix but highlights of the main sections are shown and discussed in the following.

4.6.2. Mass and energy balances

The first section implemented in the software is the reaction section, which is reported in Figure 52. Here, the unwanted water, although as small as 0.5 %wt., is removed by the TSO stream by sedimentation and the purified stream is pumped to the reactor. Methanol and catalyst are mixed to allow the formation of the active species. Then, the reaction media are mixed with the oil and brought to the optimal reaction conditions. The temperature is around 60°C for both scenarios, to keep the reaction mixture near the methanol boiling condition. The pressure is set as 4 bar for the heterogeneous catalyst and 1 bar for the homogeneous catalyst to optimize the process yield as reported in the literature (Kouzu et al., 2009; Giuffrè et al., 2017; Fayyazi et al., 2018).

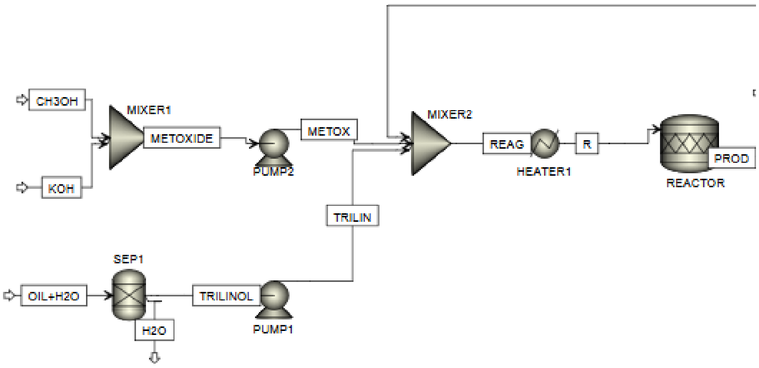


Figure 52 *Highlight of the reaction section for the first scenario*

The transesterification reactor was simulated by the means of an ideal block, i.e., *RStoic*, in Apsen Plus®, which requires as input the operating conditions and the stoichiometric reaction with the relative yield. Here the transesterification of trilinolein into its methyl ester and glycerin was considered:

$$C_{57}H_{98}O_6 + 3CH_3OH \rightarrow 3C_{19}H_{34}O_2 + C_3H_8O_3$$

The reaction conversion was set at 96.2% for the reaction with KOH as the catalyst and 96.2% for the reaction with CaO. The reactor outlet (PROD) contains the products (biodiesel and glycerin) and the unreacted reagents. Since the two products are partially miscible, their separation is induced through a water washing unit, since glycerin is hydrophilic. At the industrial scale, the separation of the methyl esters and glycerin is carried out with centrifugation because the natural occurring sedimentation of the phases would be too slow. Figure 53 shows the washing section and the equilibrium diagram for the water-biodiesel-methanol mixture.

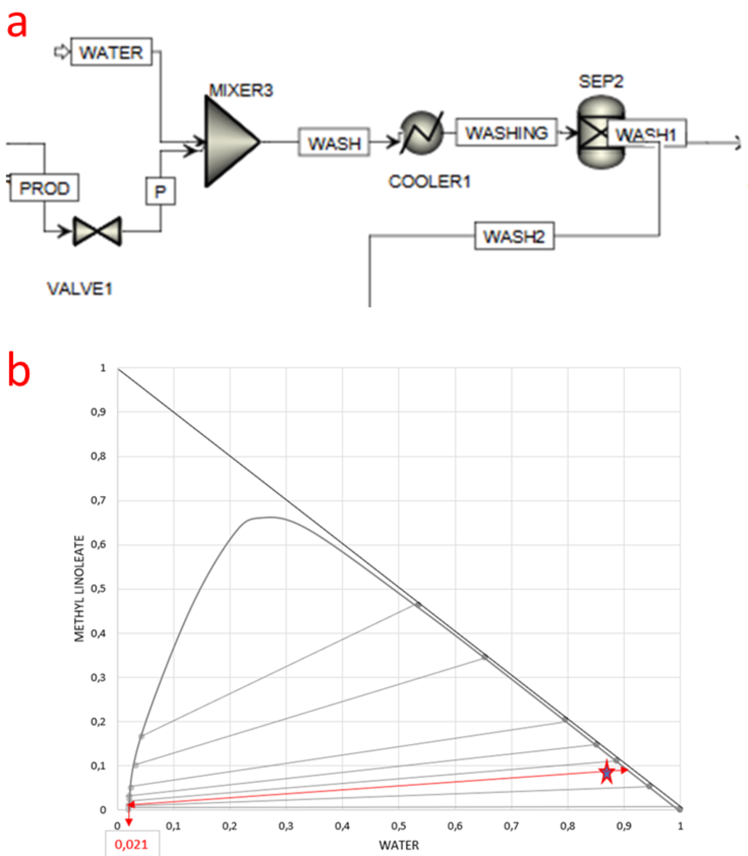


Figure 53 *a) Highlight of the washing section, b) LLE equilibrium diagram: the red star indicates the stream entering the SEP2*

The optimal value of the water feed rate (WATER) was evaluated with the Sensitivity tool of the software that allows performing a 'what if' analysis by varying a parameter. In the specific case, the water flow varied in a range of defined values, to choose the minimum flow rate that would allow the highest recovery in biodiesel. The optimum water flow rate was found to be 14.68 kg/h for both scenarios. The split fraction implemented in the SEP2 block was based on the water-methanol-methyl linoleate liquid-liquid equilibrium (LLE) data, as reported in the literature, used for the construction of the triangular diagram reported in Figure 53 (Lee, Lo and Lin, 2010). In this way, it was possible to draw the miscibility gap and the tie-lines, to evaluate the fraction of water and methanol in biodiesel (WASH1), and in glycerin-rich phase (WASH2) by difference. For both scenarios, the water molar fraction in biodiesel is 0.021 while that one for methanol is 0.0369. WASH1 and WASH2 are sent to the biodiesel purification and glycerin purification sections, respectively. The methyl ester-rich stream, identified in the flowsheet as WASH1, contains biodiesel (methyl linoleate in the simulation), and small amounts of methanol and water. This stream is sent to a distillation tower for the separation of biodiesel, i.e., RADFRAC1. Then the distilled biodiesel is furtherly purified from remaining free fatty acid impurities using centrifugation (SEP3), as reported in Figure 54.

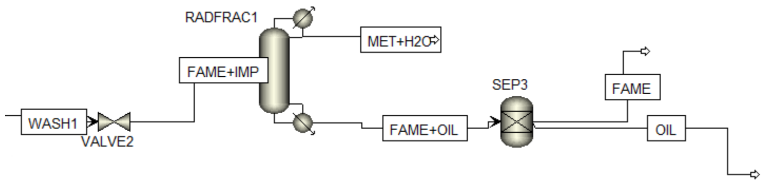


Figure 54 *Highlight of biodiesel purification section*

The operating conditions of the distillation tower are reported in Table 35:

Table 35 *Operating condition of the distillation tower for biodiesel purification*

Temperature	Pressure	Stage Number	Reflux ratio
50 °C	0.01 bar	8	8.5

Temperature is set the same as the WASH1 temperature, while the pressure is kept below the atmospheric one and selected to have the temperature of the bottom stream consistently lower than the degradation temperature of biodiesel. The stage number (N) and reflux ratio (R) were optimized using a series of sensitivity analyses to have a methyl ester recovery in the bottom stream higher than 0.9975 and the minimization of the heat at the reboiler (2.63 kW). The MET+H2O stream is considered wastewater and sent to disposal as the OIL stream (containing impurities), while the FAME stream provides a recovered product at 100% of purity with a mass flow of around 27 kg/h for both scenarios. The glycerine in the WASH2 stream, coming from the reaction section and the washing step, has very low purity, depending on the conversion method and the type of catalyst and alcohol used. Therefore, a purification step to ensure pharmaceutical grade (higher than 98%) is mandatory. This step contains two main blocks: the first for the removal and recovery of the catalyst and a train of distillation tower for glycerine purification (Figure 55).

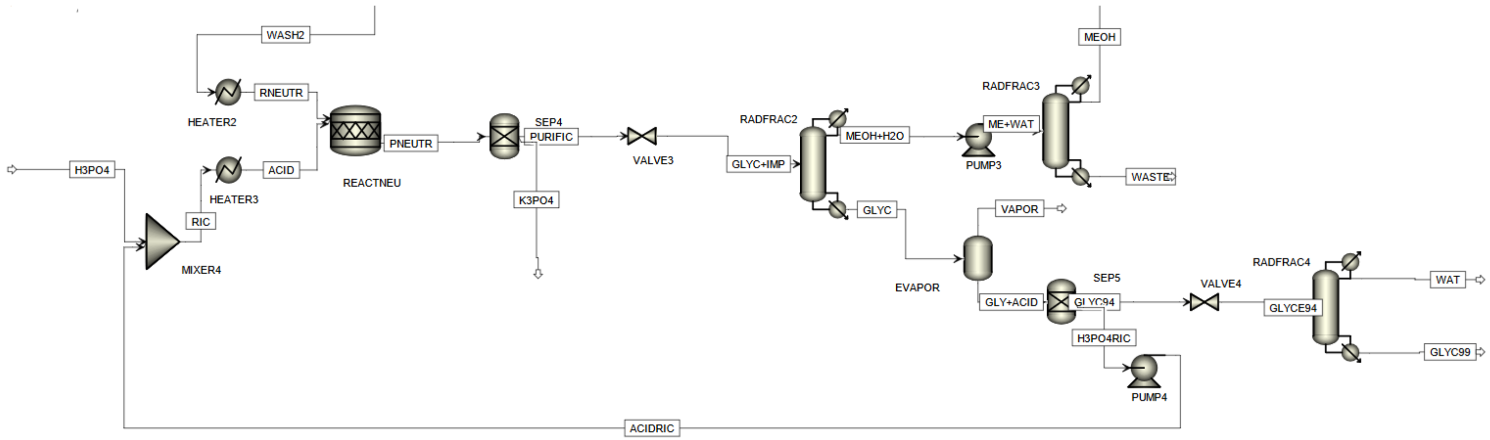


Figure 55 *Highlight of glycerin purification step for first scenario*

In the first scenario the KOH catalyst is neutralized by the means of the addition of phosphoric acid that reacts with the catalyst leading the formation of the phosphate salt:

$$KOH + H_3PO_4 \rightarrow K_3PO_4 + 3H_2O$$

The reaction is carried out in the REACTNU block at 60°C and 1 bar, then the salt is removed by centrifugation in SEP4. The phosphate salt is recovered with a mass flow rate of 0.14 kg/h and is considered an important by-product due to its utilization as fertilizer. The PURIFIC stream, containing glycerine, methanol, water, and unreacted acid is sent to the series of distillation columns that work at the following operating conditions, optimized with the same method reported for RADFRAC1:

Table 36 *Operating conditions for the distillation towers in the glycerin purification section for the first scenario*

	Temperature	Pressure	Stage Number	Reflux ratio
RADFRAC2	60 °C	0.05 bar	7	2
RADFRAC3	23 °C	1 bar	17	8
RADFRAC4	120 °C	0.02 bar	7	1

Downstream, methanol (99% pure) is recycled to the reactor while wastewater is sent to disposal, the acid is recycled to the neutralization reactor while 2.7 kg/h of glycerine is collected as a valuable product. In the second scenario, the CaO catalyst is removed by the WASH2 stream using centrifugation. Therefore, the next purification results in only two distillation towers, due to the absence of unreacted acid.

Table 37 *Operating condition for the distillation towers in the glycerin purification section for the second scenario*

	Temperature	Pressure	Stage Number	Reflux ratio
RADFRAC2	60 °C	0.05 bar	7	2
RADFRAC3	23 °C	1 bar	17	8

As in the first scenario, methanol is recycled to the reactor and wastewater is sent to disposal, the recovered CaO is recycled partially to the reactor while 2.78 kg/h of glycerine is collected as a valuable product. Regarding the energy demand of biodiesel production in the first scenario, the power allocation for the different unit operations is reported in Figure 56. The total power demand is 49.75 kW, with the glycerin purification section, as the most energy-demanding part, with 87% of allocation. In terms of energy demand, this extraction system needs 7.4 MJ for each kilogram of biodiesel produced by the plant, 7.1 MJ of thermal energy for heating streams and distillation and 0.3 MJ of electric energy for powering machines and pumps.

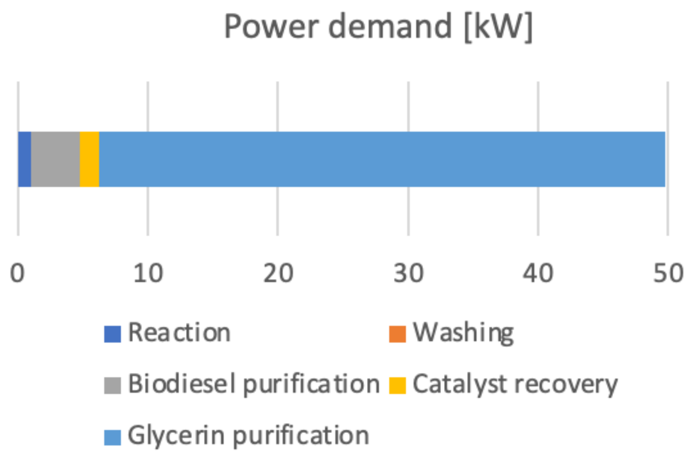


Figure 56 *Power allocation for pectin production with potassium hydroxide*

For the second scenario, the total power demand is slightly higher, namely 55 kW, with glycerin purification as the most energy-demanding section, with 89% allocation (see Figure 57). In terms of energy demand, this extraction system needs 8.2 MJ for each kilogram of biodiesel produced by the plant, 7.9 MJ of thermal energy and 0.3 MJ of electricity demand.

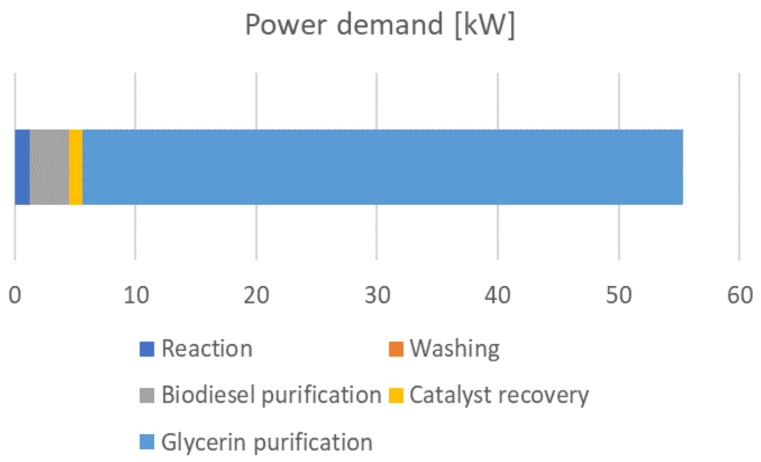


Figure 57 *Power allocation for pectin production with eggshells*

4.6.3. Biodiesel production systems comparison

This piece of work demonstrated the technical feasibility of industrial production of biodiesel from tomato seeds oil (extract from tomato pomace) using methanol in two cases differing in the approach underlying the selection of the catalyst, a traditional one (potassium hydroxide, KOH) and another "green" (calcium oxide, CaO from eggshells). The AspenPlus® software proved to be a perfect tool for simulation of the catalytic transesterification and ancillary unit operations, ensuring biodiesel productivity of 27 kg/h and glycerin production of around 2.7 in both scenarios. Great attention has been paid to the issue of recovery and recycling, according to a design approach complying with process integration and waste minimization. Therefore, the unreacted methanol in excess is recovered and recycled to the reactor with purity above 99% by a distillation column, ensuring its reduced consumption. Moreover, unwanted waste from the operations was minimized and evaluated. Table 38 reports the mass flows of unwanted side streams for both scenarios.

