POLITECNICO DI TORINO

Collegio di Ingegneria Chimica e dei Materiali

Corso di Laurea Magistrale
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Tesi di Laurea Magistrale

DEVELOPMENT OF A NOVEL GREEN PROCESS FOR SPENT TEA LEAVES VALORIZATION

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Sommario

Oggigiorno l'uomo consuma le risorse del pianeta con una cinetica nettamente superiore a quella di generazione. Anno dopo anno l'Earth Overshoot Day (EOD), ovvero il giorno in cui l'umanità consuma le risorse prodotte dal pianeta in un anno solare, arriva sempre prima. Nello specifico, ad oggi il consumo delle risorse generate dal pianeta avviene con una cinetica di 1,6 volte superiore a quella di generazione. Tale fenomeno è essenzialmente legato al trend di crescita dell'economia mondiale.

Occorre tuttavia tenere in considerazione che molti dei processi esistenti presentano numerose inefficienze che via via si fanno più marcate a partire dai processi di commodity, chimica fine fino a agroalimentari in cui è ampia la possibilità di intensificare i processi. In questo contesto partono tutta una serie di iniziative, a partire dall'accademia volte a generare conoscenza, che via via si stanno traslando al mondo dell'industria mirate all'uso più efficiente delle risorse.

Sostanzialmente è possibile delineare i tre paradigmi seguiti:

Futuristico: sponsorizzazione di iniziative per cercare risorse al di fuori del nostro pianeta. Esempio esplorazione di astri e pianeti come possibile fonte di risorse. Questo scenario, pur avendo una visione ottimistica, è attualmente lontano dall'obiettivo di poter generare profitto. Il programma dichiarato dalle grandi compagnie investitrici per i prossimi decenni è quello di organizzare e pianificare ulteriori missioni esplorative al fine di sviluppare nuove tecnologie.

Ingegnerizzazione negli ultimi cinquant'anni le conoscenze tecnologiche hanno avuto un notevole sviluppo, permettendoci di migliorare anche le tecniche di ingegneria genetica sulle colture per aumentare i vari aspetti legati alla produttività. Questo ovviamente pone tanti interrogativi, sia sulla manipolazione genetica, sia sull'interferenza all'interno della filiera del cibo, sia l'impatto dell'intensificazione selvaggia delle tecniche agricole su deforestazione, clima e così via.

Ottimizzazione a 360° dei processi già esistenti: a differenza di alcuni settori in cui lo sviluppo delle tecniche di sfruttamento delle risorse permette di avere quantità marginali di residui inutilizzati (anche al di sotto del 5%), esempio l'industria petrolchimica, nella filiera agroalimentari mediamente solo il 25% diventa prodotto mentre il restante viene classificato come residuo a cui viene attribuito un basso valore economico se non addirittura un costo aggiuntivo di smaltimento.

L'ottimizzazione dei processi permette così di ottenere un maggior quantitativo di prodotti senza dover aumentare l'estensione e lo sfruttamento delle colture esistenti.

Va inoltre tenuto presente che molti dei processi esistenti presentano numerose inefficienze che via via si accentuano a partire dai processi delle materie prime e della chimica fine fino ad arrivare al settore agroalimentare dove vi sono grandi possibilità di intensificazione del processo. In questo contesto si sviluppa il concetto di economia circolare che ridefinisce le linee guida per creare capitale economico, naturale e sociale. La chiave dell'economia circolare è ridisegnare la produzione partendo dai rifiuti che diventano una nuova risorsa. Da qui l'idea del circolo chiuso, che prevede che quando una risorsa entra nel ciclo produttivo poi vi rimanga il più a lungo possibile.

L'idea di questo lavoro nasce quindi con l'intenzione di sviluppare e progettare un processo estrattivo innovativo e sostenibile, applicabile al recupero degli scarti di lavorazione dell'industria del tè.

Il tè è una bevanda aromatica comunemente ottenuta facendo un infuso con foglie di Camellia sinensis L., un arbusto sempreverde di origine asiatica, e rappresenta oggi la seconda bevanda più consumata al mondo dopo l'acqua, con 3 miliardi di tazze bevute ogni giorno nel mondo.

L'aumento della domanda di tè nel mondo è dovuto non solo all'economicità del prodotto, ma è soprattutto legato alle sue implicazioni benefiche sulla salute. Risulta infatti ricco di polifenoli, composti aromatici largamente diffusi nel mondo vegetale, che costituiscono uno dei più importanti gruppi di metaboliti vegetali secondari, prodotti come meccanismo di difesa contro fattori esterni.

Questi composti, responsabili delle caratteristiche organolettiche di cibi e bevande, svolgono un ruolo molto importante anche nell'alimentazione grazie alle loro molteplici attività benefiche e, non essendo sintetizzabili dall'organismo umano, devono essere consumati attraverso la dieta. Le proprietà salutistiche dei polifenoli sono legate al loro potere antiossidante, a volte anche superiore a quello delle vitamine.

Nonostante questa grande varietà di composti, non tutti vengono estratti completamente dalla matrice durante la produzione di bevande al tè. Ciascuno di essi, infatti, presenta una diversa solubilità che dipende da fattori di processo. Il residuo post estrazione viene classificato come "*spent tea leaves*" (STL) che rappresenta, per le industrie, un sottoprodotto destinato allo smaltimento.

Questa etichetta di scarto, si rivela oggigiorno inappropriata in quanto esiste la possibilità di valorizzare la biomassa la quale contiene ancora quantità significative di composti nutraceutici, motivo per il quale possa esser ritenuto in futuro un potenziale asset economico.

Ad oggi, non esistono tecnologie su scala industriale adatte a valorizzare i sottoprodotti e gli scarti dell'industria del tè attraverso l'estrazione dei componenti a valore aggiunto.

Le tecnologie finora consolidate puntano essenzialmente ad una valorizzazione energetica, che inizialmente rappresentava la via più pratica per creare circolarità all'interno della filiera.

Analizzando però lo stato dell'arte attraverso la letteratura scientifica, si ha una chiara visione di quanto, al giorno d'oggi il dominio intellettuale sia particolarmente affollato e di quanta attenzione tale matrice stia suscitando.

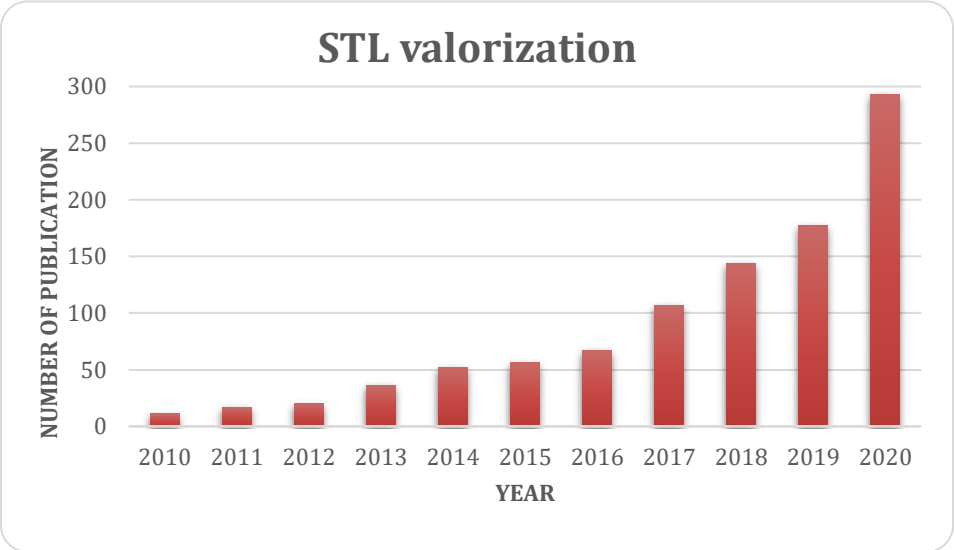

Grafico 1: Risultato dell'indagine all'interno della letteratura sul numero di pubblicazioni scientifiche riguardanti la valorizzazione dello spent tea leaves

Il diagramma sintetizza in maniera schematica i risultati ottenuti da un'indagine all'interno della letteratura scientifica inserendo come parole chiavi "spent tea leaves-waste tea-valorization".

Come è possibile osservare nell'ultimo decennio l'interesse verso questa matrice ha avuto un netto trend di crescita, indice della consapevolezza che in futuro lo STL possa passare da un'etichettatura di scarto a quella di risorsa.

Come anticipato, il progetto di tesi ha come obbiettivo lo sviluppo di un processo innovativo di valorizzazione dello STL attraverso l'*estrazione* dei suoi componenti ad alto valore aggiunto.

I metodi di estrazione possono essere classificati in due macro-categorie, metodi convenzionali e non convenzionali. I primi sono largamente diffusi in ambito industriale per via della facilità di implementazione dell'operazione unitaria e della svariata applicabilità. Tuttavia, le performance prevedono rese estrattive che raramente superano valori del 50% ottenute con enormi quantità di solvente e tempi di residenza dell'ordine delle ore.

L'efficienza di separazione dipende da diversi fattori, intrinseci alla matrice, quali dimensione delle particelle, composizione etc., oltre che da fattori legati al processo come affinità del solvente, rapporto solvente/solido, temperatura, regime fluidodinamico durante l'operazione e così via. I metodi non-convenzionali, introdotti nel mondo industriale in tempi più recenti, identificano una serie di tecniche il cui obiettivo è quello di intensificare il processo andando a migliorare in maniera combinata i parametri che influenzano l'estrazione.

I metodi tradizionali di estrazione, distillazione, estrazione con solvente, compressione a freddo, richiedono lunghi tempi di processo e impiego di grandi quantità di solvente, con la possibilità che si verifichino fenomeni degradativi delle molecole target e la parziale perdita di sostanze volatili.

Per tale motivo, considerando la natura dei composti target, il processo di valorizzazione è stato condotto attraverso lo sfruttamento della tecnologia **CAE** "*cavitation assisted extraction*" ottenendo un estratto idroalcolico con un elevato tenore di polifenoli, nonché estratti acquosi ricchi rispettivamente di proteine vegetali e dietary fiber.

Il metodo di estrazione non-convenzionale CAE si trova ad oggi all'interno di processi continui o semicontinui in loop che forniscono un'intensificazione del processo coerente in linea con i principi della "*Green Extraction*".

In maniera analoga a quanto fatto con lo STL è stata fatta un'indagine all'interno della letteratura scientifica riguardo alla tecnologia CAE. Come si può vedere nel grafico sottostante, l'interesse suscitato negli anni si dimostra in continua crescita grazie allo sviluppo di apparecchiature sempre più performanti.

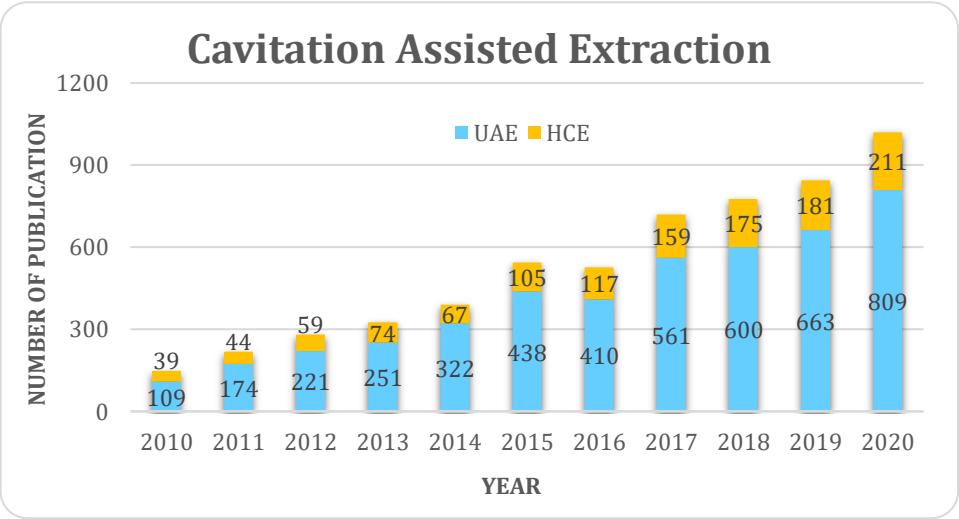

Grafico 2:Risultato dell'indagine all'interno della letteratura sul numero di pubblicazioni scientifiche riguardanti la tecnologia CAE

Tra le ultime innovazioni ritroviamo l'apparecchiatura chiave del processo sviluppato, ovvero l'estrattore solido-liquido cavitazionale TURBEX EX30 (a 3 gruppi rotore-statore), inventato da Giuliano Cavaglià e oggi licenziato in esclusiva alla multinazionale austriaca ANDRITZ AG che ne cura lo sfruttamento commerciale. Su un prototipo di TURBEX EX 30 sono state svolte le attività sperimentali sui cui risultati si basa lo sviluppo di processo svolto. Tale tecnologia, unica nel suo genere, presenta una configurazione multistadio che utilizza in modo combinato le tre tecniche di intensificazione di processo volte a generare area interfacciale e area di scambio, ovvero alta turbolenza, alto sforzo di taglio e cavitazione idrodinamica.

Il prototipo TURBEX permette di incrementare il mass transfer, impedendo il surriscaldamento del medium liquido e dunque, il verificarsi di degradazioni termiche: l'effetto meccanico indotto dalle onde di pressione della cavitazione idrodinamica promuove il rilascio di sostanze bioattive dal cuore della matrice, distruggendo le pareti cellulari e facilitando l'accesso del solvente o del mezzo estraente al contenuto cellulare.

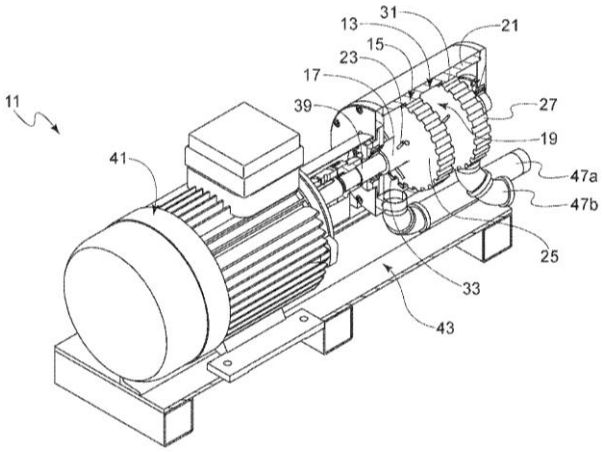

Figura b: Prototipo TURBEX a 2 gruppi rotore-statore

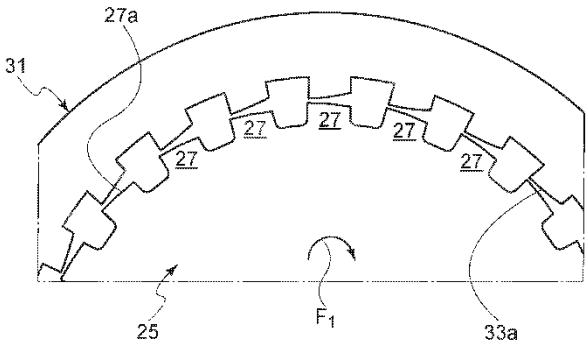

Figura a: Profilo superficiale rotore-statore parabolico

La tecnologia di intensificazione è in grado di gestire flusso di solido e di liquido in controcorrente, così facendo, la forza spingente del trasporto di materia viene mantenuta alta e pressoché costante lungo tutto l'hold-up del sistema, e il sistema TURBEX oggetto di analisi, composto da 3 stadi fisici rotore/statore, ha dimostrato sperimentalmente il raggiungimento di prestazioni equivalenti a quelle di un sistema costituito da 15 stadi di equilibrio teorici.

I gruppi rotore-statore (TG/TH) a dentatura con profilo parabolico proprietario, responsabili della generazione di alto sforzo di taglio e di cavitazione idrodinamica, sono intercalati a stadi (TB) ad alta turbolenza (Re > 500.000), realizzati con elementi mescolanti anch'essi di disegno proprietario, solidali con l'albero rotante.

La velocità di rotazione dell'apparecchio può essere modulata al fine di ottimizzare l'intensità della cavitazione, dello sforzo di taglio e della turbolenza all'operazione specifica di estrazione che si vuole effettuare.

L'implementazione di tale tecnologia all'interno di un impianto industriale, permette di soddisfare i requisiti della Green Chemistry e Green Engineering in quanto le alte rese estrattive ottenibili sono associate a rapporti (L/S) (i.e. portata di estraente liquido/portata di solido) minimizzati, con conseguente abbattimento dell'impatto delle sezioni di separazione e concentrazione e di postprocessing in genere, sia dal punto di vista CAPEX, sia dal punto di vista OPEX.

Le attività sperimentati sono state svolte su Spent Tea Leaves ("STL") provenienti da un "tea estate" ubicato in Malawi.

Durante il lavoro sperimentale sono state svolte diverse prove volte alla determinazione delle variabili necessarie alla progettazione dell'impianto di valorizzazione della matrice su scala industriale.

In particolare, sono state effettuate numerose prove con l'obiettivo di apportare migliorie graduali sull'operazione unitaria.

La prima fase infatti, ha avuto come focus l'identificazione della configurazione di estrazione più adatta (es. numeri di step estrattivi, tipo di solvente) con successiva determinazione del contenuto di polifenoli (*analisi con metodo di Folin-Ciocalteau*) per un confronto tangibile. La fase successiva di affinazione della tecnica ha permesso di valutare quali fossero le condizioni fluidodinamiche e processistiche ottimali (rapporto S/L, temperatura, contenuto di umidità, velocità di rotazione del rotore, etc.).

L'intero lavoro è stato condotto su di un impianto "pilota", costituito da una sezione di estrazione tramite estrattore cavitazionale TURBEX EX-30 accoppiato ad apparecchiature periferiche in grado di gestire i flussi in uscita all'estrattore. Nel caso specifico, come mostrato in figura, l'apparecchiatura viene alimentata attraverso uno screw feeder che riceve in maniera continua la matrice umidificata contenuta nella tramoggia sovrastante. L'estrattore inoltre, per gestire i flussi in uscita è stato accoppiato con un decantatore centrifugo seguita da una pressa a vite che permettono di completare la rimozione del liquido imbibito nella matrice solida in uscita.

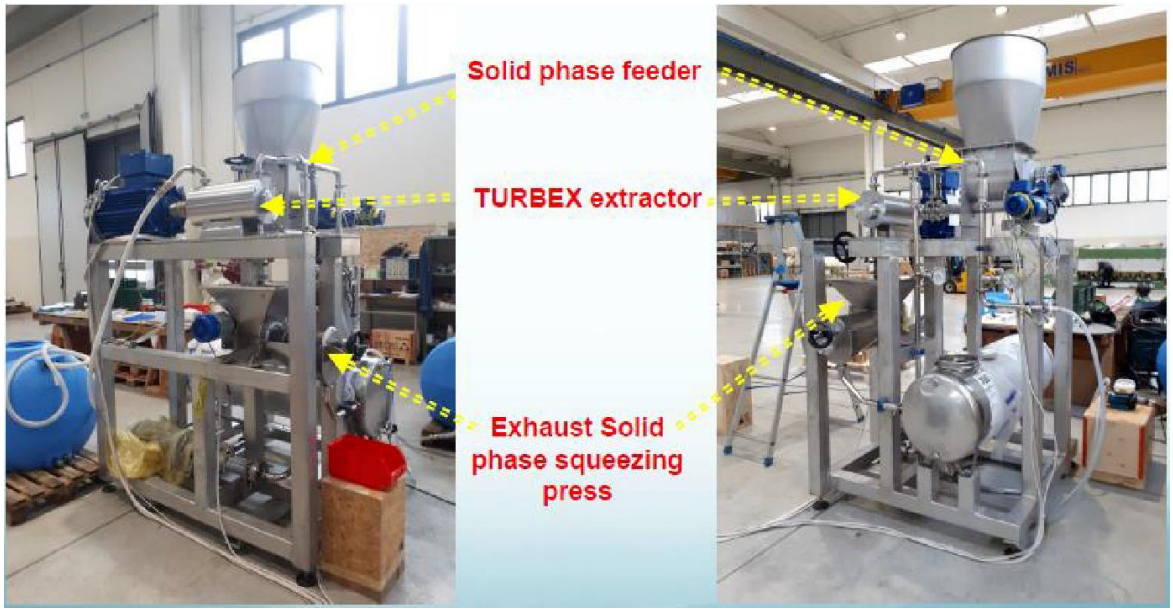

Figura c: Unità di estrazione con prototipo TURBEX EX30 (su cortesia di Giuliano Cavaglià)

Tale liquido viene recuperato nel drum di raccolta insieme al solvente fresco pronto per essere nuovamente inserito nel processo.

Per poter analizzare e confrontare i risultati delle prove di estrazione con dati oggettivi, il residuo è stato precedentemente caratterizzato sia dal punto di vista fisico (granulometria e tenore di umidità) sia dal punto di vista chimico. In tabella vengono riportati i risultati ottenuti tramite analisi HPLC sul feedstock iniziale caratterizzandone il profilo polifenolico.