***Table 38** Unwanted side streams for both scenarios in biodiesel production*

	1st scenario	**2nd scenario**
Wastewater [kg/h]	15.30	16.19
Spent oil [kg/h]	0.83	0.92
Solid waste [kg/h]		0.05
CO_2 emission [kg/h]		0.04

As reported in the table, both scenarios have a comparable amount of wastewater (composed of a mixture of water, methanol, and unreacted materials) and spent oil. It is worth noticing that 2nd scenario causes a direct emission of CO_2 due to the calcination of eggshells to produce CaO catalyst. After the simulation of the two scenarios that assessed the technical feasibility of biodiesel production from TSO, the EROI, namely the energy return of the investment, was evaluated by using the following equation:

$$EROI = \frac{LCV_{biodiesel} \times F_{biodiesel}}{E_{harvesting} + E_{tansport} + E_{transeterification}}$$

where $LCV_{biodiesel}$ is the lower calorific value of biodiesel. $F_{biodiesel}$ is its mass flow rate, $E_{harvesting}$ is the energy needed for harvesting tomato (allocated for TSO mass flow rate) (Campiotti, 2016), $E_{transport}$ is the energy needed to transport tomato by-products to the production plant and $E_{transesterification}$ is the energy for operating the production plant. The EROI index must be greater than 5 for non-renewable energy sources in order to rate the fuel production plant technically feasible (Rana et al., 2020). The energy consumption for the harvesting was considered 187 kcal/kg, as partly allocated from tomato harvesting process, the contribution from transportation was considered negligible due to the short, while the $E_{transesterification}$ was considered as the energy needed for operating the plant (from reaction to purification step). Eventually, the EROI for the conventional scenario with KOH as catalyst was 5.83 while it was 5.5 when the alternative catalyst, CaO from eggshells, is used. After the mass and energy balances, to assess the economic feasibility of the plant for biodiesel production, operative costs and gross profit were evaluated. Firstly, considering that, in first analysis, the costs for working the two separation systems are: the cost of methane for heating, the cost of electricity, the cost of refrigeration, the cost of raw materials and the cost for waste streams treatment, an operating cost comparison was carried out.

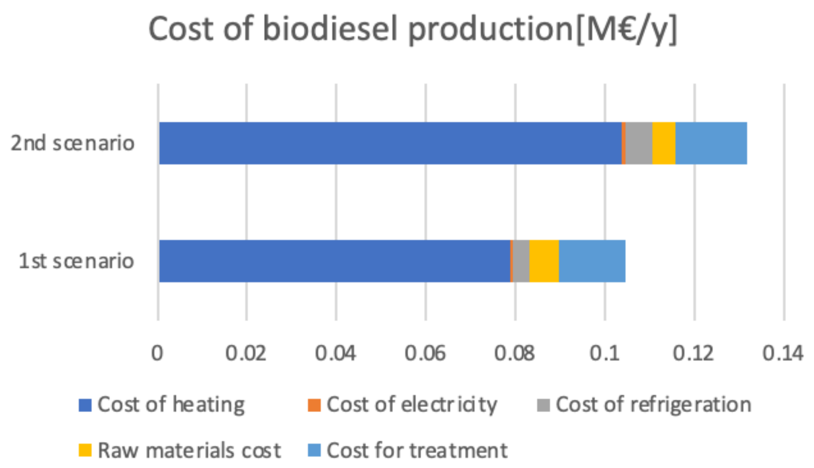


Figure 58 *Operative cost for biodiesel production in both scenarios*

As reported in Figure 58, the 2nd scenario has higher operating costs. Indeed 0.138 M€/y are needed to process 27 kg/h of tomato seed oil, while in the 1st scenario, only 0.104 M€/y are needed to process the same amount of oil. It is worth noticing, that the operating costs are almost all due to the heating demand in both scenarios. Considering the following values for the plant products:

Table 39 *Commercial values for biodiesel, glycerin and tripotassium phosphate*

	Value [€/kg]
Biodiesel	1.144
Glycerin	57.46
Tripotassium phosphate	7.04

the gross profit for a plant that uses KOH as a catalyst is 0.88 M€/y, while when eggshells are used as catalyst precursor is almost 0.87 M€/y, making the economic profitability of both plants comparable.

4.7. Torrefaction of the solid residues for pellets production

In 2016, Brachi et al. (Brachi et al., 2016b) investigated the mild thermal treatment of tomato processing residues (TRs) and reported that torrefaction led to substantial improvement in their chemical and physical properties while maintaining the mass and energy yields at satisfactory levels. This finding suggested that TRs be a valuable and convenient candidate for torrefaction treatment. Their outcomes also highlighted that sand-assisted fluidized-bed torrefaction technology was particularly suitable to cope with the exothermicity associated with the thermal degradation of nonwoody biomass, which easily tends to ignite or carbonize during torrefaction (Brachi et al., 2016b). During torrefaction, biomass is heated in an inert environment to a temperature of 200−300 °C. Conventionally, it is characterized by a low particle heating rate (typically <50 °C/min) and by a relatively long reactor residence time that, depending on the feedstock, technology, and temperature, ranges from 30 min to 120 min. In addition, Guerriero in his master thesis entitled "Studio di un processo integrato di torrefazione di bucce di pomodoro: flowsheeting, dimensionamento, analisi economica " (Guerriero, 2017), reported that the torrefaction process can be considered autothermal when 5% of the initial biomass is burned together with torgas produced by the torrefaction itself, and the generated thermal energy used to preheat the materials (biomass and CO_2) entering a continuous fluidized bed reactor. Finally, the produced torrefied biomass can be pelletized to produce a solid fuel alternative to woody pellets commercially available (Ruiz Celma, Cuadros and López-Rodríguez, 2012). With this background, a plant section producing pellets from the solid residues coming from both the pectin extraction and the tomato seed oil extraction units was developed. From the outcome of these process units, a calculation basis of 111 kg/h was considered for the flow rate of dried solid residues. Aspen Plus® software was used to simulate the torrefaction reactor, with reaction yields taken from the literature (Brachi et al., 2016b).

4.7.1. Process parameters and flowsheeting

The best reaction condition is implemented here as published by Brachi et al. (Brachi et al., 2016b). They reported that when tomato residues are treated at 285 °C for 30 min with N_2 as an inert fluidizing gas and fine silica sand as solids of the fluidized bed reactor, the mass yield of biochar is 89.6% wt. on a dry basis. A fluidized bed reactor is considered for continuous torrefaction to biochar here. CO_2 is employed as an inert fluidizing gas instead of nitrogen to consider the increasing availability of carbon dioxide from the ongoing and future carbon sequestration processes [67]. Downstream of the torrefaction reactor, the biochar is pelletized in commercial machinery, i.e., Euro Tools, 380 V, 15 kW, 50 Hz to produce pellets. The schematic diagram of the developed torrefaction plant is reported in Figure 59.

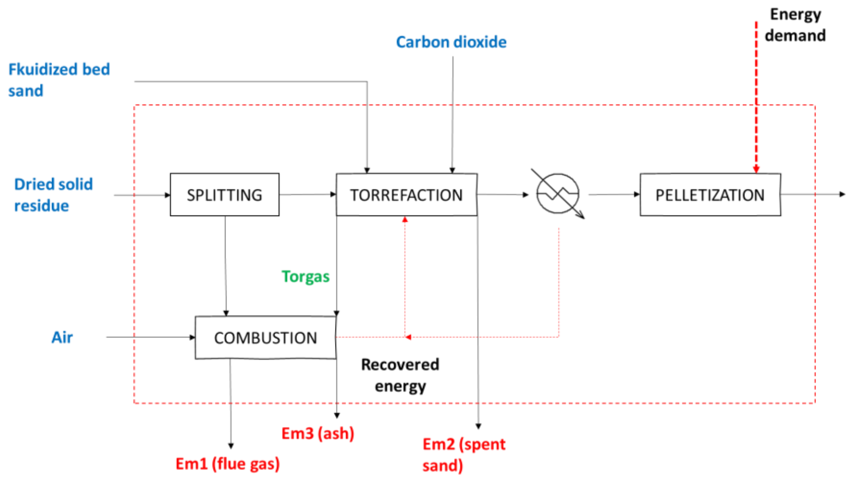


Figure 59 *Block diagram for torrefaction of dried solid residue from tomato pomace processing*

4.7.2. Mass and energy balances

As already said, torrefaction and combustion sections were implemented in Aspen Plus ® software to evaluate the mass balances and to check if the thermal energy produced by combustion was enough to sustain the torrefaction step. The entire flowsheet developed in the Aspen Plus® software is presented in the Appendix for better readability. Anyway, some highlights of the crucial sections are shown and discussed here. Figure 60, the implantation of the biomass splitting in Aspen Plus. The biomass feed (SOLRES), i.e., dried solid residue coming from the tomato seed oil extraction and pectin extraction sections, considered previously dried to low residual moisture, is separated into two flows: IN-COMB (5 % of SOLRES), which is burned to produce the needed heat for torrefaction, and BIOM (95 % of SOLRES) that is sent to the torrefaction reactor.

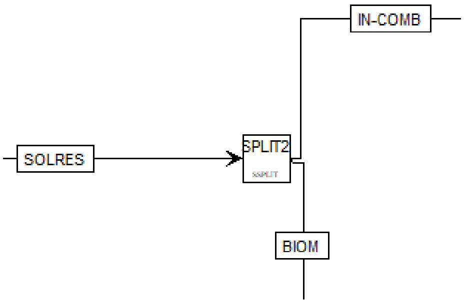


Figure 60 *Splitting of the residual biomass as feedstock in the torrefaction process section*

The biomass entering the plant (SOLRES) is specified as “non-conventional components”. The HCOALGEN and DCOALIGT models are invoked to evaluate the enthalpy of formation, the thermal capacity, and the density, starting from the data provided by the ultimate and proximate analyses. Ultimate (ULTANAL) and proximate (PROXANAL) analyses have been obtained experimentally by tomato residues samples provided by the Industria Conserviera Di Alfonso Sellitto S.P.A. (Alfonso Sellitto S.p.A. - da più di cinquant’anni nel settore agro-alimentare, no date) and then implemented in the Aspen software.

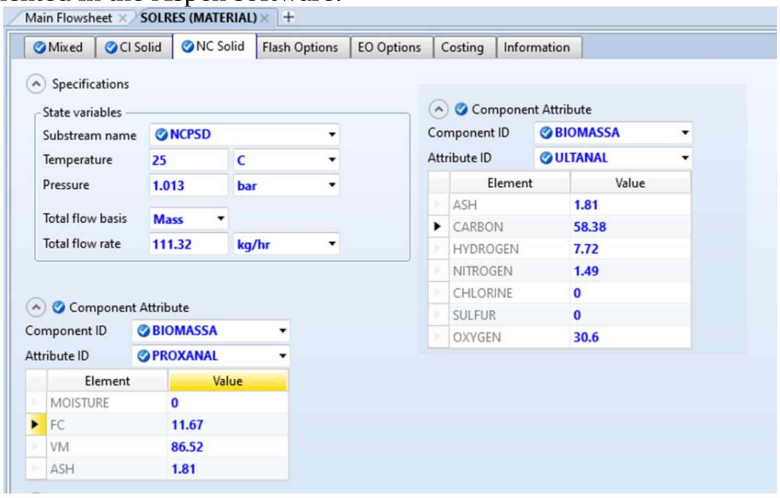


Figure 61 *Tomato solid residue implemented in Aspen Plus software as "Non-Conventional Components"*

After the splitting, the solid stream to be torrefied (BIOM) is sent to the torrefaction reactor together with gaseous carbon dioxide (CO2C). The torrefaction section developed in Aspen Plus is reported in Figure 62.

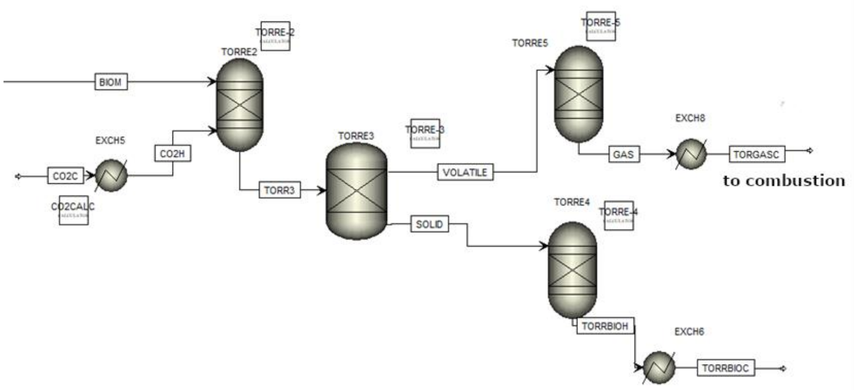
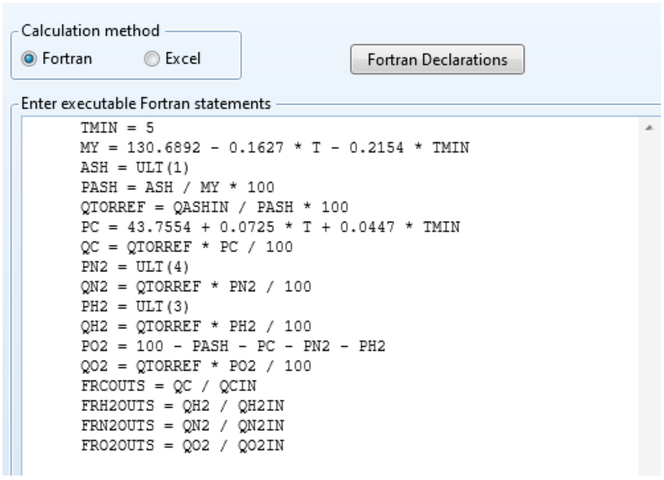


Figure 62 *Screenshot of the AspenPlus® flowsheet implementing the torrefaction section*

As it is shown in the flowsheet, the fluidized bed reactor for torrefaction is simulated through four different blocks:

- TORRE2: the decomposition of biomass in terms of its constituent elements is simulated through an *RYield* block.
- TORRE3: the splitting of the constituent elements between the solid and gaseous torrefaction products is represented by a *Sep* block; it is complemented by simple Fortran code (Figure 63) implementing the mass yield (MY), the evolution of C, O and H during torrefaction using the correlations obtained by Brachi et al. (Brachi et al., 2016b) as a function of torrefaction temperature and residence time of biomass.




```
TMIN = 5
MY = 130.6892 - 0.1627 * T - 0.2154 * TMIN
ASH = ULT(1)
PASH = ASH / MY * 100
QTORREF = QASHIN / PASH * 100
PC = 43.7554 + 0.0725 * T + 0.0447 * TMIN
QC = QTORREF * PC / 100
PN2 = ULT(4)
QN2 = QTORREF * PN2 / 100
PH2 = ULT(3)
QH2 = QTORREF * PH2 / 100
PO2 = 100 - PASH - PC - PN2 - PH2
QO2 = QTORREF * PO2 / 100
FRCOUTS = QC / QCIN
FRH2OUTS = QH2 / QH2IN
FRN2OUTS = QN2 / QN2IN
FRO2OUTS = QO2 / QO2IN
```

Figure 63 *Fortran code for torrefaction reaction*

- TORRE4: the re-combination of the constituent elements into torrefied solids is made by an *RYield* block.

- TORRE5: the evaluation of the gas is made by an *RYield;* it is complemented by a simple Fortran code (Figure 64) implementing the correlations by Tito Ferro et al. (Ferro et al., 2004) providing the torgas composition as a function of torrefaction temperature. In addition, TORGASC includes the CO_2 stream used as an "inert" fluidizing gas in the torrefaction reactor.

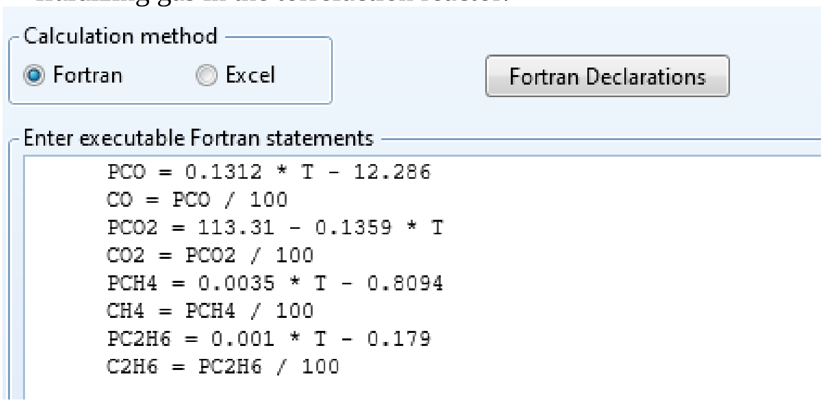


Figure 64 *Fortran code for gas composition evaluation*

The carbon dioxide feed rate (CO2C) to the torrefaction reactor was calculated by a calculator block (CO2CALC) as proportional to the dried biomass flow:

$$\dot{m}_{CO_2} = 0.786 * \dot{m}_{biomass}$$

The factor of 0.786 was estimated from the investigation of continuous torrefaction of tomato peels reported by Guerriero (Guerriero, 2017). Finally, the diverted solid residue IN-COMB is sent to a combustion chamber with air to generate the heat needed for the torrefaction reaction. The combustion of the biomass is simulated in Aspen Plus software with two blocks as reported in Figure 65.

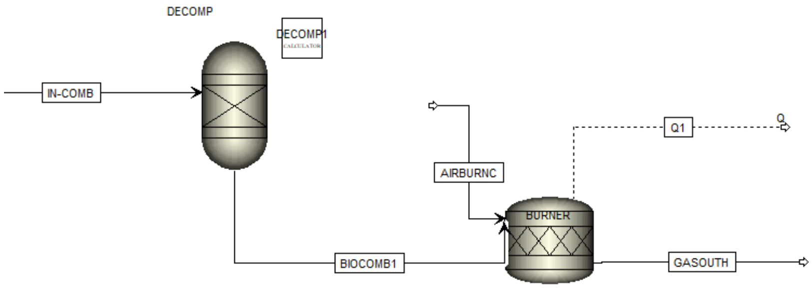


Figure 65 *Screenshot of the AspenPlus® flowsheet implementing the combustion section*

The decomposition of biomass in terms of its constituent elements is simulated through an *RYield* block (DECOMP). Then the elements, mixed with stoichiometric air (AIRBURNC), are fully oxidized in an *RStoic* block (BURNER), generating energy (Q1 as heat) and flue gas (GASOUTH) containing mainly CO_2, H_20, and N_2. As the outcome of the AspenPlus® code run and the related simple calculations regarding both fresh bed sand make-up (due to entrainment in the reactor) and the pelletization step, the obtained mass flows are reported in Table 40:

Table 40 *Mass balances for tomato solid residues torrefaction*

Raw Materials [kg/h]	
Dried solid residue	111.32
Fresh fluidized bed sand make-up	1.29
Carbon dioxide	83.12
Air	56.51
Emissions [kg/h]	
Em1 (flue gas)	156
Em2 (spent sand)	1.29
Em3 (ash)	0.09
Products [kg/h]	
Pellets	94.82

As the table shows for the torrefaction of 111.32 kg/h of dried tomato solid residues, 83.12 kg/h of carbon dioxide and 1.29 kg/h of bed sand make-up are needed. The reaction produces 94.82 kg/h of biochar that can be fully converted into pellets. Further, the combustion sub-section (GASOUTH) causes the emission of 156 kg/h of flue gas, with the following composition: 28.9 % N_2, 2.5% O_2, 66.4% CO_2 and 2.2% H_2O, which will require a waste treatment, causing a cost for the company. Regarding the energy demand, the simulation in Aspen confirmed the process is auto-thermal when 5% of biomass is sent to combustion, therefore the only power demand is for pelletizing (15 kW). 570 MJ of energy is required to produce one tonne of pellets.

4.7.3. Economic sustainability and CO_2 recovery

In conclusion, the Aspen simulation demonstrated the feasibility of pellets production starting from dried solid residues, produced by high-value compounds extraction from tomato processing by-products. The torrefaction reaction is auto-thermal when a small amount of biomass is burned to pre-heat the biomass entering the fluidized bed reactor. After the process simulation, to assess the economic feasibility of the plant for biodiesel production, operating costs and gross profit were evaluated. Unfortunately, even if only pelletizing is considered in the energy balance, the gross profit of a plant producing pellets from dried solid residues would be very low.

Indeed, high operating costs due to the treatment of the flue gas emission were found (**Figure 66**).

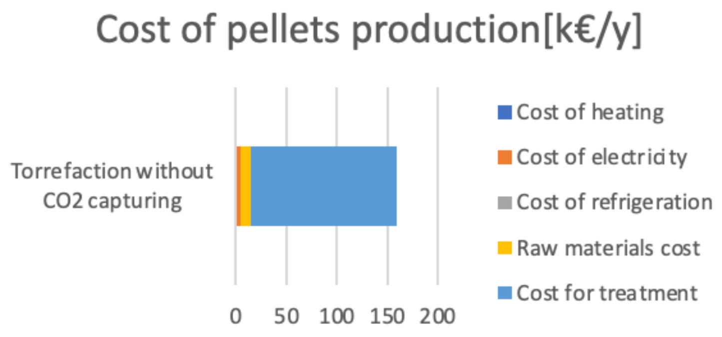


Figure 66 *Cost of pellets production*

Therefore, to avoid the cost of flue gas treatment a new scheme, reported in Figure 67, with a CO_2 recovery system was developed. For operating cost evaluation, chemical adsorption was considered a CO_2 capturing system. As reported by Yang et al. (Yang et al., 2011), both CO_2 recovery and purity are greater than 90% when chemical adsorption is used, and the cost ranges from 40-50 $/t of recovered CO_2. With this innovation in the torrefaction plant section, the treatment cost drops down, and the total operating cost was found 31 k€/y. While considering a market price of 379 $/t for the pellets, the gross profit turned positive, and it is 146 k€/y when 94.82 kg/h of residual tomato pellets are produced.

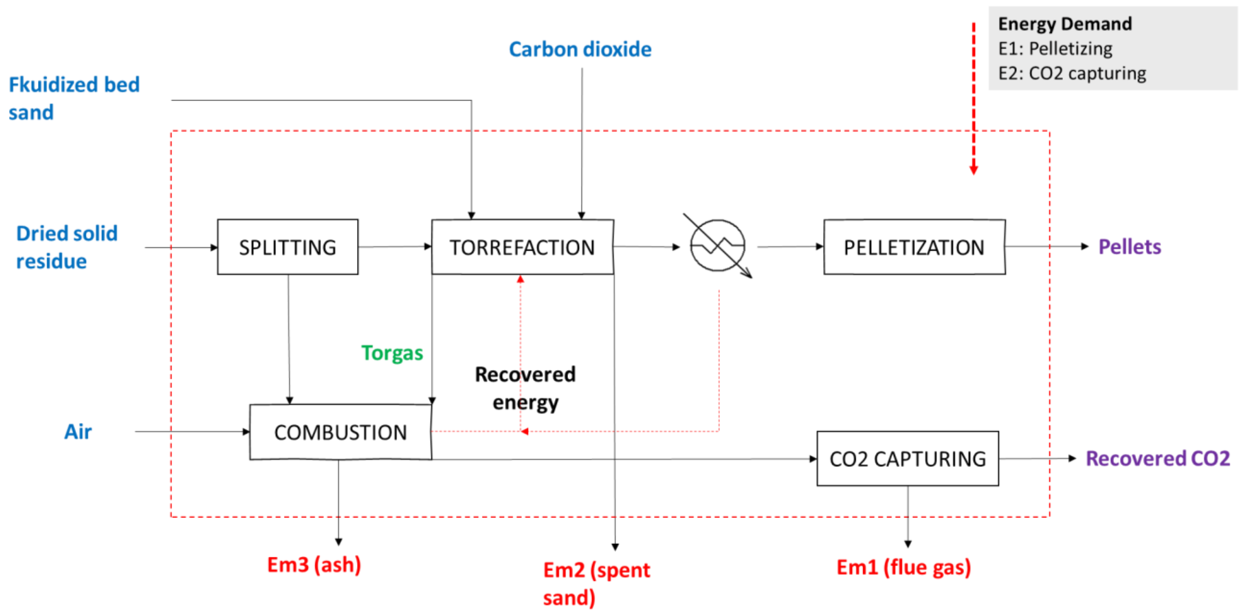


Figure 67 *Block diagram for the torrefaction with CO_2 recovery system*

5. LCA of Conventional and Alternative biorefining

Life cycle assessment (LCA) is the method typically recommended by international institutions, such as the European Commission and the United Nations Environment Programme, to support sustainability policies by quantitatively assessing environmental impacts throughout a product's life cycle. The application of LCA minimizes trade-offs between comparable alternatives, avoiding shifting environmental burdens from one life cycle stage or process to another, and from one environmental impact category to another. LCA is defined as collecting and calculating the inputs/outputs and potential environmental impacts of a product or product system during its life cycle. Standard practice for LCA is recorded in the 14040 series of standards issued by the International Organization for Standardization (ISO). The LCA methodology comprises four iterative steps: goal and scope definition, inventory analysis, impact assessment and interpretation (Life Cycle Assessment - Theory and Practice, 2018; ISO 14044:2006(en), Environmental management — Life cycle assessment — Requirements and guidelines, no date; ISO 14040:2006(en), Environmental management — Life cycle assessment — Principles and framework, no date; Cucurachi et al., 2019).

- Goal and scope: defining the goal and scope is the first step in any LCA study. Here, the aim of the study is carefully outlined and described. This step focuses on formulating the research question and providing the context for answering that question. The plan for the LCA study is defined as clearly and unambiguously as possible. The purpose of the LCA should address the intended application, e.g., comparing environmental impacts for specific goods or services or identifying the parts of a product system that contribute most to its environmental impact, the reason for conducting the study, e.g., as decision support, and the intended audience. Thus, the conditions and assumptions under which the study results are valid must be made explicit in this phase. The functional unit is one of the main aspects of the scope definition. It describes quantitatively the function that is fulfilled by the product system. Therefore, the LCA quantifies environmental impacts concerning the function performed by a system (Life Cycle Assessment - Theory and Practice, 2018; Cucurachi et al., 2019). During this phase, the “boundaries of the system” are defined, specifying the activities that are included or omitted from the study. The system boundaries should ideally cover the entire life cycle, upstream and downstream. In practice, simplifications are necessary to limit the increase in complexity when additional upstream and downstream ramifications are added to the analysis. The system boundaries are generally divided into a foreground and a background system. The former identifies all those processes that are at the center of the study and can be directly influenced by decisions based on its results; the latter includes all other processes that exchange materials and energy with the foreground, usually through a homogeneous market (Clift, Doig and Finnveden, 2000; Paulillo et al., 2021).

- Life Cycle Inventory (LCI): this step involves the collection of data, identification of relationships, and quantification of the inputs and outputs of the system under consideration. Starting with the functional unit, a flow chart is developed that maps all the individual subunits (i.e., unit processes) that together make up the system. The inventory records the "elemental flows," i.e., the natural resources extracted from the natural environment and the substances released into the natural environment. These extractions and emissions occur within the technosphere and are subject to human transformation. Given the complexity of the systems typically under evaluation, an LCA study requires the collection of primary data to model all processes comprised in the “foreground”. Instead, it relies on existing commercial inventory databases to model the "background" system, which includes, for example, data on irrigation water demand or the electricity grid mix at a specific geographic location (Clift, Doig and Finnveden, 2000). The output of the LCI step is an inventory table of exchanges (resources and emissions) between the system under consideration and the natural environment (Life Cycle Assessment - Theory and Practice, 2018; Cucurachi et al., 2019).
- Life Cycle Impact Assessment: at this stage, predefined methods, usually implemented in dedicated LCA software, are used to group, and aggregate inventory data, i.e., resources and emissions, into environmental impact categories. For example, all greenhouse gas (GHG, e.g., CO_2 and CH_4) emissions released during the life cycle of a product and quantified in the Life Cycle Inventory phase are translated into climate change impacts expressed in terms of CO_2 equivalent. For this, LCI results are multiplied by their respective global warming potentials (GWP), as provided by the

Intergovernmental Panel on Climate Change. The result is a climate change impact score, which we often refer to as a carbon footprint. However, the purpose of an LCA is broader than simply assessing climate impacts, and GWPs are just one example of a broader range of characterization factors. Models and characterization factors have been developed to characterize water, land, and resource use, among other things, and also to characterize human health impacts and ecotoxicity as a result of, for example, the emission of a solvent into the air (Life Cycle Assessment - Theory and Practice, 2018; Cucurachi et al., 2019).

- Interpretation: inventory and impact results are analyzed and interpreted. At this stage, potential areas for improvement related to hotspots in the life cycle can be highlighted or a decision on a preferable option in a comparative assessment can be made. The relationship between the results and the methodological issues, assumptions and limitations of the study are assessed here with their influences on the decision at stake and the objective of the study. These increasingly include issues related to the uncertainty of the study results, and potential sources that influence the uncertainty of the results (e.g., lack of data, unrepresentative process data, or difference in the geographic or temporal scopes of the data collected) (Life Cycle Assessment - Theory and Practice, 2018; Cucurachi et al., 2019).

5.1. Goal and scope

In this section of the work, the life cycle assessment of two different approaches for the valorization of tomato by-products was conducted. The two approaches were based on the same biorefinery model shown in the previous chapter and reported in Figure 68.

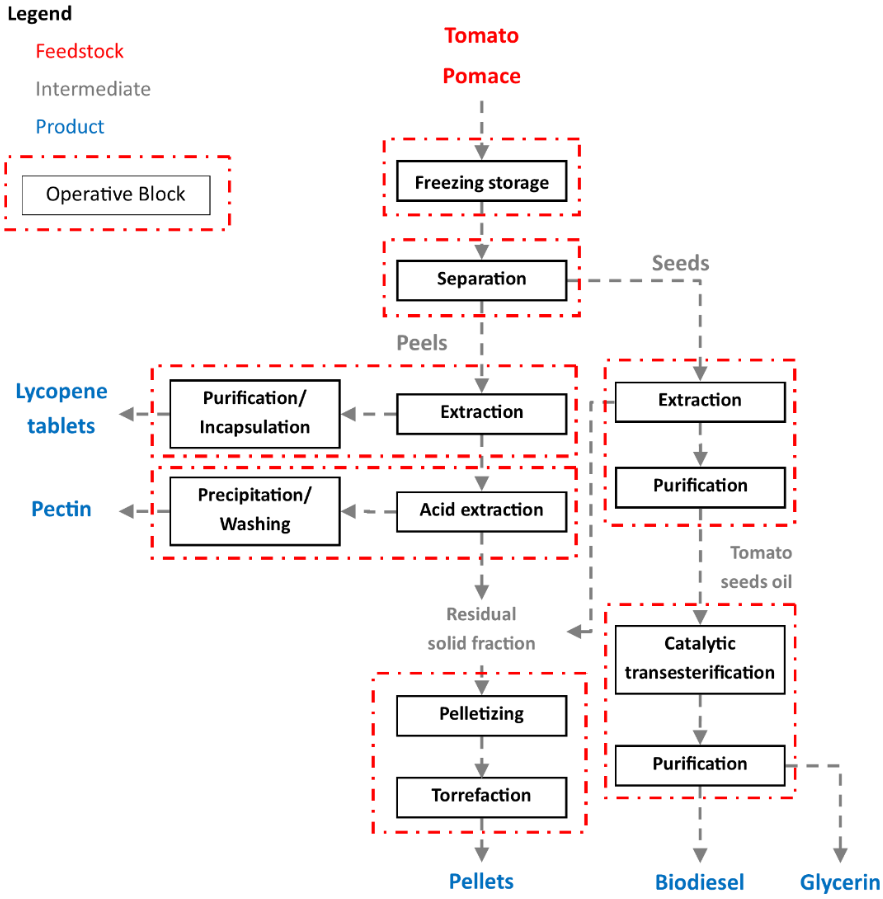


Figure 68 *Block diagram of the biorefinery modelled in the previous chapter*

It is worth noticing that dotted lines highlight the single operations that were investigated and optimized in the techno-economic assessment, reported in Chapter 4. The biorefinery of the first approach, called "conventional", comprises all the conventional technologies reported in the previous chapter, while the biorefinery of the second approach, called "alternative", is composed of operations based on "green" alternative techniques. Table 41 shows the processes considered for the modelling of the two biorefineries.

Table 41 *Technologies involved in the two biorefineries for the LCA study*

	Conventional biorefinery	Alternative biorefinery	Product
Storage	Freezing storage		-
Pomace separation	Floatation-cum-sedimentation	Air separation	-
Lycopene extraction	Extraction with ethyl acetate	Extraction with limonene	Lycopene containing tablets
Pectin production	Extraction with hcl	Extraction with citric acid	Pectin (food grade)
Seed oil extraction	Extraction with hexane	Expeller pressing	-
Biodiesel production	Transesterification with koh	Transesterification with eggshells	Biodiesel, glycerin, fertilizer (only 1st scenario)
Pellets production	Torrefaction without co_2 recovery	Torrefaction with co_2 recovery	Pellets

The goal of the LCA study is to assess the environmental performance and to identify the main sources of the impact of the proposed biorefineries in relation to the conventional processes for treating tomato residues and for producing the five compounds exiting the systems (i.e., lycopene, pectin, biodiesel, glycerin, and pellets). It is worth noting that two different current scenarios were developed: one related to the conventional biorefining and the other one related to the alternative biorefining. For the two developed biorefineries, the system boundaries reported in Figure 69 were considered.