SPENT BLACK TEA LEAVES	
Componenti	Contenuto [mg/g *dry basis*]
EpiGalloCatechin (EGC)	0,4
Catechin	0,3
EpiGalloCatechin 3-O-Gallate (EGCG)	9,7
EpiCatechin (EC)	3,2
GalloCatechin 3-O-Gallate (GCG)	1,3
EpiGalloCatechin 3-O-MetilGallate (EGCMG)	0,5
EpiCatechin 3-O-Gallate (ECG)	10,21
TOTAL CATECHINS (TC)	**25,61**
CAFFEIN	32,25
Gallic Acid	2,92
P-coumaric acid	0,23
Chlorogenic Acid	0,53
Quercetin	0,86
Caffeic Acid	5,73
Sinapic Acid	0,59
TOTAL PHENOLIC ACIDS	**10,86**
Theaflavin	0,71

Tabella 1: Risultati analisi HPLC sul feedstock

Il lavoro sperimentale, brevemente anticipato, si è focalizzato sull'estrazione dei principali composti ad alto valore aggiunto contenuti nello STL in modo da esaurire il più possibile la matrice sviluppando così una intensificazione a 360°.

In quest'ottica, l'attività svolta può essere divisa nei due step principali:

- estrazione dei polifenoli e caratterizzazione dell'estratto,
- estrazione di proteine e dietary fiber e analisi sull'estratto.

Per quanto riguarda l'estrazione dei polifenoli la configurazione migliore è stata ottenuta utilizzando una soluzione idroalcolica etanolo/acqua in rapporto 60:40 in volume. Tale solvente si dimostra essere efficiente in quanto permette la rottura dei legami ad idrogeno tra biomassa e metaboliti secondari favorendone così il rilascio.

L'individuazione dei parametri fluidodinamici e di processo è stata fatta mantenendo in considerazione un maggior numero di aspetti, che vanno oltre la singola resa estrattiva. Infatti, elevati valori di L/S, nonostante permettano di esaurire la matrice, si dimostrano essere controproducenti in quanto l'estratto risulta essere eccessivamente diluito rendendo difficile la fase successiva di post processing e purificazione.

Durante la sperimentazione, si è dimostrato di fondamentale importanza l'identificazione del valore ottimale legato alla velocità di rotazione dei rotori TURBEX. Infatti, all'aumentare della velocità, si ha un incremento della turbolenza del sistema, con fenomeni cavitazionali più rilevanti. Quest'ultimo fenomeno potrebbe essere considerato vantaggioso in termini di performance estrattive. Le analisi sui campioni di estratto, mostrano però come l'aumento dell'intensità dei fenomeni cavitazionali si traduca in una minore quantità di polifenoli totali contenuti. La spiegazione di questo, all'apparenza anomalo comportamento, è da ricercare analizzando a livello molecolare ciò che avviene durante la fase di estrazione.

I fenomeni di cavitazione infatti, oltre una certa soglia, provocano la formazione di radicali liberi all'interno del mezzo estrattivo con conseguente ossidazione dei polifenoli estratti, riducendone l'attività biochimica.

L'estratto ottenuto è stato successivamente caratterizzato sia dal punto di vista qualitativo, valutando il contenuto di polifenoli totali (*metodo Folin-Ciocalteau*), sia quantitativo tramite analisi HPLC (tabella) permettendo di calcolare le rese performate dalla tecnologia TURBEX.

Componenti	**Contenuto [mg/g *dry basis*]**	**Resa [%]**
EpiGalloCatechin (EGC)	1,78	61,4%
Catechin	1,56	71,8%
EpiGalloCatechin 3-O-Gallate (EGCG)	48,9	69,6%
EpiCatechin (EC)	12,8	55,2%
GalloCatechin 3-O-Gallate (GCG)	6,75	71,7%
EpiGalloCatechin 3-O-MetilGallate (EGCMG)	2,31	63,8%
EpiCatechin 3-O-Gallate (ECG)	51,64	69,8%
TOTAL CATECHINS (TC)	**125,74**	**67,8%**

CAFFEIN	121	51,8%
Gallic Acid	**15,45**	**73,0%**
P-coumaric acid	1,23	73,8%
Chlorogenic Acid	2,88	75,0%
Quercetin	4,54	72,9%
Caffeic Acid	28,12	67,7%
Sinapic Acid	3,41	79,8%
TOTAL PHENOLIC ACIDS	**55,63**	**70,7%**
Theaflavin	4,46	86,7%

Tabella 2: Risultati analisi HPLC sull'estratto ricco di polifenoli e rese estrattive (basate sul feedstock secco)

Le analisi sugli estratti ottenuti dimostrano che il TURBEX permette di ottenere rese di estrazione > 60%, superiori a quelli ottenuti con altre tecnologie convenzionali e non-convenzionali e con rapporti liquido/solido inferiori.

A questo punto la matrice presenta con ancora un contenuto di proteine e fibre solubili elevato, motivo per il quale è stata utilizzata per implementare il secondo step estrattivo.

La seconda fase di estrazione è stata eseguita utilizzando lo stesso estrattore TURBEX precedentemente analizzato.

In questo caso pero, per poter estrarre le macromolecole è indispensabile idrolizzare i legami idrogeno che le tengono intrappolate.

Nell'ottica di un processo più sostenibile, con l'obbiettivo di ridurre il più possibile il quantitativo di solvente, si è deciso di effettuare l'operazione di idrolisi separatamente della fase di estrazione. In particolare, questa operazione è strata effettuata mantenendo la biomassa esausta della frazione polifenolica (36% di solidi), in condizioni batch, a contatto con una soluzione alcalina 8M di idrossido di potassio ottenendo così un miscuglio con le caratteristiche di una pasta. In questa maniera si ha la possibilità di garantire un tempo di residenza sufficiente affinché la soluzione alcalina esplichi la sua funzione.

Terminata l'operazione di soaking dopo un tempo di 20 minuti, la pasta alcalina è stata alimentata all'estrattore utilizzando come solvente estrattivo esclusivamente acqua.

Ottenuto così un estratto acquoso ricco di proteine e dietary fibers si è proceduto nella separazione dei composti solubilizzati tramite precipitazione e successiva centrifugazione a bassa temperatura

L’estratto ricco proteico è stato successivamente analizzato (*metodo Kjeldahl*) mostrando un contenuto di proteine totali del 32%.

La figura 2 rappresenta il diagramma a blocchi dell’esperimento svolto, con indicazione dei principali parametri di processo ottimali e rese estrattive ottenute.

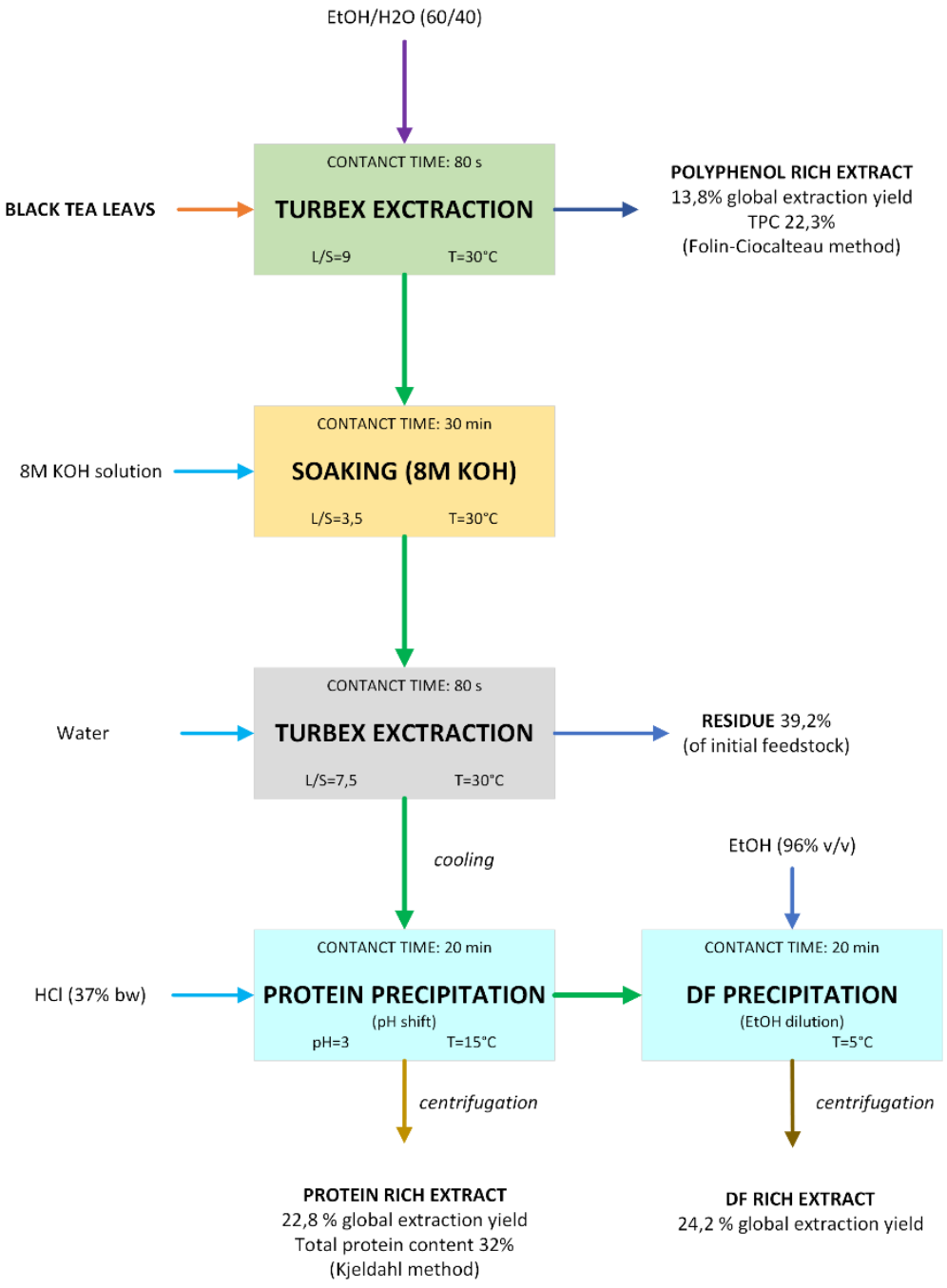

Figura d: Schema di flusso dell'attività sperimentale con rese estrattive

Sulla base dei risultati di detto esperimento, è stato progettato un impianto industriale in grado di trattare lo scarto industriale del tè, con capacità di targa pari a 1.000 ton/anno di STL (100% secco) in arrivo da un impianto door-to-door di produzione di ready to drink tea.