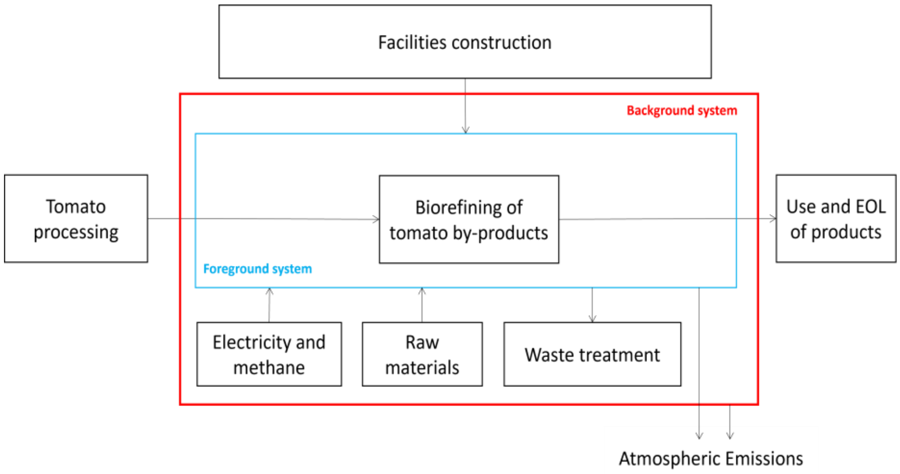


Figure 69 *System boundaries for tomato residues valorization via biorefining*

The system boundaries are “gate-to-gate” because only operations inside the two biorefineries were considered; in addition, the study is made specific to the Italian context. As the figure shows, in the study of environmental impact, energetic demand, raw materials use and waste treatment connected to the processing of tomato pomace was considered as background system, while the foreground system comprises all processes related to the biorefining of tomato residues. Impacts connected to tomato processing, facilities construction, and the use of the products of the biorefinery were not considered. The functional unit for this study does not simply correspond to the amount of a product or a feedstock due to the complexity of the scenarios. Indeed, biorefineries are multiproduct systems, that is, a series of processes that starting from an organic feedstock produce in a cascading fashion different compounds like high-value molecules, food-grade fractions and biofuels. In our case study, starting from tomato pomace (which comes from a tomato processing plant) the biorefineries produce (with different product yields) lycopene, pectin, glycerin, biodiesel, and pellets. Therefore, considering 1 t of tomato pomace entering the boundaries, as a functional unit, would neglect the fact that the two biorefineries have different product outputs. On the other hand, considering only a single product (e.g., 1 kg of lycopene or 1 MJ contained in biodiesel) as a functional unit would require a different amount of tomato by-products, making results less meaningful, due to a different size of the biorefineries. Therefore, we defined two functional units, for the two biorefining systems, including the amount of tomato pomace produced by 5 medium tomato processing companies in a year and the corresponding amounts of the products generated by the conventional and alternative biorefineries, respectively. For the conventional system, addressed as Conventional Biorefinery in the following, the functional unit is a biorefinery treating 4020 t of tomato pomace and producing 7.7 t of lycopene-containing lipophilic extract, 129 t of pectin, 25.6 t of glycerin, 248 t of biodiesel, and 669 t of pellets. For the alternative system, referred to as Alternative Biorefinery, in the following, the functional unit is a biorefinery treating 4020 t of tomato pomace still, but producing 1.9 t of lycopene-containing lipophilic extract, 75 t of pectin, 11.1 t of glycerin, 106 t of biodiesel and 835 t of pellets. Table 42 shows the details of the two functional units for the two scenarios:

Table 42 *Functional unit for the two scenarios*

	Functional unit	
	Conventional Biorefinery	**Alternative Biorefinery**
Tomato pomace [t]	4020	4020
Lycopene-containing lipophilic extract [t]	7.7	1.9
Pectin [t]	129	75
Biodiesel [t]	248	106
Glycerin [t]	25.6	11.1
Pellets [t]	669	835

The product amounts were evaluated from the mass balances obtained in the techno-economic analysis, reported in Chapter 4. Once the two functional units were defined, two different current scenarios were modelled for comparing the actual situation with the two developed biorefineries. The boundaries considered for the current scenarios are reported in Figure 70.

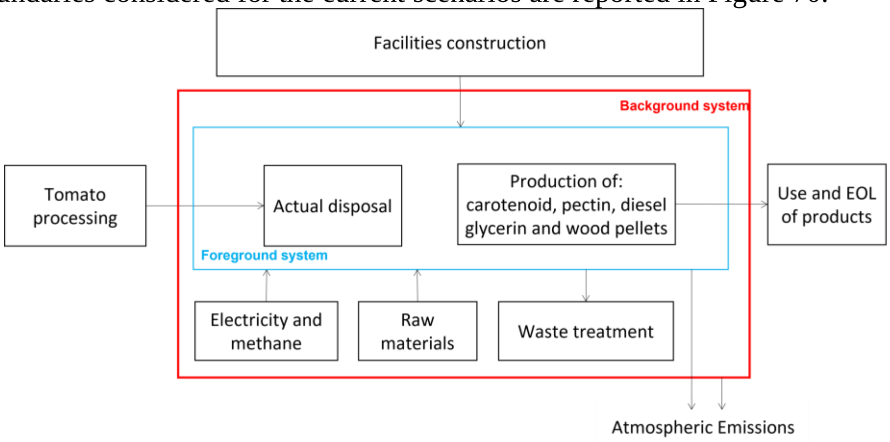


Figure 70 *System boundaries for Current Scenarios*

The system boundaries of the current scenarios include both the end-of-life of tomato pomace, which is the current way of disposal and the production systems of the 5 compounds coming out of the biorefineries. For developing the models of the two current scenarios, it was considered that tomato pomace is sent to disposal as reported in the literature, while the biorefinery products are considered to be produced conventionally, for example, pectin from citrus peels or diesel from the refinery. When no conventional process or source was found for a biorefinery's product, like in the case of lycopene, similar compounds were used for modelling. As reported in Figure 70, for the environmental assessment of the current scenarios, energetic demand, raw materials use and waste treatment connected to the tomato pomace disposal and compounds production were considered as the background system, while the foreground system comprises all processes related to tomato pomace disposal and compound's production. The two modelled current scenarios will be referred to in the text as Current Scenario 1 and Current Scenario 2. Their functional unit corresponds to that of the conventional and alternative biorefineries, as reported in Table 42. Therefore, as already mentioned at the beginning of this chapter, the goal of this study is to compare the environmental performances of the Conventional Biorefinery with Current Scenario 1 and the Alternative Biorefinery with Current Scenario 2, to understand how the transformation of tomato pomace in two alternative biorefineries differs from the current scenario when the same functional unit is considered and from an environmental perspective. Then, the environmental impact of tomato pomace transformation in Conventional and Alternative Biorefinery and of the Current Scenarios (1 and 2) were estimated using the GaBi software tool for Life Cycle Assessment (Kupfer et al., 2020), and by applying the Environmental Footprint 3.0 methodology (European Commission, 2018; Joint Research Centre (European Commission) et al., 2018). The Environmental Footprint (EF) is an initiative of the European Commission, establishing a common methodological approach for quantifying the environmental performance of any good or service throughout its life cycle, developed by the Joint Research Centre (JRC). The following impact categories were examined:

Table 43 *Impact categories considered in the LCA study*

Impact Category	Unit
Acidification terrestrial and freshwater	Mole of H^+ eq
Cancer human health effects	CTUh
Climate Change	kg CO_2 eq
Ecotoxicity freshwater	CTUe
Eutrophication freshwater	kg P eq
Eutrophication marine	kg N eq
Eutrophication terrestrial	Mole of N eq
Ionizing radiation – human health	kBq U^{235} eq
Land Use	Pt
Non-cancer human health effects	CTUh
Ozone depletion	kg CFC-11 eq
Photochemical ozone formation – human health	kg NMVOC eq
Resource use, energy carriers	MJ
Resource use, mineral and metals	kg Sb eq
Respiratory inorganics	Disease incidences
Water scarcity	m^3 world eq

A brief description of the impact categories included in the study is reported in the Appendix.

5.2. Life cycle inventory

Energy demand, raw materials, emissions, and waste flows for the modelling of the two biorefineries were provided by the previous techno-economic assessment for each biorefinery section, reported in Chapter 4. The overall Life Cycle Inventory of the Conventional and Alternative Biorefineries is reported in Table 44 and Table 45.

Table 44 *Life Cycle Inventory of Conventional Biorefinery for its Functional Unit*

			FREEZING STORAGE				
Raw materials	Tomato pomace	4020	t				
Auxiliary facilities	Allocated Surface	4985	m^2				
	Electricity	132E5	MJ				
			FLOATATION-CUM-SEDIMENTATION				
Raw materials	Tomato pomace	4020	t	**Output**	Dried Tomato Peels	511	t
	Water	237E3	t		Dried Tomato Seeds	712	t
Auxiliary facilities	Electricity	0.8E5	MJ	**Emission and waste**	Wastewater	240E3	t
	Thermal Energy	68E5	MJ				
			LYCOPENE EXTRACTION WITH ETHYL ACETATE				
Raw materials	Dried Tomato Peels	511	t	**Output**	Lycopene oleoresin	7.7	t
	Ethyl acetate	1.3E3	t		Dried Dewaxed Peels	460	t
	Molecular sieve	4.8	t	**Emission and waste**	Spent oleoresin	0.3	t
Auxiliary facilities	Electricity	8.5E5	MJ		Water to air	39.6	t
	Thermal Energy	22E5	MJ		Spent solvent	1.3E3	t
					Spent sieve	4.8	t
			PECTIN PRODUCTION WITH HCL				
Raw materials	Dried Dewaxed Peels	460	t	**Output**	Pectin Food Grade	129	t
	HCl	16	t		Solid residue	331	t
	Water	258	t	**Emission and waste**	Spent air	8027	t
	Ethanol	656	t		Spent solvent	910	t
Auxiliary facilities	Electricity	9E5	MJ				
	Thermal Energy	40E5	MJ				
	Cooling Energy	394E5	MJ				
			SEED OIL EXTRACTION WITH HEXANE				
Raw materials	Dried Tomato Seeds	712	t	**Output**	Tomato Seed Oil	256	t
	Hexane	0.51	t		Solid Residue	456	t
Auxiliary facilities	Electricity	17E5	MJ	**Emission and waste**	Spent solvent	0.51	t
	Thermal Energy	15E5	MJ				
	Cooling Energy	29E5	MJ				
			BIODIESEL PRODUCTION WITH KOH				
Raw materials	Tomato Seed Oil	256	t	**Output**	Biodiesel	248	t
	KOH	2.55	t		Glycerin	25.6	t
	Methanol	28	t		Phosphate	3.2	t
	Water	154	t	**Emission and waste**	Wastewater	157	t
	Phosphoric acid	1.5	t		Spent oil	8.5	t
Auxiliary facilities	Electricity	0.8E5	MJ				
	Thermal Energy	17E5	MJ				
	Cooling Energy	2.7E5	MJ				
			TORREFACTION WITHOUT RECOVERY				
Raw materials	Solid Residue	788	t	**Output**	Pellets	669	t
	Fluidized bed sand	9.1	t	**Emission and waste**	Flue gas (66% CO_2)	1100	t
	Carbon dioxide	586	t		Spent sand	9.1	t
Auxiliary facilities	Electricity	3.8E5	MJ		Ash	0.6	t

Table 45 *Life Cycle Inventory of Alternative Biorefinery for its Functional Unit*

		FREEZING STORAGE					
Raw materials	Tomato pomace	4020	t				
Auxiliary facilities	Allocated Surface	4985	m^2				
	Electricity	132E5	MJ				
		AIR SEPARATION					
Raw materials	Tomato pomace	4020	t	Output	Dried Tomato Peels	483	t
	Air	1E6	t		Dried Tomato Seeds	724	t
Auxiliary facilities	Electricity	0.7E5	MJ	Emission and waste	Wastewater	2.7E3	t
	Thermal Energy	63E5	MJ				
		LYCOPENE EXTRACTION WITH LIMONENE					
Raw materials	Dried Tomato Peels	483	t	Output	Lycopene oleoresin	1.93	t
	Limonene	111	t		Dried Dewaxed Peels	444	t
	Water	203	t		Spent oleoresin	0.08	t
Auxiliary facilities	Electricity	11E5	MJ	Emission and waste			
	Thermal Energy	590E5	MJ		Spent solvent	314	t
		PECTIN PRODUCTION WITH CITRIC ACID					
Raw materials	Dried Dewaxed Peels	444	t	Output	Pectin Food Grade	75	t
	Citric acid	18	t		Solid residue	369	t
	Water	40	t	Emission and waste			
	Ethanol	17	t		Spent solvent	78	t
Auxiliary facilities	Electricity	3.6E5	MJ				
	Thermal Energy	38E5	MJ				
	Cooling Energy	38E5	MJ				
		SEED OIL EXTRACTION BY EXPELLER PRESSING					
Raw materials	Dried Tomato Seeds	724	t	Output	Tomato Seed Oil	111	t
					Solid Residue	613	t
Auxiliary facilities	Electricity	8E5	MJ				
		BIODIESEL PRODUCTION WITH EGGSHELLS					
Raw materials	Tomato Seed Oil	111	t	Output	Biodiesel	106	t
	Eggshells	0.4	t		Glycerin	11.1	t
	Methanol	12	t				
	Water	70	t	Emission and waste	Wastewater	71	t
					Spent oil	4	t
Auxiliary facilities	Electricity	0.3E5	MJ		Solid waste	0.22	t
	Thermal Energy	8E5	MJ		CO2 emission	0.17	t
	Cooling Energy	4E5	MJ				
		TORREFACTION WITH RECOVERY					
Raw materials	Solid Residue	982	t	Output	Pellets	835	t
	Fluidized bed sand	11	t		Flue gas (low CO_2)	458	t
	Carbon dioxide	731	t	Emission and waste	Spent sand	11	t
Auxiliary facilities	Electricity	13E5	MJ		Ash	0.8	t

Then the two models were developed in Gabi and reported in Figure 71 and Figure 72.

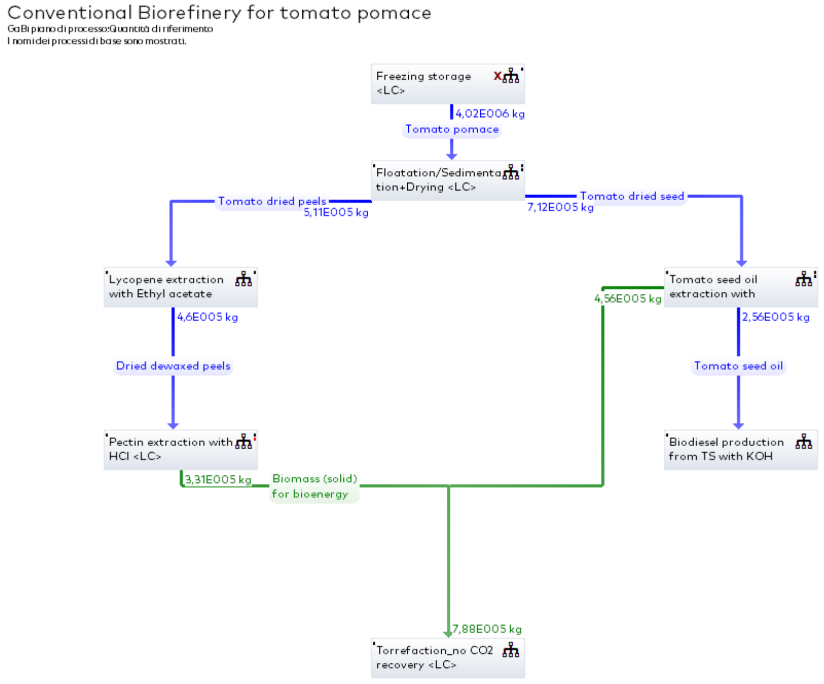


Figure 71 *Gabi model for Conventional Biorefinery*

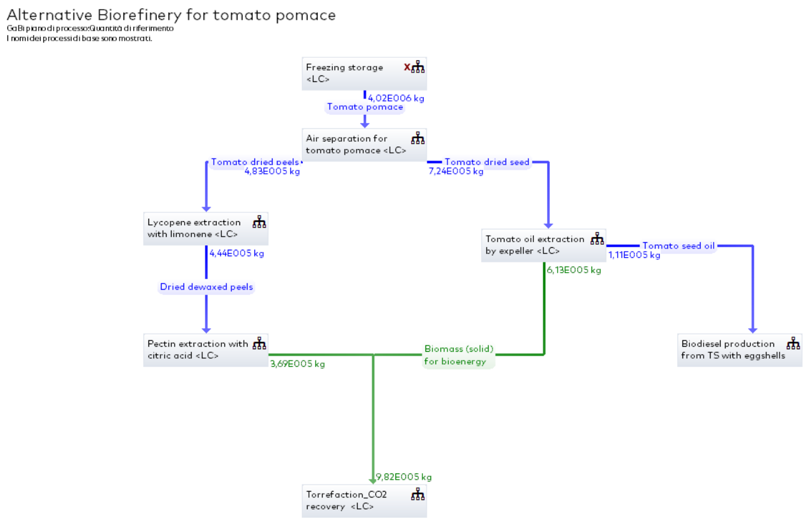


Figure 72 *Gabi model for Alternative Biorefinery*

For the raw materials, inventory datasets provided by the ecoinvent 3.0 database were used. For electricity demand, the Italian Grid mix was considered while natural gas was considered to produce thermal energy. Regarding the comparative scenarios, namely Scenario 1 and Scenario 2, comprising the current disposal of tomato pomace and the production of the 5 compounds exiting the biorefineries, the following assumptions were made:

- Tomato pomace is disposed of in the following way: 75% by composting, 18% by anaerobic digestion, 4% by incineration, and 3% by landfill as reported by Xue et al. for the Italian current situation (Xue et al., 2021). Figure 73 reports the model developed in Gabi software for the current pomace disposal.