All'interno dell'impianto è possibile distinguere tre sezioni principali:

- sezione di pretrattamento
- sezione di estrazione dei polifenoli e concentramento
- sezione di estrazione delle proteine e dietary fiber e concentrazione
- Sezione di recupero del solvente e stoccaggio

La sezione di pretrattamento si rende necessaria in quanto, nei periodi estivi la produzione di STL supera la capacità giornaliera gestibile dall'impianto. Per tale motivo l'eccesso subisce una riduzione del contenuto di umidità a valori al di sotto del 10% evitando così fenomeni degradativi della biomassa.

Il cuore dell'intero processo sviluppato è ancora la tecnologia chiave oggetto di indagine, ovvero l'estrattore TURBEX EX30. Tramite una sequenza di due estrattori, in grado di gestire fino a 200 kg/h ognuno, è risultato possibile esaurire la matrice dei suoi composti ad alto valore valore aggiunto, con rese di estrazione estremamente elevate.

La sezione di recupero di solvente ha lo scopo fondamentale di recuperare l'etanolo utilizzato all'interno del processo riducendo sia l'impatto economico sia quello ambientale.

Sulla base del feedstock in ingresso e delle rese ottenute tramite l'estrattore TURBEX, l'impianto permette di produrre circa 145 ton/y di estratto ricco in polifenoli (CTP=22%), 230 ton/y di estratto proteico (32% contenuto di proteine totali) e 243 ton/y di dietary fiber.

Considerando i valori commerciali di tali prodotti, è stata stimato in questa fase preliminare un ricavo annuale di oltre 8 milioni di € con dei costi di gestione relativamente bassi per via del contenuto dispendio di utilities.

Il principale vantaggio dell'impianto considerato è sicuramente l'elevata resa di estrazione con ridotti consumi di solvente. Ciò comporta minori costi sia nell'acquisto degli stessi che nelle fasi di recupero. Inoltre, la temperatura relativamente bassa (30 °C) consente un ulteriore risparmio energetico molto consistente se si considerano le quantità di liquido circolanti e quindi la grande quantità di energia che sarebbe richiesta. La sezione di concentrazione tramite membrane consente il recupero del solvente e la concentrazione del flusso di prodotto a costi ridotti, evitando un elevato dispendio energetico nelle apparecchiature evaporative.

Il potere antiossidante è una delle caratteristiche più importanti del tè nero, di interesse sia per l'industria alimentare che per l'industria farmaceutica e cosmetica. Dalle analisi

effettuate si è riscontrato che questo è fortemente influenzato dalle condizioni operative del sistema TURBEX, indipendentemente dalle rese di estrazione. In particolare, è di fondamentale importanza identificare la velocità di rotazione ottimale dei rotori TURBEX per ottimizzare l'attività biochimica nonché il potere antiradicalico e il potere antiossidante dell'estratto ricco di polifenoli.

Al termine di questo lavoro sono stati ottenuti risultati che supportano l'utilizzo della tecnologia estrattiva tramite cavitazione assistita, rappresentando un'innovazione dal punto di vista della sostenibilità. Dai confronti effettuati con metodologie convenzionali e non-convenzionali è stato possibile dimostrare come la tecnologia TURBEX inserita all'interno di un contesto industriale rappresenti una valida alternativa. Lo sfruttamento di tale innovazione permette di convertire i materiali di scarto in prodotti ad alto valore aggiunto, richiedendo minimi costi di gestione dell'impianto e delle utenze necessarie.

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Chapter 1

Chapter 1

1 Introduction

1.1 Definition of thesis target and of the enviroment in which this thesis program has been developed

Nowadays, humans consume the planet's resources with a kinetic higher than that of generation. Year after year, the Earth Overshoot Day EOD (the day in which humanity consumes entirely the resources produced by the planet throughout the year) always comes earlier. Compared to 20 years ago, the EOD date has moved back by two months. Today, we consume resources 1,6 times faster than the Earth can regenerate [1]. This is essentially linked to the growth trend of the global economy and industrial development. The progressive pauperisation of the planet and its renewable resources requires radical innovation.

Thus a series of ideas and innovations take shape, starting with the academy aimed at generating knowledge, which are gradually being transferred to the industrial world, improving the efficiency of the steps involved.

Basically, the paradigms followed are three:

Futuristic: investiments and sponsorships of initiatives to seek resources outside our planet. Companies such as Space Exploration Technologies (SpaceX), Rocket Lab, Virgin Galactic and Astrobotic, together with the space agencies that use them, are opening new avenues of exploration in the cosmic world in search of resources that can represent the new "extraterrestrial gold" [2]. Space offers unlimited access to a precious resource for the Earth: solar power. In space there is no night, nor clouds or other bad weather which reduce the radiation power. This is why the dream of solar energy obtained from space has fascinated many researchers and potential investors for several decades. This scenario, even in an optimistic view, is currently far from the goal of being able to generate profit, the declared program for the next decades is to organize and plan further exploration missions in order to develop new technologies.

Engineerization: in the last fifty years the technological knowledge has had a notable development, allowing us to improve also the techniques of genetic engineering on crops to increase the various aspects related to productivity (yield per hectare, resistance to diseases, etc.). Experimental bases of the genetic improvement of agricultural productions were essentially empirical in the initial phase of the change, today resistant varieties can be developed with genetic improvement methods, which allow to insert genetic resistance factors in the same genotype. This obviously raises many questions, from the point of view on genetic manipulation, both on interference within the food supply chain, and on the impact of the wild intensification of agricultural techniques on deforestation, climate and so on.

Optimization of existing processes at 360°: unlike some sectors, where the development of resource exploitation techniques allows to have small amount of unused residues (even below 5%), for example in the petrochemical industry, in the supply chain agri-food on average only 25% becomes product while the remainder is classified as a waste to which a low economic value or even an additional disposal cost is attributed.

The optimization of processes thus allows to obtain a greater quantity of products without having to increase the extension and exploitation of existing crops.

The current industrial process is still based on a linear concept as schematically represented in figure 1.

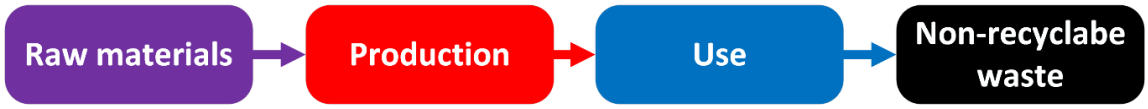


Figure 1.1: Schematic representation of linear economy

It should also be take in mind that many of the existing processes have numerous inefficiencies that gradually become more marked starting from the commodity and fine chemical processes up to the agri-food sector where there is great possibility for the intensification of the process. In this context, the concept of **circular economy** develops which redefines guide lines to create economic but also natural and social capital. This concept focuses on the benefits for the whole society and not just for the individual. The key to the circular economy is to redesign production starting from waste that becomes a new resource. Hence the idea of the closed circle, which provides that when a resource enters in the production cycle then it remains there for as long as possible. The concept turns out be clearer through the R scheme which highlights the principles that describe the multi-product and closed-loop life cycle system as a basis for sustainable production [3].

The circular economy can be seen as "eco-innovation", that is, as an innovation path that increases efficiency and competitiveness, while having a positive effect on the environment and society. Therefore, by developing as an initial change within a small part of the industry, it can initiate a green transition process that is passed on to the whole society. The last decade has seen from industries, and supply chains in general, a growing commitment aimed at reducing production waste and maximizing the value of those inevitably generated. The foundations are being built for an industrial world that pays particular attention to the protection of the environment and also regarding human health [4]. The new process concepts follow a series of criteria defined by the Green Chemistry and Engineering which thus make it possible to guarantee sustainability.

The table summarizes the 24 principles collected in the two keywords IMPROVEMENT and PRODUCTIVELY[5].

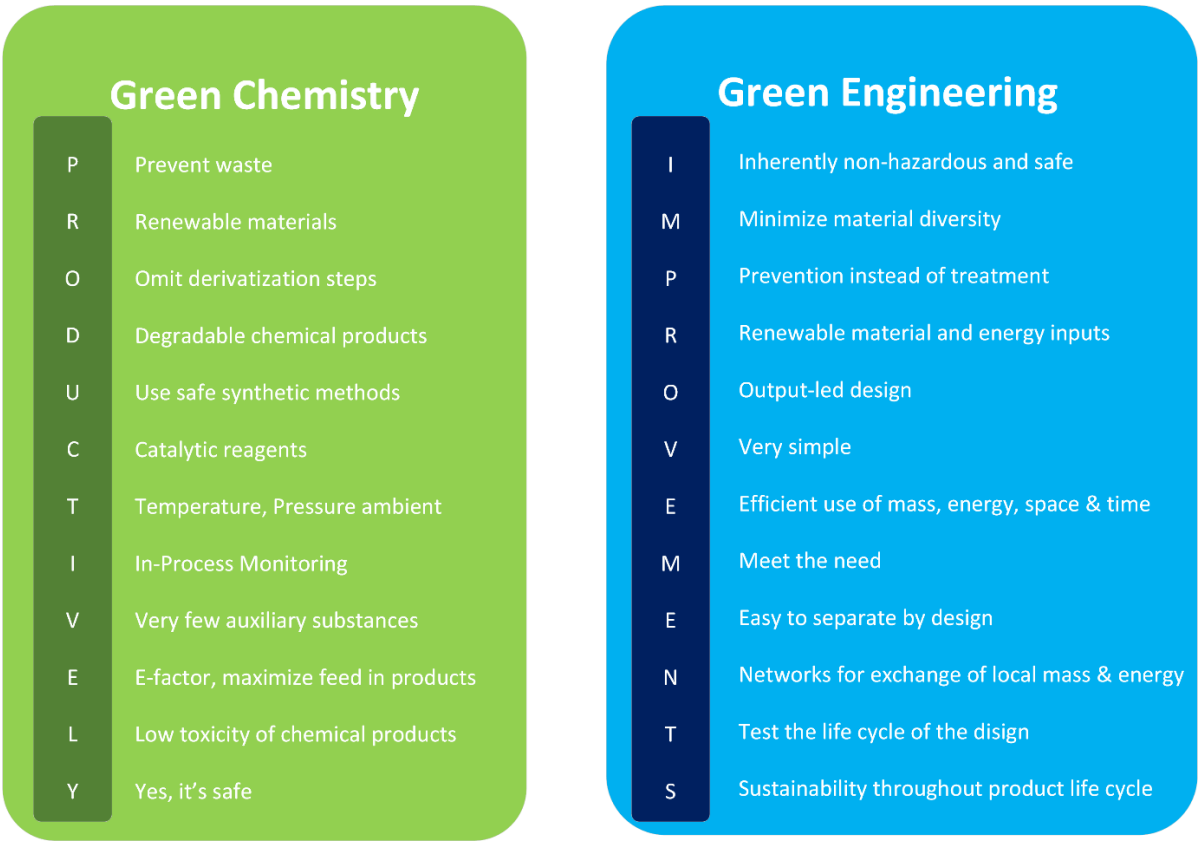


Figure 1.2 Priciples of Green Chemistry&Engineering [5]

To obtain satisfactory results, it is necessary to start from the design phase, because, although the step traditionally consumes few resources, equal to about 15% of production costs, it is responsible for the destination of the remaining 85% [3].