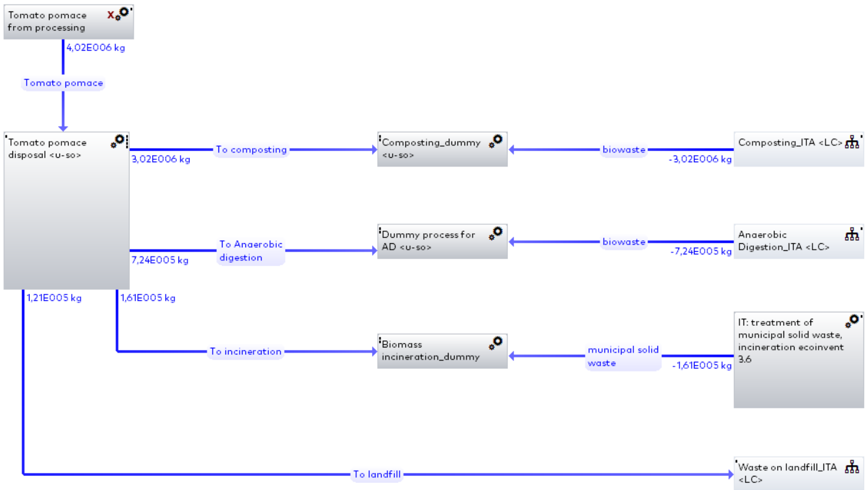


Figure 73 *Gabi model for tomato pomace disposal*

- Lycopene was considered a carotenoid and its actual production from algae was modelled in Gabi using the process scheme and inventory reported by Espada et al. (Espada et al., 2020). The block diagram of the process for carotenoid production is reported in Figure 74.

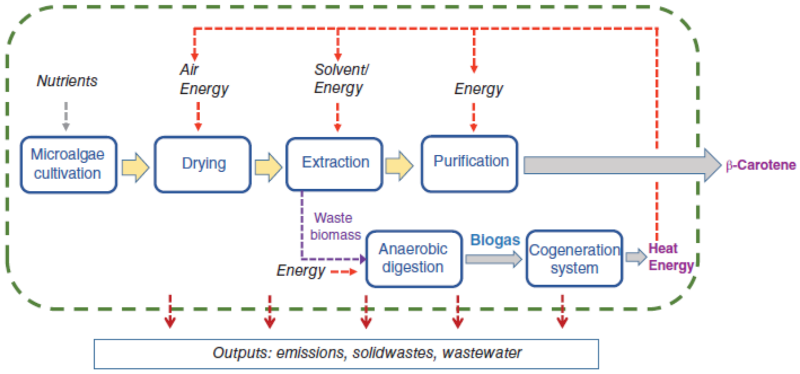


Figure 74 *General scheme for carotenoid production by algae (Espada et al., 2020)*

- The production of pectin from orange peels with hydrochloric acid was modelled by using the process scheme and inventory reported by Garcia-Garcia et al. (Garcia-Garcia et al., 2019). Figure 75 shows a simplified block diagram and the inventory of the process.

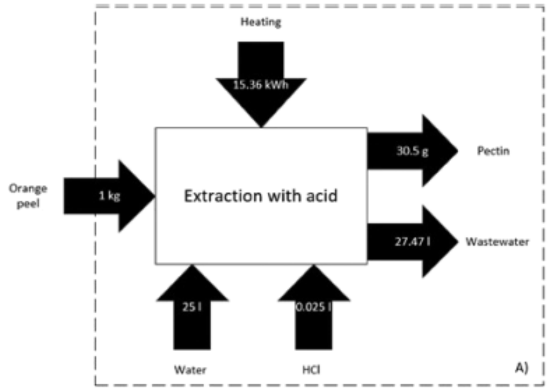


Figure 75 *Inventory for pectin production from orange peels*

- For the production of pellets (from wood), biodiesel (from refinery) and glycerin (from epichlorohydrin), processes already present in the GABI database were used.

5.3. Life Cycle Impact Assessment and hotspot analysis

The impact assessment for all the considered categories for processing 4020 t of tomato pomace in a Conventional Biorefinery and producing 7.7 t of lycopene-containing lipophilic extract, 129 t of pectin, 25.6 t of glycerin, 248 t of biodiesel, and 669 t of pellets, is reported in Table 46.

Table 46 *Impact assessment for Conventional Biorefinery*

Acidification terrestrial and freshwater [Mole of H+ eq.]	6.65E4
Cancer human health effects [CTUh]	9.46E-3
Climate Change [kg CO2 eq.]	3.97E7
Ecotoxicity freshwater [CTUe]	4.12E8
Eutrophication freshwater [kg P eq.]	4.18E3
Eutrophication marine [kg N eq.]	1.93E4
Eutrophication terrestrial [Mole of N eq.]	1.54E5
Ionizing radiation - human health [kBq U235 eq.]	1.30E6
Land Use [Pt]	7.45E7
Non-cancer human health effects [CTUh]	3.31E-1
Ozone depletion [kg CFC-11 eq.]	2.16
Photochemical ozone formation - human health [kg NMVOC eq.]	5.85E4
Resource use, energy carriers [MJ]	5.89E8
Resource use, minerals and metals [kg Sb eq.]	1.91E2
Respiratory inorganics [Disease incidences]	5.20E-1
Water scarcity [m^3 world equiv.]	8.74E6

The hotspot for the operative blocks included in the biorefinery is reported in Figure 76.

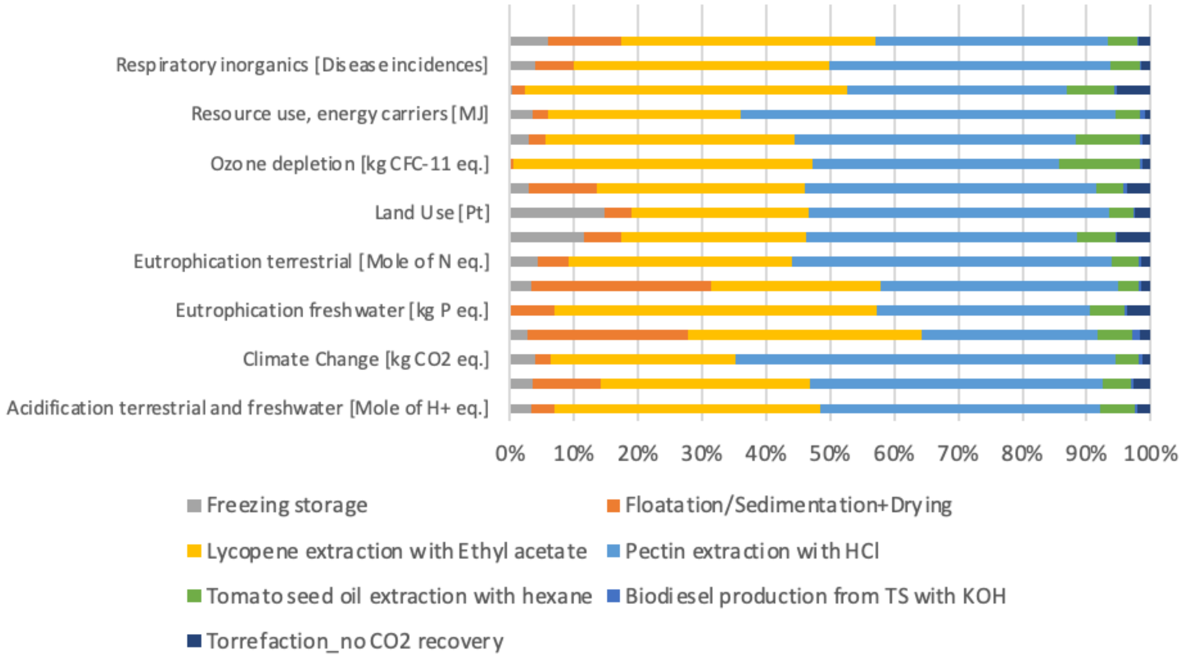


Figure 76 *Hotspot analysis for Conventional Biorefinery*

Figure 76 shows that for all the impact categories, the main impacting processes of the biorefinery are pectin extraction with hydrochloric acid and lycopene extraction with ethyl acetate. This is mainly due to the fact that pectin production is the most energy demanding block, because of the thermal and cooling energy required by the distillation columns, while the lycopene extraction step has both high energy demand due to the flash operations and presents high waste output. On average, pectin extraction with HCl contributes 49% to impacts, in particular, from a minimum value of 24% in ecotoxicity of freshwater category to a maximum value of 59% in climate change. Regarding lycopene extraction, the second most contributing operative block, it contributes 36% to impacts on average; from a minimum value of 29% in the climate change category to a maximum value of 50% in the use of metals and minerals. The sedimentation block contribution is significant only in the marine eutrophication (28%) and in the freshwater ecotoxicity (24%) categories. All the other operative blocks contribute to impacts with a percentage lower than 15%. Table 47 reports the impact assessment for all the considered categories for processing 4020 t of tomato pomace in Alternative Biorefinery, producing 1.9 t of lycopene-containing lipophilic extract, 75 t of pectin, 11.1 t of glycerin, 106 t of biodiesel and 835 t of pellets.

Table 47 *Impact assessment for Alternative Biorefinery*

Acidification terrestrial and freshwater [Mole of H+ eq.]	1.97E4
Cancer human health effects [CTUh]	3.04E-3
Climate Change [kg CO2 eq.]	1.35E7
Ecotoxicity freshwater [CTUe]	8.37E7
Eutrophication freshwater [kg P eq.]	9.15E2
Eutrophication marine [kg N eq.]	4.43E3
Eutrophication terrestrial [Mole of N eq.]	4.72E4
Ionizing radiation - human health [kBq U235 eq.]	3.72E5
Land Use [Pt]	2.09E7
Non-cancer human health effects [CTUh]	8.52E-2
Ozone depletion [kg CFC-11 eq.]	8.96E-1
Photochemical ozone formation - human health [kg NMVOC eq.]	1.50E4
Resource use, energy carriers [MJ]	1.98E8
Resource use, minerals and metals [kg Sb eq.]	6.17E1
Respiratory inorganics [Disease incidences]	1.31E-1
Water scarcity [m^3 world equiv.]	2.45E6

The hotspot for the operative blocks included in the biorefinery is reported in Figure 77. For the Alternative Biorefinery, the most impacting operations is pectin extraction with citric acid, similar to what was found for the conventional biorefinery, again due to the distillation operations. The second most impacting operating block becomes freezing storage for the alternative approach;, indeed, even though the energy demand of freezing storage remains the same for both biorefineries due to the same amount of stored by-products, this contribution becomes by far more significant than in the conventional biorefinery scenario. On average, pectin extraction with citric acid contributes 65% to impacts, from a minimum value of 25% in the land use category to a maximum value of 84% in ozone depletion. Regarding freezing storage, in green, it contributes 15% to impacts on average; from a minimum value of 1% in the ozone depletion category to a maximum value of 40% in ionizing radiation. All the other operative blocks contribute to impacts with a percentage lower than 11%.

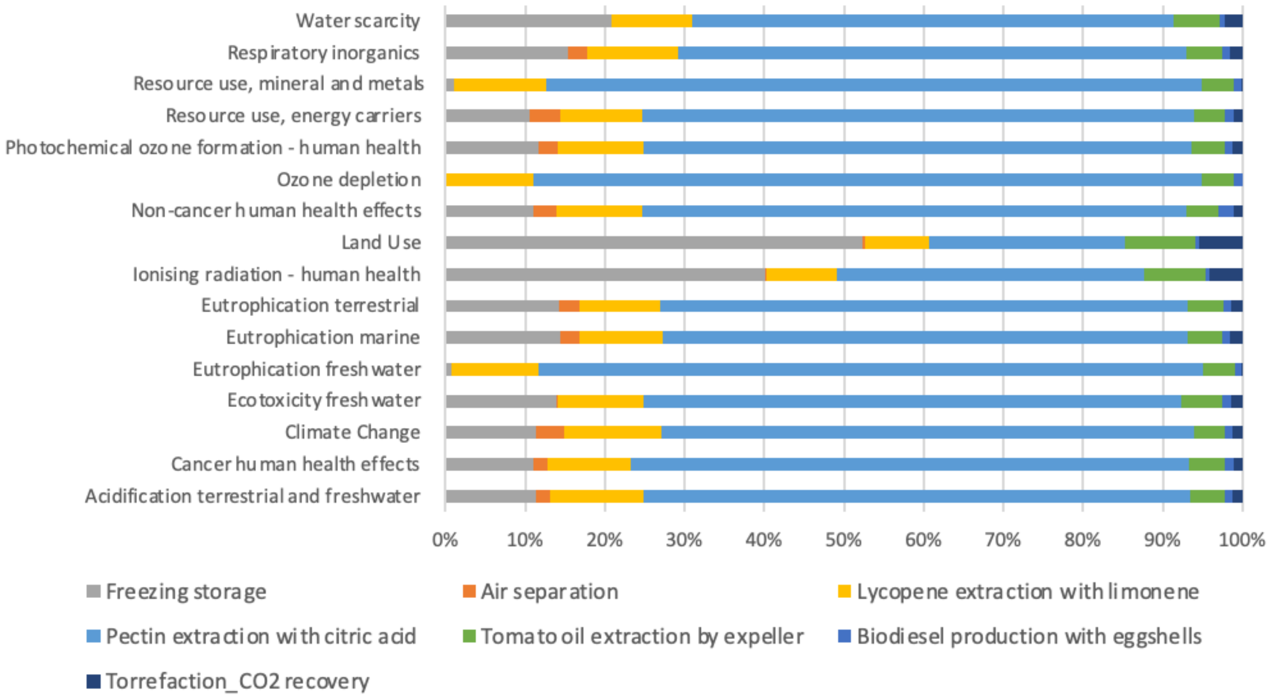


Figure 77 *Hotspot analysis for Alternative Biorefinery*

After the LCA was carried out for Conventional and Alternative Biorefinery, the impact assessment for all the considered categories for the two comparative current scenarios, namely Current Scenario 1 (with the functional unit equal to Conventional Biorefinery) and Current Scenario 2 (with the functional unit equal to Alternative Biorefinery) are evaluated and reported in Table 48. The latter also shows, next to the impacts of comparative scenarios, the impacts of the two biorefineries; Conventional and Alternative (Table 46 and Table 47), to which the reference systems are related. The impact on each category for the two comparative scenarios has been assessed as the sum of the impacts due to the disposal of tomato pomace plus the impacts due to the conventional production of the compounds (lycopene, pectin, biodiesel, glycerin, pellets) that form the functional unit.