This thesis project is part of the current of innovation that is committed to the development of technologies for process intensification. In particular, attention is paid to extraction technologies and methods, that play a crucial role within the industry.

The main objectives are to reduce the use of solvents and, where possible, to replace them with more environmentally sustainable equivalents. Obviously, these replacements can guarantee satisfactory results in terms of the trinomial cost-quality-time only if accompanied by an intensification of the process.

The development of innovation, as in any other context, in green extraction starts from the design of processes aimed at the use of renewable resources, alternative solutions to traditional solvents, enhancement and reduction of residues. Huge steps forward have been made thanks to the use of unconventional techniques, such as ultrasound extractions[6][7], microwaves[8][9], supercritical fluids [10][11], rapid extraction[12][13].

These techniques are now widespread in laboratories rather than on an industrial scale, although in recent years are arousing more and more interest.

There are numerous studies that confirm the effective convenience of these techniques. The main advantages translate into time savings, reduction of energy consumption, greater stability of the extracts, greater biological activity thanks to the protection of thermolabile compounds [14].

1.2 Introduction on tea leaves, spent tea leaves and tea leaves offspec (sources, characteristics, applications, market)

Tea is an aromatic drink commonly obtained by making an infusion with leaves of Camellia sinensis L., an evergreen shrub of Asian origin, and represents the second most consumed drink in the world today after water, with 3 billion cups drunk every day in world [15].

Usually the plant is grown in tropical and sub-tropical areas, since its growth is favored by a humid warm climate, however, some varieties like the British one, can tolerate the marine climate [16]. Tea production remains however limited to some areas in the world, as its growth is subject to strong changes according to climate change. According to Global Tea Production 2015 the 90% of the world tea supply is concentrated in the top seven producing countries [16].

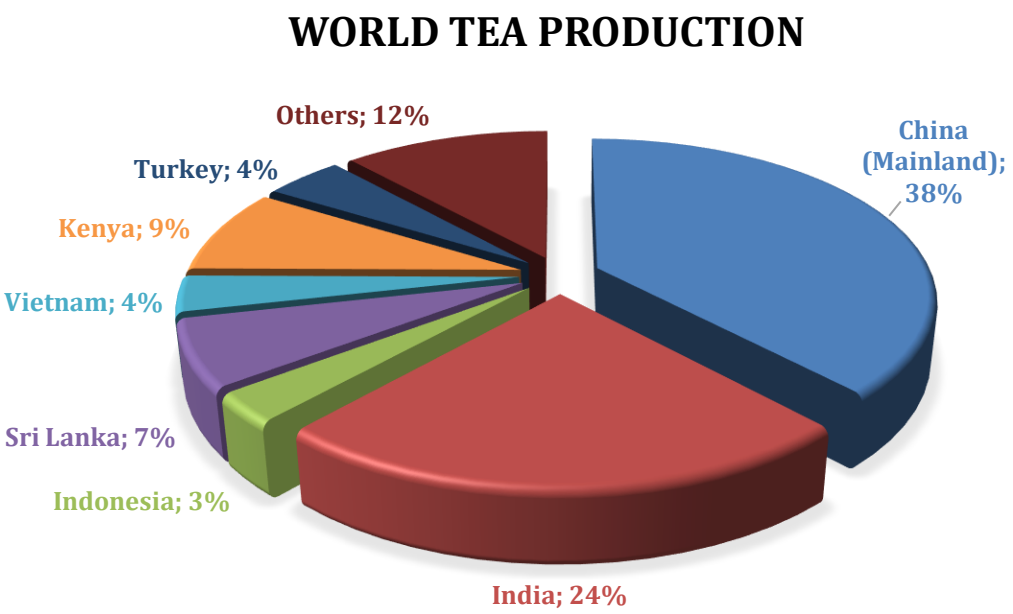


Figure 1.3 World Tea Production [16]

Harvesting process in milder areas takes place throughout the year, but as the altitude increases, the frequency drops to 3-4 times a year. To date it is available in different variants, as reported in table 1.1, which differ in the oxidation techniques and fermentation applied to the leaves and shoots of the plant [15][17].

Table 1.1: Characteristics of different types of Tea

Tea types	Characteristic features	References
Green Tea	It is particular popular in East Asia.	Tran, 2013
	Is represents 20% of the total tea production.	Fatima and Rizvi, 2011
	Green tea is known for its beneficial effects due to the presence of phytochemical and bioactive compounds.	Tran, 2013
	thanks to the minimal processing of green tea, the catechins are in high concentration.	Tran, 2013
	The main active compound (around catechins) in green tea is Epigallocatechingallate.	Schneider and Segre, 2009; Tran, 2013
	It has various pharmacological properties such as anti-diabetic, hypocholestrolemic, anti-inflammatory, anti-carcinogenic, anti-cavity, thermogenic, robiotic, antimicrobial, anti-viral, anti-bacterial, antimutagenic and anti-oxidant.	Cabrera *et al*., 2006; Tran, 2013; Jayakeerthana, 2016

Tea types	Characteristic features	References
Black Tea	80% of the tea production is black tea.	Fatima and Rizvi, 2011
	India is the large producer.	Ruxton, 2008
	It undergoes a strong oxidation with subsequent complete fermentation.	Ruxton, 2008; Fatima and Rizvi, 2011
	It is particularly consumed in China Japan and India	Chaturvedula and Prakash, 2011
	Flavan-3-ol monomers are oxidized and polymerized to form polyphenols i.e., theaflavins and thearubigins while manufacturing black tea.	Wright et al., 2002
	It possesses properties like anti-oxidative, anti-thrombogenic, anti-inflammatory, anti-mutagenic, anti-carcinogenic, antidiabetic.	Das et al., 2008; Fatima and Rizvi, 2011
Oolong Tea	It is made by withering followed by semifermentation resulting into partial oxidation.	Fatima and Rizvi, 2011

	It is traditional in South China.	Komatsu et al., 2003
	Its composition is intermediate between green tea and black tea.	Graham, 1992
	Major compounds are caffeine, polyphenols and amino acids with fewe amount of catechins and theaflavins.	Fatima and Rizvi, 2011; Komatsu et al., 2003
	It is sweeet in taste compare to green tea.	Chaturvedula and Prakash, 2011
	It has the potential to scavenge superoxide radicals and therefore, possesses anti-oxidative and antibacterial Properties.	Su et al., 2007; Ng et al., 2017
White Tea	It is unfermented tea produced by young shoots.	Teixeira et al., 2012
	It is produced in India, China, Kenia, Vietnam and Sri Lanka.	Blair, 2006
	It has delicate and light taste.	Dias et al., 2013
	It has great effects in reducing oxidative stress and obesity treatment.	Teixeira et al., 2012
	The main active compound (around catechins) is Epigallocatechingallate. Lower caffein content compare green tea.	Saha et al., 2017
Yellow Tea	It is partial fermented type	Hashimoto et al., 2007; Bhattacharjee, 2015; Teng et al., 2018
	It conteins high cathechins content and vitamins	
	Strong aroma with mild taste	
	It is popular in China.	
Dark Tea	It is unfermented type	Chaturvedula and Prakash, 2011
	It is brownish in color, has a smoky taste.	

The tea is processed directly in the original plantations and then exported as a finished product. The most important phases of the preparation of orthodox teas are: withering, rolling, fermentation, drying and finally classifying in leaves or broken by order of size.

The increase in demand for tea in the world is due not only to low prices and widespread information about this, but it is mostly linked to his benefict implications in health [17]. In fact, it turns out to be rich in polyphenols, aromatic compounds widely spread in the plant world, which constitute one of the most important groups of secondary plant metabolites, produced as a mechanism defense against external factors, such as UV radiation, pollution and parasite attacks.

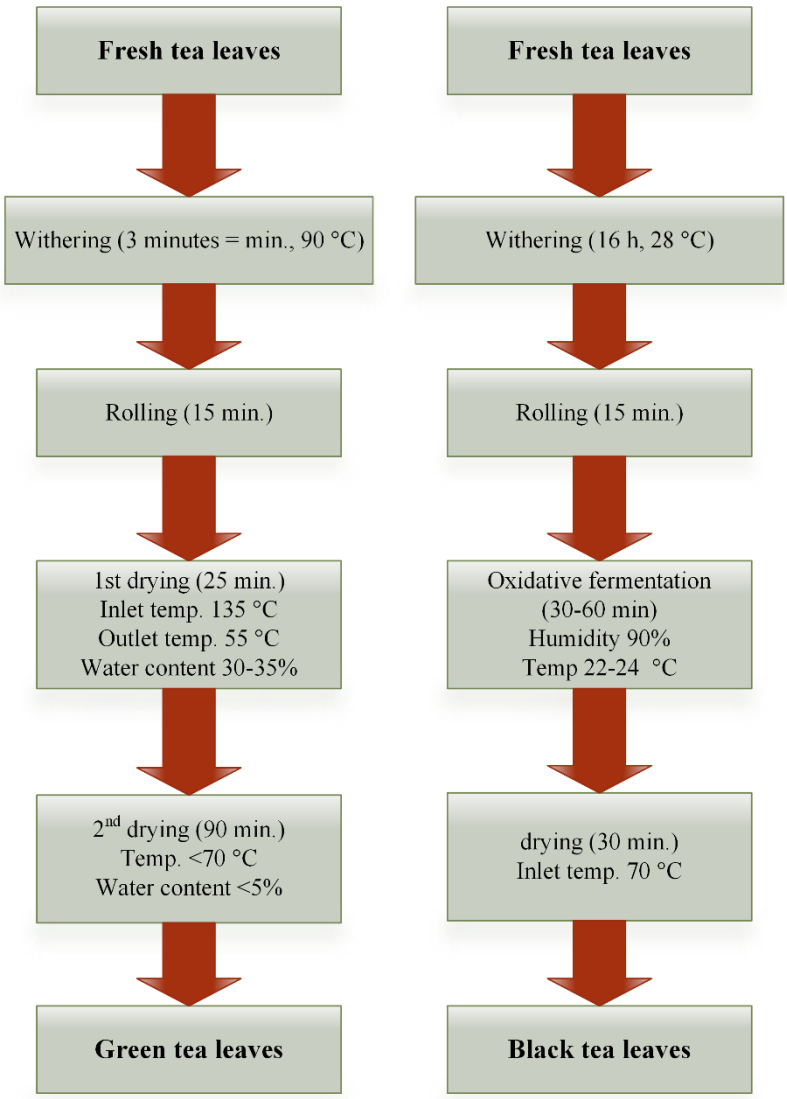


Figure 1.4: Typical sequence of green and black tea manufacturing in Indonesia [3].