Table 48 *Impact assessment for the comparative scenarios*

	Current Scenario 1	Conventional Biorefinery	Current Scenario 2	Alternative Biorefinery
Acidification terrestrial and freshwater [Mole of H+ eq.]	9.50E4	6.65E4	4.22E4	1.97E4
Cancer human health effects [CTUh]	8.86E-3	9.46E-3	3.87E-3	3.04E-3
Climate Change [kg CO2 eq.]	3.53E7	3.97E7	1.76E7	1.35E7
Ecotoxicity freshwater [CTUe]	8.78E8	4.12E8	2.83E8	8.37E7
Eutrophication freshwater [kg P eq.]	4.66E3	4.18E3	2.10E3	9.15E2
Eutrophication marine [kg N eq.]	1.90E4	1.93E4	8.91E3	4.43E3
Eutrophication terrestrial [Mole of N eq.]	2.55E5	1.54E5	1.20E5	4.72E4
Ionising radiation - human health [kBq U235 eq.]	1.05E6	1.30E6	3.58E5	3.72E5
Land Use [Pt]	7.88E7	7.45E7	4.13E7	2.09E7
Non-cancer human health effects [CTUh]	3.77E-1	3.31E-1	1.64E-1	8.52E-2
Ozone depletion [kg CFC-11 eq.]	1.25	2.16	4.54E-1	8.96E-1
Photochemical ozone formation [kg NMVOC eq.]	7.27E4	5.85E4	3.40E4	1.50E4
Resource use, energy carriers [MJ]	6.50E8	5.89E8	3.32E8	1.98E8
Resource use, minerals and metals [kg Sb eq.]	5.11E2	1.91E2	1.60E2	6.17E1
Respiratory inorganics [Disease incidences]	8.85E-1	5.20E-1	3.77E-1	1.31E-1
Water scarcity [m³ world equiv.]	4.64E7	8.74E6	1.26E7	2.45E6

5.4. Results of the comparison between current disposal and biorefineries

When the impacts for all categories are compared between the biorefinery and its related current scenario - Scenario 1 for the Conventional Biorefinery and Scenario 2 for the Alternative Biorefinery - it is possible to state if the valorization of tomatoes by-products is environmentally sustainable, in comparison with the current state. Figure 78 reports the relative reduction in the impact categories when tomato pomace is processed in the conventional and alternative biorefinery. The relative reduction was evaluated as:

$$Relative\ Reduction = \frac{Impact_{biorefinery} - \ Impact_{current\ scenario}}{Impact_{current\ scenario}}$$

Figure 78 shows that both biorefineries perform better than their related current scenario in all categories except ozone depletion and, only slightly, ionizing radiation. The conventional biorefinery performs worse than the actual scenario also in cancer effects, climate change and marine eutrophication.

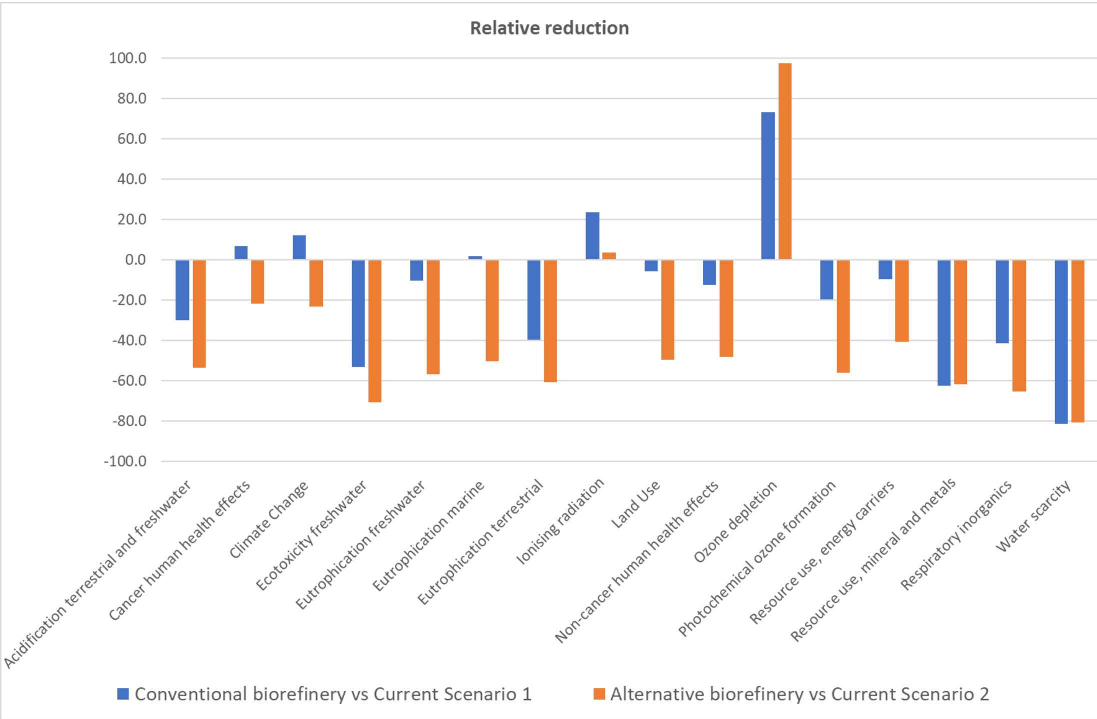


Figure 78 *Relative reduction for the two biorefineries*

In particular, the Conventional Biorefinery yields 10-81% less environmental impacts than the reference system, Scenario 1, in almost all impact categories. It shows a limited reduction of around 10% in resource use – energy carriers and eutrophication freshwater, and a significant reduction in water scarcity, resource use - mineral and metals and ecotoxicity freshwater of about 81%, 62% and 53% respectively. However, increases of 7%, 12%, 2% and 73% were found in the following categories: cancer human health effects, climate change, eutrophication marine, and ozone depletion, respectively. On the other hand, when the Alternative Biorefinery is used for treating tomato pomace, the proposed process becomes environmentally advantageous in comparison to the reference system, Current Scenario 2, in the majority of categories, yielding reductions of around 53% in the acidification category, 23% in climate change, 70%, 50% and 61% in freshwater, marine and terrestrial eutrophication respectively, 48% in human toxicity (non-cancer effects), 70% in ecotoxicity freshwater, 50% in land use, 56% in photochemical ozone formation, 40 and 61% in resource use energy carriers and mineral and metal respectively and 81% in water use. In the remaining categories, ionizing radiation, and ozone depletion, the Alternative Biorefinery generates 4 and 97% higher impacts. On average, the reduction is 15.4% for Conventional Biorefinery and 39.7% for Alternative Biorefinery. The results of the comparative analysis suggest that from an environmental perspective processing tomato pomace in an alternative biorefinery is environmentally preferable to the actual situation. Choosing a conventional strategy would be less environmentally effective, even though it is worth noticing that the product output is higher in this case.

5.4.1. Sensitivity analysis on moisture and pectin yield

A Sensitivity analysis (SA) was carried out for studying the robustness of results and their response to uncertainty factors in life cycle assessment. It was studied how the environmental impacts varied for two of the main parameters of the alternative biorefinery developed in Chapter 4. The parameters selected were the amount of moisture present in the by-products, due to its wide range of variation (65%-85% wt.), and the yield of pectin extraction with citric acid, which as this stage is the most impactful as shown in section 5.3 and due to the low TRL of this technology. For this sensitivity, in addition to the standard case, that was studied in the previous paragraphs, 4 new scenarios were developed: two in which the moisture content of the by-products varies and two in which the productivity of pectin extraction varies. Moisture, which in the standard case is 72%, is 65% in the "low moisture" scenario and 85% in the "high moisture" scenario. Pectin extraction yield, which in the standard case is 17g/100g of dried dewaxed peels, is reduced by 30% in the "low pectin yield" scenario and 15% in the "medium pectin yield" scenario. Table 49 shows the various cases schematically

Table 49 *Schematic description of the scenarios introduced for the sensitivity analysis*

Name	Description
Standard case	The alternative biorefinery considered in the TEA (Chapter 4) and LCA study (Chapter 5), with 75% moisture contained in the pomace and a pectin extraction yield of 17g/100g of DDP
Low moisture	Same as standard case except for moisture content of 65%
High moisture	Same as standard case except for moisture content of 85%
Low pectin yield	Same as standard case with 30% reduction of pectin yield
Medium pectin yield	Same as standard case with 15% reduction of pectin yield

Regarding the sensitivity on moisture, after the two new cases were designed, the impacts for the categories considered were evaluated using the same methodology as at the beginning of Chapter 5. Figure 79 shows the results of the LCA on the standard case and the two new scenarios: "low moisture" and "high moisture".

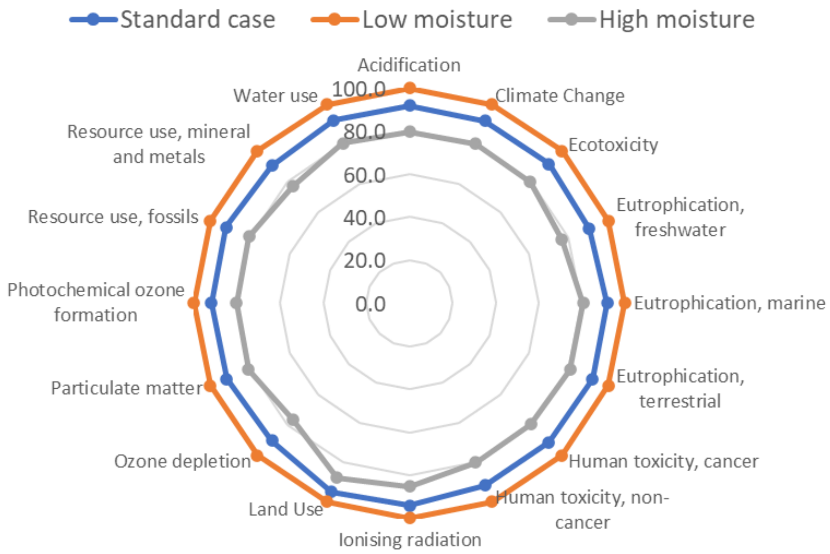


Figure 79 *Sensitivity analysis on moisture content*

As can be seen from the graph, for all categories, the impacts are greater as the amount of moisture decreases. This can be explained because as the amount of moisture decreases, the dry fraction of the by-products increases: it is worth noting that the case study and hence the comparison of the scenarios is carried out at fixed mass feed rate of tomato pomace. Thus, the raw materials (solvents and reagents) and energy required for the various biomass valorization steps increase at “low moisture”.

To understand in more detail how this parameter influences the environmental performance of the biorefinery, the new scenarios were compared with their current reference ones with updated functional units (considering that the output products of the biorefinery increase as humidity decreases). Figure 80 shows the relative reduction of impacts in the various categories due to the implementation of the alternative biorefinery compared to the current scenario, in the three cases considered in this sensitivity.

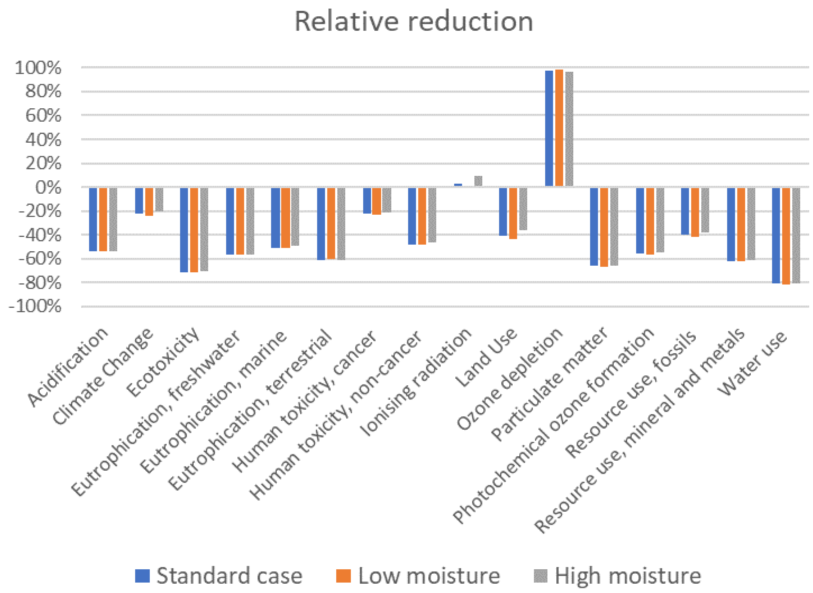


Figure 80 *Relative reduction of impact for scenarios with different moisture amount respect to their current scenarios*

As can be seen from the results, humidity minimally influences the environmental performance of the alternative biorefinery, as the impacts remain lower than in the conventional scenario, except for the categories, of ionising radiation and ozone depletion, even when the above parameter changes.

Regarding the sensitivity on pectin, after the two new cases were designed, the impacts for the categories considered were evaluated using the same methodology as at the beginning of Chapter 5. The new scenarios were compared with their current reference scenarios with updated functional units (considering that the pectin output of the biorefinery decreases as extraction yield decreases). Figure 81 shows the relative reduction of impacts in the various categories due to the implementation of the alternative biorefinery compared to the current scenario, in the three cases considered in this sensitivity.

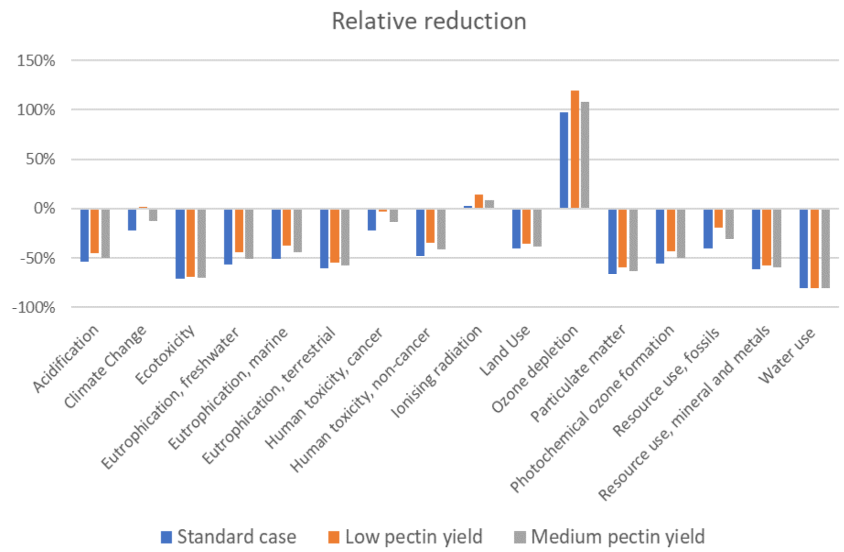


Figure 81 *Relative reduction of impact for scenarios with different pectin yield respect to their current scenarios*

In this case, the pectin yield has a more pronounced favorble effect, although the alternative scenarios have lower impacts than the standard scenario (except for ozone depletion and ionising radiation categories) even though the pectin yield decreases by 30%. In conclusion, it is possible to state that even if the moisture content in the tomato processing by-products were to increase or decrease sharply, or the pectin extraction section was not able to reach the desired yields, the implementation of the biorefinery would allow a decrease in environmental pressure in almost all impact categories.

5.4.2. The effect of pectin extraction on ozone depletion

To better understand why biorefineries perform worse in ozone depletion, an in-depth hot-spot analysis of the Alternative Biorefinery was conducted to identify which operative block or auxiliary operations impact most on the ozone depletion. As already reported in Figure 77, It was found that the extraction of pectin with citric acid is responsible for 67% of the impact on average, and in particular, is responsible for 84% of the ozone depletion caused by the Alternative Biorefinery. Therefore, the pectin extraction impact assessment was deeply studied. Figure 82 reports the Gabi model for the pectin extraction with citric acid, implemented with data obtained from the techno-economic assessment.

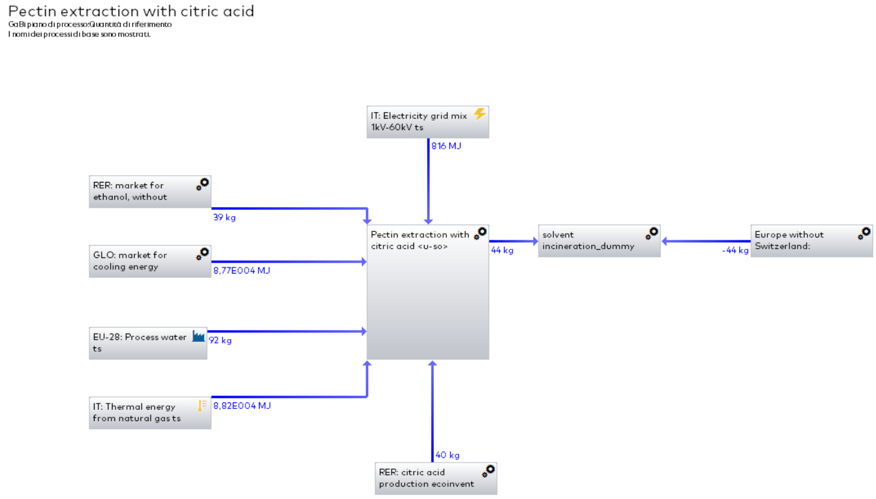


Figure 82 *Gabi model of pectin extraction with citric acid*

From the impact assessment (reported in Figure 83), it was found that cooling energy is responsible for 98% of ozone depletion.