These compounds, which are also responsible for the organoleptic characteristics of food and beverages, play a very important role in nutrition thanks to their many beneficial activities and, since they cannot be synthesized by the human body, they must be consumed through the diet. The health properties of polyphenols related to their antioxidant power, sometimes even higher than that of vitamins. We can define an antioxidant as a substance which, when present at low concentrations compared to an oxidizable substrate, delays or inhibits its degradation processes in a consistent way. In particular, the health effects ascribed to tea are involved in the prevention of diseases resulting from aging such as cardiovascular ones; acting as stabilizers or deactivators of free radicals, antioxidants protect cellular components from damage due to reactions involving these extremely reactive species.

The chemical composition of tea leaves (table 1.2) contains different compounds such as polyphenols, proteins, sugars, lipids, vitamins, fibers and minerals [18].

composition	*green tea (g/kgDM)*	*black tea (g/kgDM)*
DM	937 ± 3,56	942 ± 5,61
OM	938 ± 1,67	939 ± 1,73
CP	240 ± 1,02	242, ± 1,38
EE	20,8 ± 3,29	12,6 ± 4,06
ASH	61,8 ± 1,67	61,4 ± 1,73
S	2,74 ± 0,15	2,53 ± 0,22
NDF	254 ± 12,0	323 ± 15,6
ADF	211 ± 7,89	309 ± 9,02
TP	231 ± 17,0	151 ± 9,61
TT	204 ± 12,1	133 ± 6,79
CT	176 ± 4,73	101 ± 22,8
TS	276 ± 15,6	86,1 ± 3,69

Table 1.2: Chemical composition of green and black tea [18]

DM, dry matter (g/kg sample); OM, organic matter; CP, crude protein; EE, ether extract; S, sulfur; NDF, neutral detergent fiber; ADF, acid detergent fiber; TP, total phenols; TT, total tannins; CT, condensed tannins; TS, total saponins.

Despite this large variety of compounds, not all of them are extracted completely from the matrix during the production of tea drinks. In fact, each of them has a different solubility which depends on process factors. What remains after the extraction process is classified as spent tea leaves (STL) which represents, for industries, a waste product.

This labeling as waste nowadays turns out to be inappropriate as there are numerous possibilities to enhance this matrix. Despite its low commercial value, it contains significant quantities of nutraceutical compounds, which is why the waste is thought to become a potential commercial asset, pushing the valorisation beyond just combustion. The chemical composition of the STL is shown in the table 1.3 [18].

composition	*green tea (g/kgDM)*	*black tea (g/kgDM)*
DM	141	131
WHC	61,1	66,4

OM	955	959
CP	252	240
EE	23,0	14,4
ASH	45,4	41,4
S	2,90	2,58
NDF	394	461
ADF	285	410
TP	130	99,0
TT	126	90,2
CT	105	77,3
TS	70,1	39,3

Table 1.3: Chemical composition of green and black STL [18]

DM, dry matter (g/kg sample); WHC, water-holding capacity (g H_2O/kg DM); OM, organic matter; CP, crude protein; EE, ether extract; S, sulfur; NDF, neutral detergent fiber; ADF, acid detergent fiber; TP, total phenols; TT, total tannins; CT, condensed tannins; TS, total saponins.

The enhancement strategies consolidated to date are mainly [19]:

Nutrients: the caffeine extracted from the residue has a widespread use, medical, cosmetic, fertilizer and nutritional, which makes STL a potential source of extraction. In addition, the high protein and fiber content makes its use interesting as a feed for livestock, after a previous treatment to remove the tannin acids that interfere with the metabolization of proteins.

Adsorption: the increasingly widespread necessity to treat and clean process flows has led research to study the adsorbing capacities of the biomass. This possibility in recent years has been experiencing enormous growth given the intrinsic characteristics of the STL. Among the various components, it is particularly effective for the removal of heavy metals, antibiotics, dyes and other toxic effluents that are generated as a process byproduct.

Fertilizer: the matrix is mixed with further compounds to improve its fertilizing capacity (phosphorus, nitrogen, potassium).

Energy: to date the most immediate and widespread practice to obtain a small circular economy. The residue is thermally decomposed in a fluidized bed in the absence of oxygen at temperatures around 500-700 °C. The pyrolysis conversion product turns out to be a bio oil and biochar.

From a nutraceutical point of view, in addition to the presence of caffeine, fiber and proteins, STL contains a high content of polyphenols. These natural molecules, adequately extracted from the processing waste of the agri-food industry, have recently aroused great interest in the market as antioxidant products. They can be used, as well as in the food

industry, in various sectors as additives for plastics, elastomers, lubricants, as well as oils and fuels.

1.2.1 Polyphenols

Phenolic compounds include a broad spectrum of structurally heterogeneous substances, but all characterized by the presence of an aromatic ring with one or more hydroxyl groups with a strong antioxidant action. The antibacterial and anti-fungal activity is due to the combined action of the antioxidant power and the chelating capacity of phenolic hydroxyls, which can also bind the proteins of the cell wall of microorganisms with hydrogen bonds. The polyphenols can be in free form or glucosylated or esterified with organic acids. The most important groups of polyphenols that affect the appearance and "sensory" properties of food are *anthocyanins*, responsible for the red-purple color of fruits and flowers, *cateches* and *proanthocyanidins* which, like the precursors of tannins, are responsible for color, astringent taste and aroma. The *flavonoids*, on the other hand, are known for their protective function on blood vessels and the capillary microcirculation. There is no toxic effect due to polyphenols obtained from plants present in human nutrition, although their role in the metabolism of the human body is still being studied.

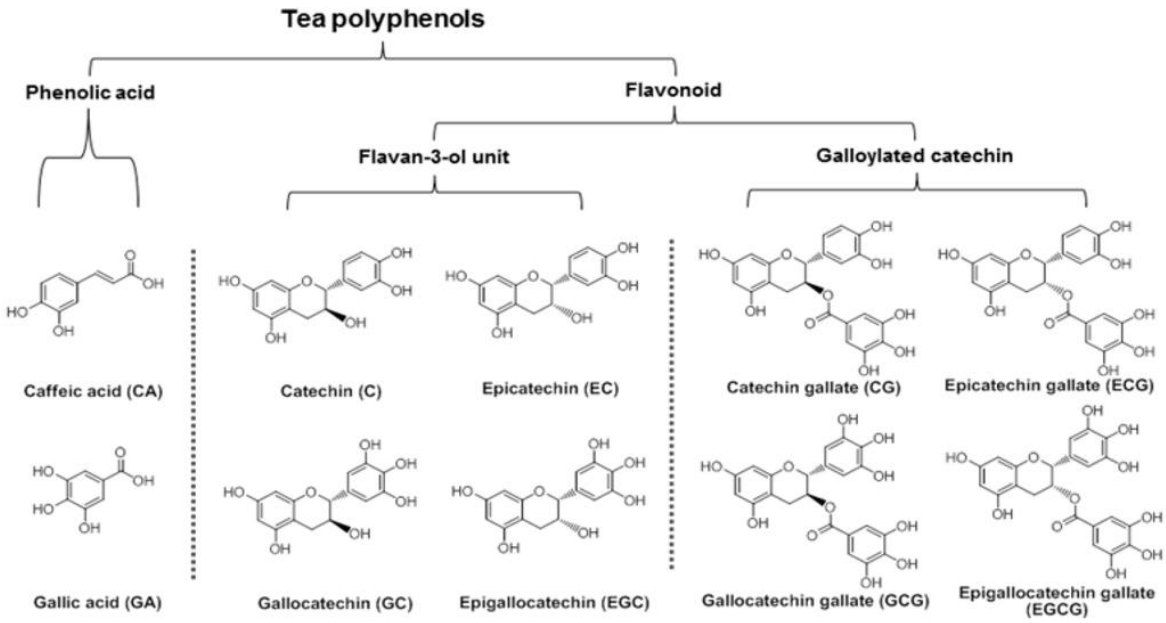


Figure 1.5:Principal polyphenols structure present in tea [20]

Polyphenols are classified from a chemical and structural point of view according to the presence of aromatic rings, the hydroxyl group and the presence of bonded monosaccharides of different nature. The table 1.4 summarizes those most commonly found in tea [20].

Flavonoids	
Flavanols	Catechin
	Catechin 3-O-gallate
	Gallocatechin

	Epicatechin
	Epicatechin 3-O-gallate
	Epigallocatechin
	Epigallocatechin 3-O-gallate
	Procyanidin dimer B1
	Procyanidin dimer B2
	Procyanidin dimer B4
	Prodelphinidin dimer B3
	Theaflavin
	Theaflavin 3'-O-gallate
	Theaflavin 3,3'-O-digallate
	Theaflavin 3-O-gallate
Flavonols	Kaempferol
	Kaempferol 3-O-rutinoside
	Quercetin 3-O-glucoside
	Quercetin 3-O-glucosyl-rhamnosyl-glucoside
	Quercetin 3-O-rutinoside
Phenolic acids	
Hydroxybenzoic acids	5-O-Galloylquinic acid
	Gallic acid
Hydroxycinnamic acids	4-Caffeoylquinic acid
	4-p-Coumaroylquinic acid
Alkaloids	
Methylxanthine	Caffeine
	Theobromine

Table 1.4:Principal polyphenols present in tea [20]

Their quantities within the STL depend on the quality of the tea leaves and the intensity of extraction, that is linked to the tea-to-water ratio, to which they were previously subjected for the preparation of tea drinks. The study conducted by Ramdani, 2014 shows that SGTL "*spent green tea leaves*" contains a higher amount of total alkaloids and catechins but less of theaflavins than SBTL "*spent black tea leaves*", while the caffeine content is approximately equal. As regards the extraction process, it has been shown that by increasing the tea-to-water ratio, the content of non-extracted polyphenols increases. The results of the study are shown in the table 1.5 below [21].