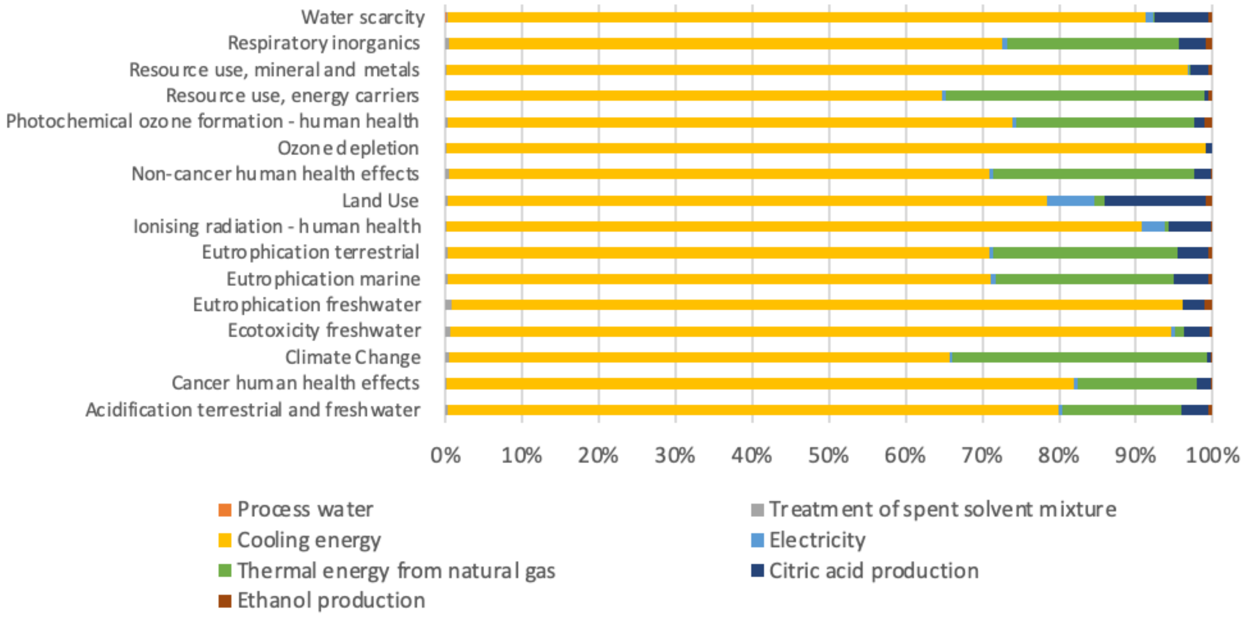


Figure 83 *Impact assessment for all the considered categories of the pectin extraction with citric acid*

With this information, a scenario in which heat integration is conducted to reduce the required cooling and thermal energy was hypothesized. With this, it was found that a 60% of cooling and thermal energy reduction would make the ozone depletion of alternative biorefinery lower than the one for the reference system. Figure 84 reports the relative reduction of the alternative biorefinery with respect to Current Scenario 2, its comparative scenario when 60% of energy recovery is achieved.

As reported in the figure, the alternative biorefinery with 60% of energy recovery would perform better in all the impact categories with respect to Current Scenario 2, with an average reduction of 63%.

In conclusion, LCA results show that both biorefineries perform better than the current scenarios in all categories except for the ozone depletion and slightly ionizing radiation. Conventional Biorefinery performs worse than the current scenario also in cancer effects, climate change and marine eutrophication. In general, the average reduction is 15.4% for Conventional Biorefinery and 39.7% for Alternative Biorefinery. This result suggests that from an environmental perspective processing tomato pomace in an Alternative Biorefinery is better than the actual situation; moreover, if heat integration or optimization is conducted on the pectin extraction process to reduce the cooling demand by 60%, the Alternative biorefinery would outperform the Current Scenario in all impact categories considered in this study.

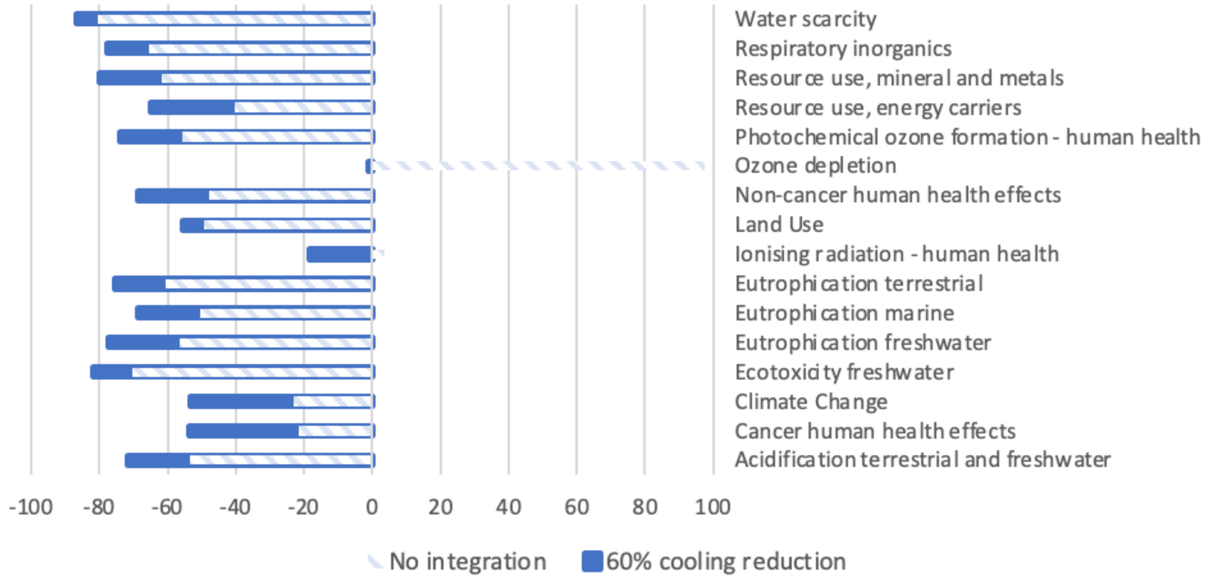


Figure 84 *Relative reduction with and without heat integration for Alternative Biorefinery*

Conclusions

The scientific literature is rich in articles investigating the valorization of tomato pomace; however, most works lack holistic thinking. Tomato by-products are characterized and studied as a source of lycopene or cutin or fiber or energy, but only in a disjointed fashion; in other words, the biorefinery cascade approach that leads to a multi-products output has been rarely applied, and its feasibility has never been assessed, when considering tomato pomace as a feedstock. Indeed, scientific articles dealing with the recovery of more than one compound from tomato pomace are very rare.

After a study relying on a detailed literature search, an overview of the valorization of tomato by-products in R&D EU-funded projects was carried out. This analysis shows that 11% of the funded European projects dealing with tomato are centered on tomato waste and by-products. 40 projects were found with “tomato” and “waste” as keywords on CORDIS; 14 regard by-products valorization and are categorizable in the following topics: production of bioplastic or biofilm, extraction of high-value compounds, preparation of food additives or fodder, biogas production via fermentation and biorefining of tomato by-products. The overall budget amounts to around 40 M€, involving 20 European and 4 non-European countries, with project coordinators located in Germany, Netherlands, and Italy in most cases. The field of biorefining – which is the main topic of this PhD project - has one of the highest numbers of partners involved and, crucially, one of the largest budgets (but it is not the field with the highest number of funded projects). This is probably because even though the application of the biorefinery concept to tomato by-products is relatively new, the European Commission believes that research in this field could have a significant impact on waste reduction, because a substantial part of tomatoes is still sent to landfills or incinerated, and could boost the ecological transition, due to the possibility of co-production (bio-products, biodiesel, and pellets) from this underused biomass.

Gathering and analyzing all the information about the chemical and thermochemical properties of tomato pomace enabled the development of a biorefinery scheme based on the valorization of tomato by-products for a sustainable co-production of fuel and chemicals, with minimal or no generation of wastes. The preliminary scheme based on literature data, reported in Chapter 3, was used as the basis for the modelling and optimization of a multi-product biorefinery, aimed at producing lycopene-based tablet, pectin, and fuel, both liquid and solid, thus creating added value whilst reducing organic waste generation.

The multi-product biorefinery scheme was divided into several operating blocks, like tomato pomace separation, lycopene extraction, biodiesel production and others. For each operative block, two alternative process options were selected from the literature: one is commercially available nowadays, whereas other one is a "green" alternative (which is typically less studied). Each alternative process configuration was studied, modelled, and optimized to evaluate its techno-economic feasibility. Microsoft Excel® and Aspen Plus® were used to evaluate the mass and energy balances for each operative block. Furthermore, for each biorefinery block, the revenues coming from the selling of the specific product were evaluated together with operative costs. These latter included raw materials, energy demand for operational equipment, the cost for waste treatment and the cost of methane for thermal energy production. Gross Profit, evaluated as the difference between revenue and operating costs, and ROI (Return of Investment) were used as economic indicators to compare the alternatives. In general, the results show that valorizing tomato by-products via a cascade approach is technically feasible, and that economic sustainability is guaranteed for both the commercial and the 'green' alternatives. The commercial alternatives feature higher revenues due to a higher product output, while 'green' alternatives present lower operative costs to the milder operation conditions and the reduced consumption of materials.

Finally, Life Cycle Assessment was carried out to quantitatively assess the environmental impacts of the two different biorefineries, one based on the conventional techniques and the other on 'green' alternatives. Each was compared to a scenario representing the current end-of-life of tomato pomace and the conventional technology for delivering each by-product produced by the biorefinery. In the study of environmental impact, only energetic demand, raw materials usage, and waste treatment connected to the processing of tomato pomace were taken into consideration; impacts linked to tomato processing, facilities construction, and use of the products of the biorefinery were not considered, because processing and products end-of-life are the same for both biorefinery scenarios, while construction is usually negligible for chemical plants. Energy demand, raw materials, emissions, and waste flows for the modelling of each of the two scenarios were provided by the techno-economic assessment of the corresponding biorefinery. The environmental impacts were estimated using the GaBi software tool for Life Cycle Assessment, and by applying the Environmental Footprint 3.0 methodology. LCA results show that both biorefinery scenarios perform better than the actual disposal scheme in all categories except in the ozone depletion and, slightly, in ionizing radiation. The conventional biorefinery performs worse than the present disposal scenario also in cancer effects, climate change and marine eutrophication. In general, the average reduction is 15.4% for the conventional biorefinery and 39.7% for the alternative "green" biorefinery. This result suggests that, from an environmental perspective, processing tomato pomace in an alternative biorefinery is better than the present situation. Choosing a conventional strategy would be less effective, even if it is worth noticing that products output is higher in this case.

Moreover, it is possible to state that even if the moisture content in the tomato processing by-products were to increase or decrease sharply, or the pectin extraction section was not to reach the desired yields, the implementation of the biorefinery would allow a decrease in environmental pressure in almost all impact categories.

It must be underlined that a key limitation of this work lies in its fundamental theoretical basis. In fact, in the modelling and optimization of the various unit operations, it was assumed that the physical and chemical processes in series do not change the characteristics of the biomass block after block, and therefore that it is reasonable to use each unit operation yield as reported in the literature. Future works should focus on characterizing the intermediate materials and evaluating the actual yields of each unit operations in the biorefinery network.

Although this study has been quite comprehensive, successfully including the analysis of environmental impacts and the economic evaluation of tomato pomace valorization based on a robust literature study, it nevertheless deserves some improvements and insights that could be carried out in future works downstream of this thesis. The development of a pilot plant using the feedstock hypothesized in this thesis will make it possible to replace secondary data, adopted from literature or estimated using software, with primary data, thus making the results more reliable and allowing the model to be improved and validated. Once the model has been validated, the techno-economic-environmental analysis method adopted in this work can be extended to other feedstocks, also typical of Italy, and currently underused, such as coffee residues or wastes from the fish industry. Furthermore, the relative impact on both cost and environmental categories of the plant scale and location could be investigated, for instance, the construction of the biorefinery directly *in loco* at the tomato processing factory might trigger a further reduction of impacts and costs associated to transportation. Finally, the evaluation of the overall revenues of the two biorefinery scenarios, using the functional unit implemented for the LCA analysis, might be carried out, together with the evaluation of the capital costs with their associated cash flows.

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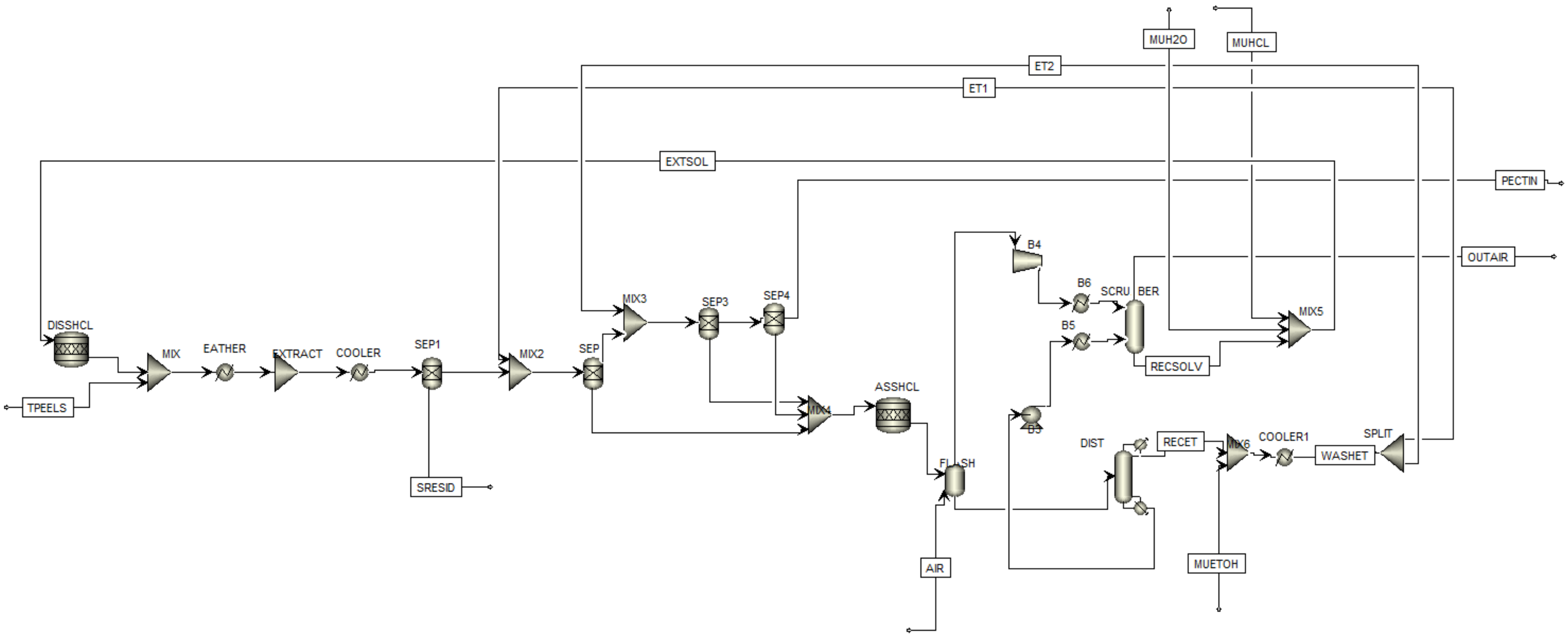
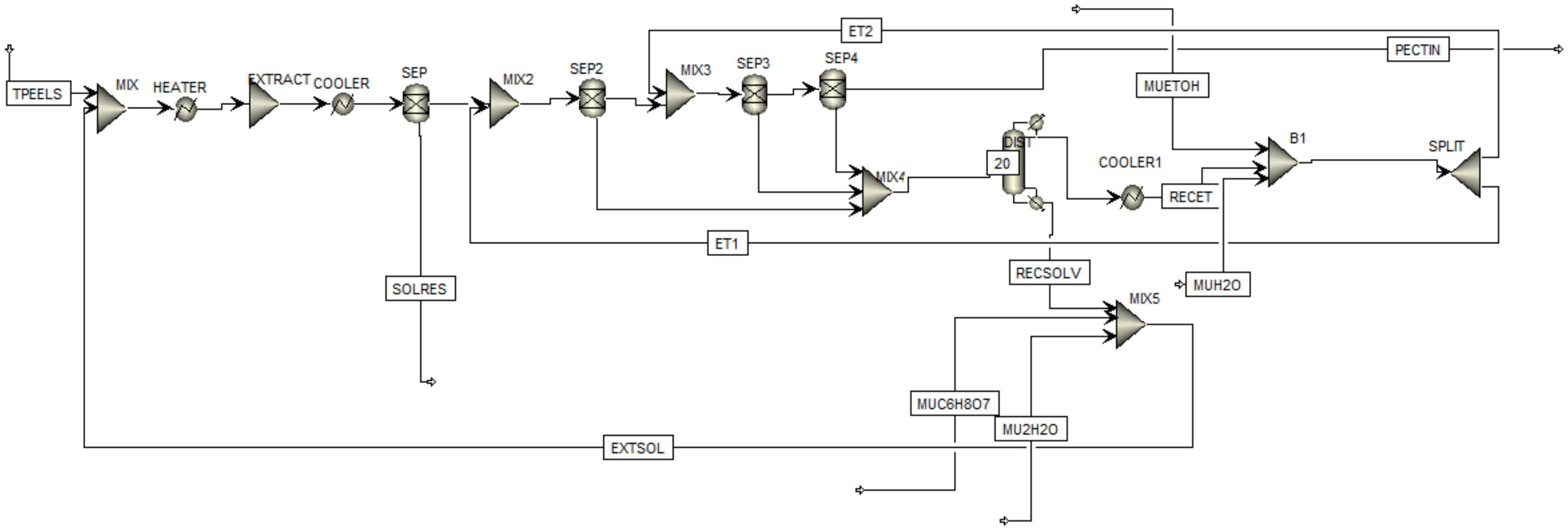
Appendix

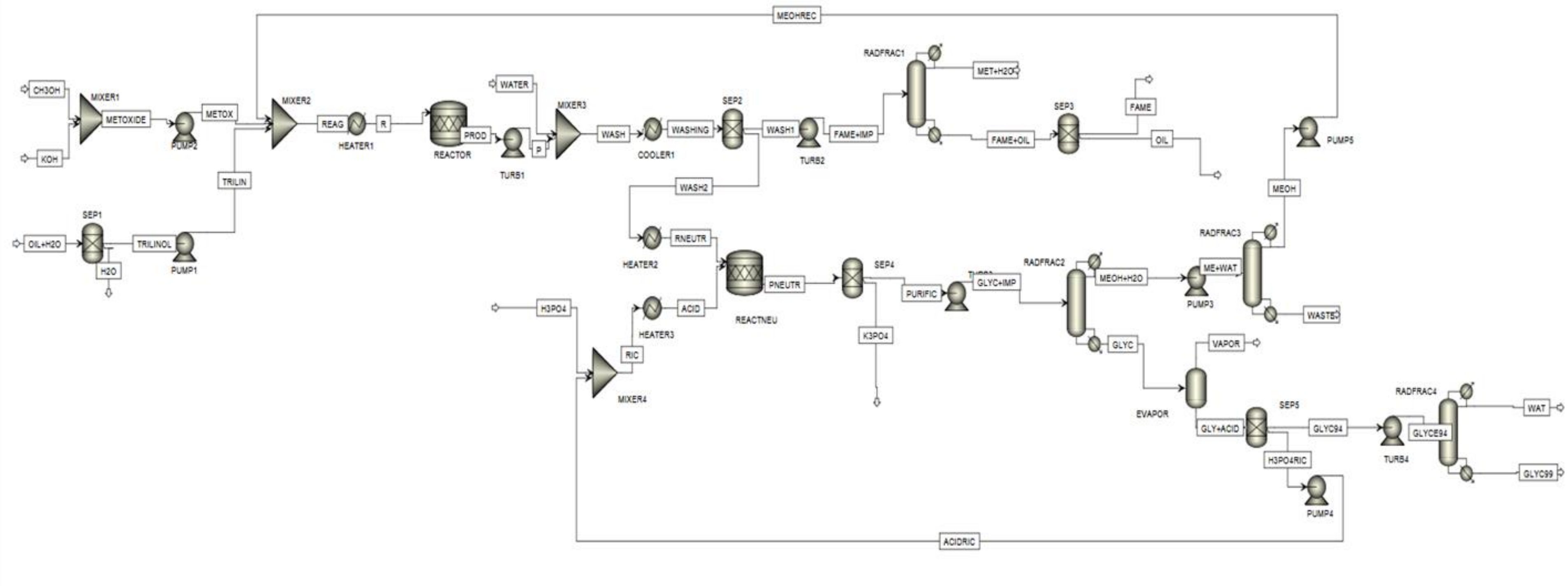
Aspen flowsheet for pectin extraction with HCl



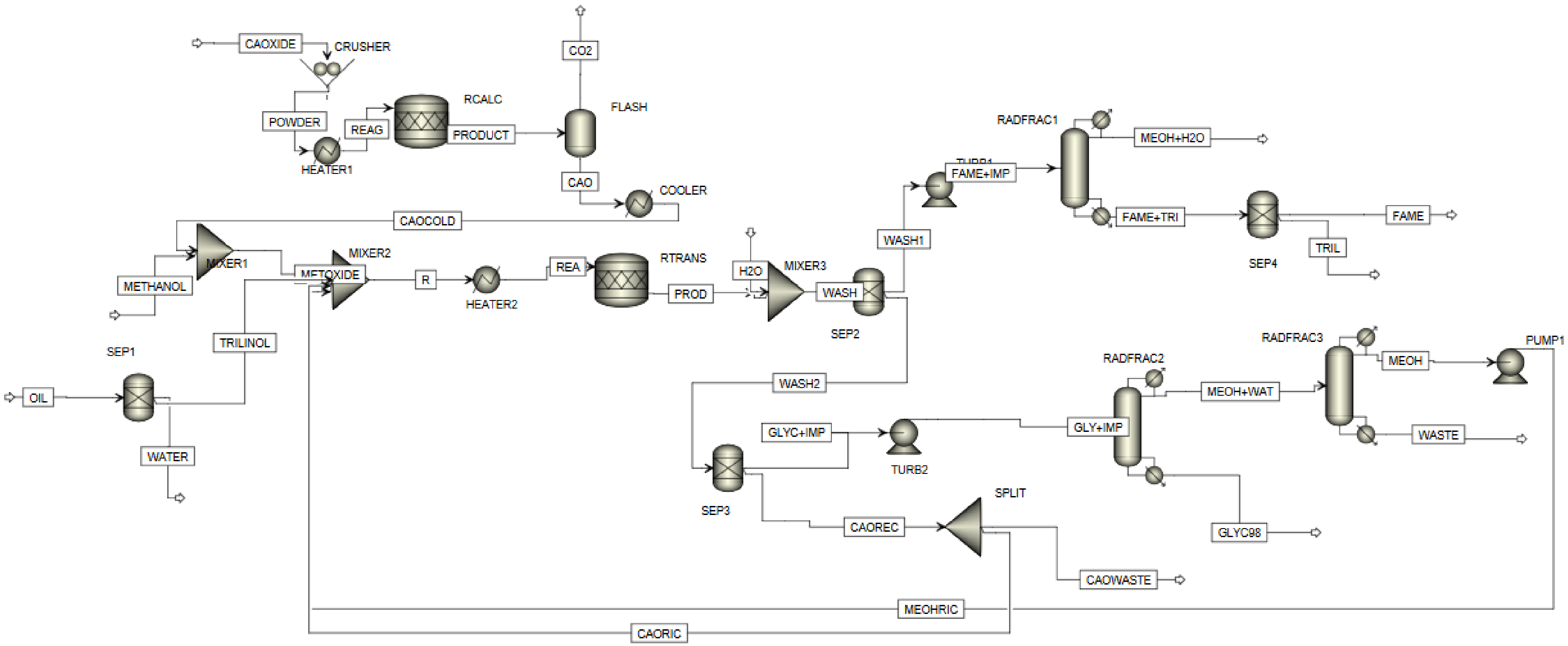
Aspen flowsheet for pectin extraction with citric acid



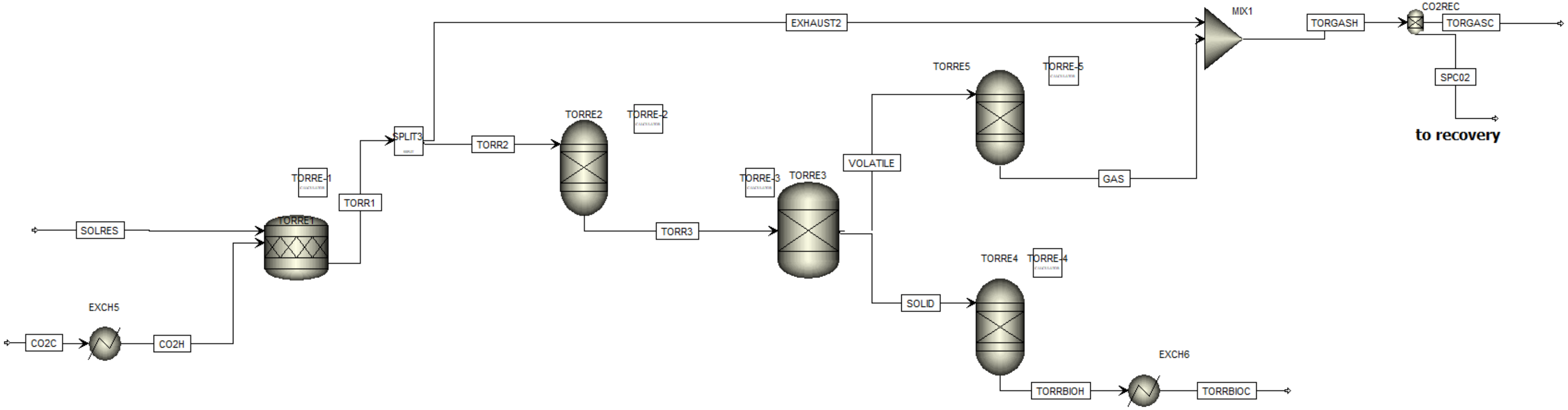
Aspen flowsheet for biodiesel production with KOH



Aspen flowsheet for biodiesel production with eggshells



Aspen flowsheet for torrefaction



Impact categories

A brief explanation of the impact categories used in the study is provided below.

Acidification

The Acidification category quantifies the impact of pollutants with the potential of causing acidifications of soil or aquatic ecosystems. Acidifying pollutants are mainly released by combustion processes occurring in thermal power plants, combustion engines, waste incinerators, e.g. sulphur and nitrogen oxides and hydrochloric acid, and agriculture, which is the main contributor to emissions of ammonia. Following the release, acidifying compounds are trapped by water in the form of rain, fog and snow, and then deposited onto different receptors. Because of their high water solubility, the atmospheric residence time of acidifying pollutants is limited to a few days, and therefore acidification represents a regional effect.

Climate Change

The Climate Change category expresses the impact of greenhouse gas (GHG) emissions based on the extent to which they increase the radiative forcing in the atmosphere. The portion of the sunlight that is not reflected back into space heats up the planetary surface and is released back into the atmosphere as infrared radiation with a longer wave-length than the absorbed radiation. This infrared radiation is partially absorbed by GHGs and kept in the atmosphere instead of being expelled into space, explaining why the temperature of the atmosphere increases with its content of GHGs. The major anthropogenic contributions to the greenhouse effect are represented by emissions of carbon dioxide, methane and nitrogen oxides mainly from burning fossil fuels and deforestation.

Freshwater Ecotoxicity and Human Toxicity

Any substance emitted may lead to toxic impacts depending on a number of factors including emitted mobility, persistence, exposure patterns and bioavailability, and toxicity. The toxicity impact categories account for these four factors and focus on the impact on freshwater ecosystems and human beings.

Eutrophication, aquatic and terrestrial

The three Eutrophication categories describe the impact of macro nutrients, the most important of which are nitrogen (N), and phosphorus (P), on aquatic and terrestrial ecosystems respectively. Excessive levels of nutrients in the aquatic ecosystem trigger a cause-effect chain that causes growth and blooming of algae and other aquatic plants, and reduction of oxygen availability, leading to degradation of water quality, altered species composition and loss of biodiversity. For terrestrial systems, eutrophication primarily causes changes in the function and species composition of nitrogen-poor ecosystems and also damages to crops and forests leading to reduced yields. Because of these environmental mechanisms, eutrophication is a regional impact category, highly dependent on local conditions.

Ionising radiations

The Ionising Radiations category covers impacts on human beings of radionuclides from direct emissions or that arise from nuclear waste disposed in a final repository. Exposure of humans to radioactive materials can lead to both stochastic and deterministic effects in terms of fatal and non-fatal cancers and hereditary effects.

Ozone Depletion

The Ozone Depletion category quantifies the effect of bromated and chlorinated substances on the depletion of the ozone layer. Ozone (O_3) is a harmful pollutant in the lower atmospheric layers, i.e. tropospheric and ground-level (See Photochemical Ozone Formation category), but it is an essential substance in the upper atmosphere (stratosphere) as it screens out more than 99% of the energy-rich ultraviolet (UV) radiation from the sun, preventing it from reaching the Earth's surface. The impact of UV on living organisms depends on its wavelength: short-wavelength UV (type C) is the most dangerous wavelength but it is almost completely filtered by the ozone layer; UV-B (medium wavelength) is of the greatest concern due to the ozone layer depletion; UV-A (long wavelength) is not absorbed by ozone. Impacts are also dependent on duration and intensity of the exposure, and include skin cancer, cataracts, immune system disease to humans, epidermal damage to animals, and radiation damage to the photosynthetic organs of plants.

Particulate Matter/Respiratory Inorganics

The category of Particulate Matter/Respiratory Inorganics quantifies toxicity-related effects on human health caused by Particulate Matter (PM). Exposure to PM leads to numerous detrimental effects including chronic and acute respiratory diseases, cardiovascular diseases, chronic and acute mortality and lung cancer. In 2013 outdoor and household PM pollution contributed alone to 71% of premature deaths attributable to environmental factors and 19% to all factors. PM can be distinguished according to formation type (primary and secondary) and aerodynamic diameter (respirable, coarse, fine and ultrafine). Primary PM includes particles that are directly emitted (e.g. from road transport or power plants), whilst secondary PM refers to particles formed by reactions with precursor substances such as nitrogen oxides, sulphur oxides, ammonia and Volatile Organic Compounds (VOCs).

Photochemical Ozone formation

The Photochemical Ozone formation category addresses the impacts caused by ozone and other reactive oxygen compounds; these are formed as secondary contaminants in the troposphere by the oxidation of the primary contaminants, mainly volatile organic compounds (VOC) and carbon monoxide, in the presence of nitrogen oxides and under the influence of light. The most important source of emissions of VOC derives from road traffic and use of organic solvents; whilst carbon monoxide is mainly emitted from combustion processes with insufficient supply of oxygen, including road traffic and other forms of incomplete combustion of fossil fuels and biomass. The negative impacts are associated with their reactive nature that enables them to oxidise organic molecules: when inhaled they can cause damages to the respiratory tract tissue and trigger respiratory diseases in humans; or they can attack surfaces of plants or even enter plant leaves damaging the photosynthetic organs.

Resource depletion, mineral, fossil and renewable

Natural resources can be classified according to their origin into biotic and abiotic, that is whether resources are or are not living at the moment of extraction, or according to their availability into stock (resources with a finite and fixed reserve), fund (resources that are regenerated but can be depleted if the extraction rate exceeds regeneration) and flows (resources that are provided as flows, e.g. solar radiation and wind). The most widely accepted method for quantifying impacts of resource use focuses on depletion of abiotic resources (stocks), using either the total estimated reserves of the resource (ultimate reserves approach) or only that part that has reasonable potential to become economically and technically feasible to exploit (reserve base approach).

Resource depletion, water

With respect to the distinction of natural resources made above, water is a resource provided as flow that cannot be depleted. There is sufficient water on our planet to meet current needs of ecosystems and humans: of the total water deposited every year on land only about 3% is used by humans and human activities. However, despite the small fraction, there are still important issues associated with water use; for instance, many rivers are running dry from overuse, leading to significant damages to local ecosystems. The issue is not about having too little water; rather it is about mismanagement of a resource that is required by both humans and ecosystems. Excessive consumption of water may lead to poor availability for humans, which may lead to deployment of backup technologies such as desalinisation of water if socio-economic resources are available, or otherwise cause deprivation and therefore water-associated diseases if socio-economics means are not sufficient.