Composition (g/kg DM)	Spent Tea Leaves		Tea-to-Water g/300 ml		
	Green	**Black**	**2,8**	**5,6**	**11,2**
Theobromine	0,79	0,42	0,44	0,58	0,80
Caffeine	10,2	9,84	7,16	9,68	13,3
Tot. Alkaloids	**11,0**	**10,2**	**7,60**	**10,3**	**14,1**
GC	1,63	n.d.	n.d.	n.d.	n.d.
EGC	9,04	0,75	4,12	4,91	5,65
C	0,41	0,14	0,22	0,27	0,34
EC	1,36	0,03	0,66	0,70	0,74
EGCG	51,6	2,32	24,3	27,0	29,5
GCG	0,85	0,17	0,46	0,50	0,58
ECG	14,4	0,85	7,62	8,35	9,05
CG	1,95	0,53	1,13	1,24	1,35
Tot. Catechins	**81,2**	**6,27**	**39,2**	**43,8**	**48,2**
TF	0,18	1,38	0,70	0,81	0,82
TF-3-G	0,13	3,15	1,50	1,70	1,72
TF-3'-G	0,22	2,02	1,03	1,15	1,17
TF-3,3'-DG	0,24	5,61	2,73	3,02	3,03
Tot. Theaflavins	**0,74**	**12,2**	**5,97**	**6,67**	**6,74**

Table 1.5: Specific polyphenol composition in green and black tea [21]

n.d., not detected; GC, gallocatechin; EGC, epigallocatechin; C, catechin; EC, epicatechin; EGCG, epigallocatechin gallate; GCG, gallocatechin gallate; ECG, epicatechin gallate; CG, catechin gallate; TF, theaflavin; TF-3-G, theaflavin-3-gallate; TF-3'-G, theaflavin-3'-gallate; TF-3,3'-DG, theaflavin-3,3'-digallate.

1.2.2 Proteins

As shown in the table 1.2-3, both tea leaves and STL are potential sources of protein, several studies show that the content is around 21-28% on dry base. Despite the lower initial interest in this class of compounds in STL, in recent years numerous researches have been conducted to evaluate the bioactive properties such as antimutagen and antioxidants [22][23]. The application of proteins is widely spread in the food and pharmaceutical sectors due to the numerous functional properties. However, these properties have been shown to

strongly depend on the method of isolation and concentration [24]. Most proteins are soluble in highly alkaline environments due to their hydrophobicity and the intermolecular disulfide bond that links them. For this reason, to date, the extraction of proteins from plant matrices is mainly carried out through the use of alkaline solutions.

In the study conducted by Wang et al [25], Conducted through an alkaline extraction, the protein content was characterized demonstrating that the proteins present have a molecular weight ranging from 17 to 72 kDa. Furthermore, the results obtained confirm that there are no differences in terms of molecular weight between the proteins extracted from fresh leaves compared to those deriving from post processing. With regard to the physico-chemical analysis, it can be concluded that the functional properties of tea proteins are comparable to those extracted from soy which, together with those of milk, represents the main source for the food industry. The characterization and composition of the proteins extracted from the tea leaves with an alkaline solution is reported below (table 1.6) [21].

Amino acid	
Aspartic acid	8,01
Threonine	3,83
Serine	3,94
Glutamic acid	10,12
Glycine	4,59
Cysteine	0,8
Valine	4,63
Methionine	1,12
Isoleucine	3,93
Tyrosine	3,05
Phenylalanine	4,46
Lysine	5,62
Histidine	1,96
Arginine	4,83
Proline	3,62
Leucine	7,78
Alanine	4,97

Table 1.6: Amino acids composition in tea protein (g/100 g protein) [21].

1.2.3 Dietary Fibers

Dietary fibers (DF) represent the vegetable portion, consisting of polysaccharides, which the human body cannot break down into simpler molecules with its own enzymes. Their classification is made on the basis of solubility in water, thus distinguishing them into

soluble dietary fiber and unsoluble dietary fiber. Although the human body is not able to break the internal bonds of these macro-structures, DF possess numerous beneficial aspects that they carry out through their immunological, anti-carcinogenic and hypoglycemic activity.

1.2.4 Sorting and Grading of Tea

Sorting is an essential phase within the tea industry. This operation, carried out mechanically, allows to sort the various grades of tea, in order to obtain the best price during the auctions.

Initially, this process, performed manually, had the main purpose of removing foreign materials and large leaves. Later, with the development of automated equipment, it was possible to perform a classification in the various grades based on the size.

In modern equipment the tea passes through a variable number of sieves, thus obtaining a classification into whole leaves, broken leaves, fanning and dusts.

The CTC "crush, tear, curl" process mainly includes a first electrostatic separation that allows the separation of the fibers and stalks, then the matrix is conducted inside a series of machines, for example Myddleton machine, rotary hexagonal sifter, Britannia Tea Sorter and wind tunnel. These allow separation based on specific gravity and size.

The relative quantities of the different grades depend mainly on the market and the quality of the crop. In orthodox production the average quantities are [26]:

- Whole leaf 15%
- Broken 60%
- Fannings 18%
- Dust 4%
- Residue 3%

The dusts, which represent the lower grade, having a very small size have an enormous specific surface. This results in excessive extraction of the matrix with an undesirable effect on the flavors. For this reason this part is classified as waste by the industries that produce high quality tea.

A further loss for the tea industry is represented by the part of the product that doesn't satisfy the greyness and bloom. The greyness refers to the superficial coloring of the leaf which is avoided as it determines the liquoring properties, this defect is typically caused by the sorting process if not conducted in an optimal way. The ideal bloom occurs when a film develops on the surface of the leaf. If this does not happen, the extract appears to be dull and for this reason classified as poor [26].

1.2.5 The market

Defining the quantities of residual tea is not easy, this is also due to the fact that the traceability of the residue is not always respected within the production chain. In general, India's Tea Board regulators state that about 2% of the entire production volume is classified as waste. Based on this indicative value, it is easy to understand the great potential that this residue can have in the market following a further extraction process. Among the various

compounds possibly extractable from the STL, those that show the greatest commercial interest are certainly the polyphenols.

According to data reported by Grand View Research, the global demand for these chemical compounds generated an economic market value of 1,28 billion US dollars in 2018 compared to 760 million US dollars in 2015. The estimates made include an increase in the demand for polyphenols (CARG) of 7,2% by 2025. The huge demand is mainly due to the application of the secondary metabolites of plants in functional foods and beverages that are constantly growing on the market. The term functional identifies those foods that play an important role in the prevention of diseases by strengthening the immune system. Other everexpanding products that require the use of polyphenols are dietary supplements which, unlike pharmaceuticals, are a natural way to treat some gastrointestinal disorders or those caused by low immune defenses. Less impact from the point of view of consumption, but still important, is the demand for antioxidant compounds in products intended for cosmetics and animal nutrition. The market is dominated by extracts rich in polyphenols deriving from grape seeds, followed by extracts rich in polyphenols deriving from green tea, and then by those deriving from apple while the remainder is represented by extracts rich in polyphenols deriving from other matrices (ie cacao, coffee, hazelnuts, tomato, olive leaves, red fruits, rosemary, carob, etc.).

The strong demand is the result of numerous researches that have proven the effective beneficial aspects that these compounds give when included in the daily diet. In addition, the advancement of the average age of the population and greater attention to physical fitness are driving forces towards the consumption of products that prevent cardiovascular problems and delay aging phenomena. However, the increase in demand for polyphenols must be preceded by the development of new technologies that make it possible to access an ever increasing quantity without the need to extend the size of the crops.

The protein market was 38,5 billion USD in 2020 with an estimated growth rate of 10,5% between 2021 and 2028. Despite the large size of this market, the ongoing research and development of a wider range of amino acids that perform specific functions allow us to conclude that they represent a growing economic opportunity in the market. To date, the main source is represented by vegetable matrices followed by those of animal and dairy origin, although the latter two classes in 2020 represented 70% in terms of turnover as they are more expensive. Being cheaper, a higher growth trend is expected for those of vegetable origin, moreover the growing trend of veganism pushes an increase in this share respect to the animal one. The demand for this macronutrient is mainly associated with their extensive use in foods and beverages intended for human and animal nutrition, in particular for infant formula.

As for the dietary fiber market, in 2019 it reached a value of 39,8 billion USD with an estimated crest rate of 8,9% over the 2020-2027 time frame. The large consumption is linked to the healthy lifestyle adopted in recent years, considering dietary fiber as an integral part of the daily diet. The increased demand for products containing dietary fiber is the result of consumers' awareness of the fact that in order to prevent certain cardiovascular disorders it is necessary to adopt a healthy lifestyle starting from adopting a healthy and balanced diet. The Havard School study shows that the daily requirement for dietary fiber for adults and children is around 20-30 g. In addition, their consumption decreases the risk associated with disorders such as diabetes (type 2), constipation and cardiovascular problems. To date, about half of the demand, 48%, is satisfied by cereal crops, while the remainder is completed by those from fruit, legumes and seeds. Their main application, as anticipated, concerns the use in food products which accounts for almost 50% of the total

demand while about 25% is destined for the pharmaceutical supply chain and the remaining part for animal consumption and other purposes.

The table 1.7 shows the market values of the components potentially extractable from the STL.

Components	**Price (€/kg)**
Polyphenols rich extract (*)	45
Hydrolysed Proteins	10
Proteins	2,6
Dietary Fibes	4,5

Table 1.7: Commercial value from potential end-users evaluation

(*) polyphenols rich extract with total polyphenol content of 22%

Chapter 2

2 State of art

2.1 Survey of industrial scale technologies available on the market

To date, there are no industrial-scale technologies suitable to valorise tea industry byproducts and wastes through the extraction of value-added components.

The technologies consolidated so far essentially aim at an energy valorization, which was initially the most practical way to create circularity within the supply chain. The energy production process, from STL, involves pressing and drying steps before feeding the residue, with a humidity of 30% on MB, to a combined heat and power station to produce heat and electricity. The initial idea of an energy enhancement arises from the need to partially satisfy the high demand of the entire process. In fact, the tea industry, among the food industry, is one of the most intensive from the point of view of energy consumption [27]. Further, the situation is even more critical considering that most of the tea industries exploit obsolete technologies with low efficiency, mainly due to the lack of monetary flows for modernization. The main sources, to satisfy the energy consumption, derive from coal, oils and firewood.

Within the process, thermal energy is needed especially in the early stages, where the fresh leaves are subjected to the drying process. As for the electrical one, the main requests come from the cutting phases and from the various motors, fans and conveyors. The scheme (figure 2.1) below shows the breakdown of the energy needs for the production of black tea.

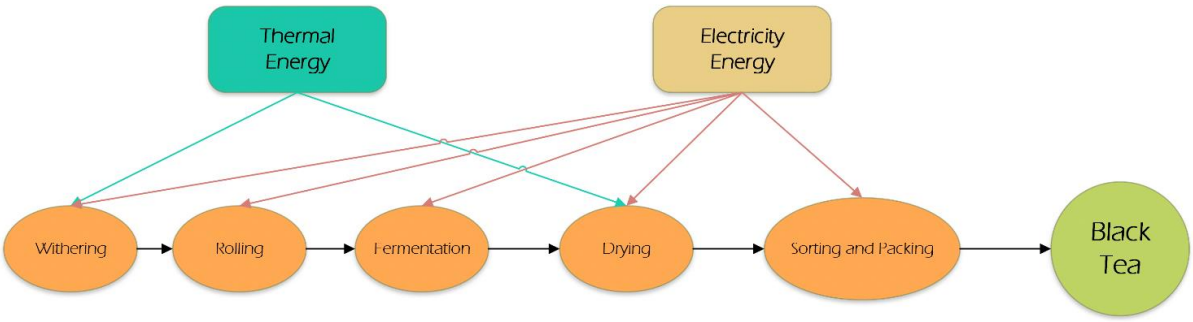


Figure 2.1:Energy requirements in tea process industry [27]

Overall the ratio between the two energy forms, thermal and electric, is 85:15. The specific energy consumption, estimated between 4-10,4 kWh/kg of tea produced, is strongly influenced by many production factors and furthermore by the geographical location.

The ways that allow to exploit the STL from an energy point of view are mainly through combustion, pyrolysis and anaerobic fermentation with the production of biogas.

As far as combustion is concerned, the residue deriving from the production of instant tea is first pre-treated to reduce the moisture content below 30% and subsequently fed together with firewood to the boiler for steam generation. About 25% of the heat generated is sent back to the dehumidification phase of the tea residue while the remainder is used in the various production phases.

In the pyrolysis process, on the other hand, the residue undergoes an incomplete thermal decomposition treatment in anaerobic conditions at a temperature of 500-700 °C, producing a bio-oil known as char. This thermal process, endothermic type, is responsible for breaking the polymers into chains of reduced size. At higher temperatures (700-850 °C) it is possible to carry out the gasification obtaining a syngas that can be destined for cogeneration systems with electricity production. In this process the thermal reaction is carried out by monitoring the quantity of oxygen necessary in order to produce a gas rich in H_2, CH_4 and CO together with an already combusted and inert quantity of N_2, H_2O and CO_2.

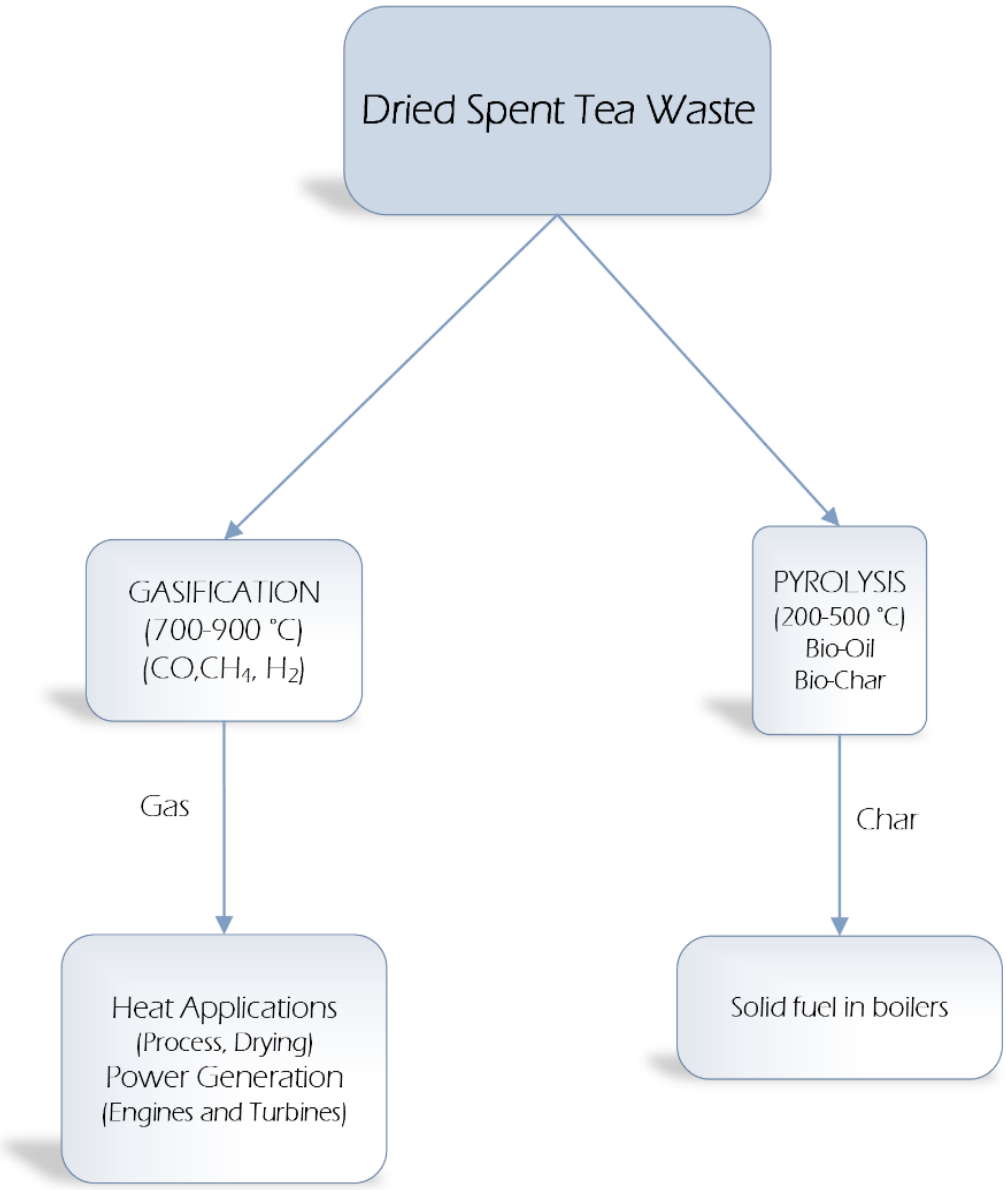
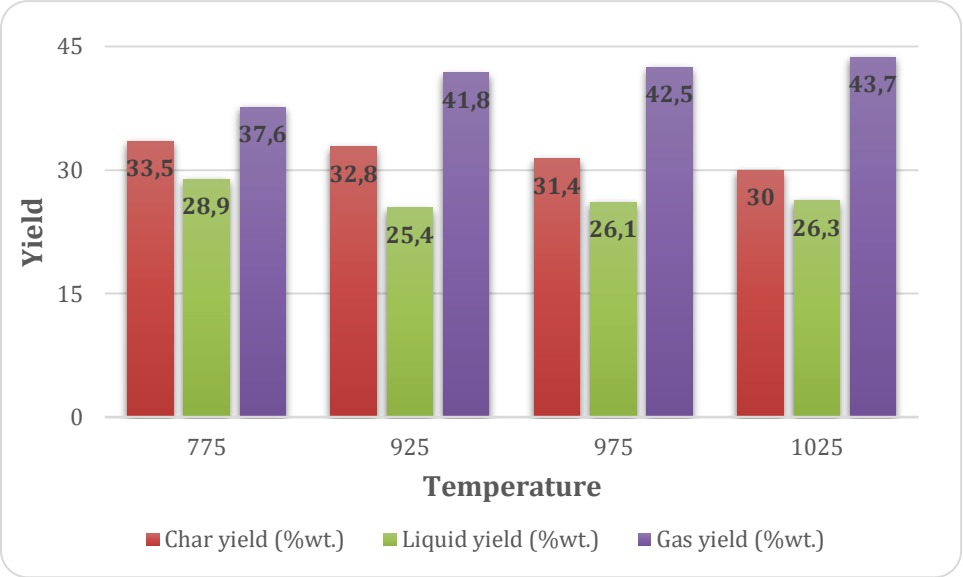


Figure 2.2: Pyrolysis and Gasification process of dried STL [28]

The pyrolysis and gasification process takes place inside fluidized bed reactors in which the various drying, pyrolysis, reduction and combustion sections can be identified. This configuration allows to couple the endothermic phases with the exothermic ones and thus have an overall self-sustainable decomposition reaction.

The overall pyrolysis and gasification yields depend on the set of operating parameters, in particular on the operating temperature. In this way, according to the energy requirements of the system, the optimal ones are identified. The yields as a function of the operating temperature are shown in graphic 2.1.



Graphic 2.1: Pyrolysis yield as a function of operative temperature [28]

An analysis conducted on pyrolysis and gasification products shows how the average energy quantity obtained is 16,19 MJ per kg of tea residue [28].

A further way of enhancing the by-product at an industrial level, confirmed to date, is the extraction of caffeine with a content in the tea waste that varies from 1,82% to 2,45%. This compound is naturally extracted from plants to be added to food and drinks. Furthermore, it is widely used in the field of medicines due to its known stimulating effects on the nervous system.

The process of extracting caffeine from the residue of tea, carried out continuously, can be divided into three main sections, the pre-treatment section, the extraction section and finally the post-treatment section. In the pre-treatment phase, the matrix is mixed with water and lime and then subjected to a heat treatment. This facilitates the release of caffeine from the matrix. The next phase is represented by the extraction which is carried out in a multi-stage configuration in counter-current, using the most suitable solvent depending on the destination of the extract. Among those used industrially we find chloroform (limited due to its toxicity), ethyl acetate, methylene chloride and supercritical CO_2. Once the extract is obtained, the solvent is removed by evaporation and recirculated while the remaining part constitutes the crude caffeine. The next step, after desolventization of the stream, is that of post treatment. In this phase, the crude caffeine is first dissolved in hot water, bleached and then filtered. At this point the purified caffeine is ready to be crystallized in an ethyl acetate solution.

Another way to valorise tea waste at an industrial level is to use it as a food for poultry and pigs. However, in order to make STL suitable for this consumption it is necessary to reduce the tannic acid content. In fact, this metabolite, with a content of about 6,3% in the STL, interferes with the metabolic proteins. To solve this problem, economic systems are adopted

in such a way as to make its use convenient. One of these, which is easy to manage, consists in keeping the matrix in a soaking of water (1:50) for a duration of 10-12 hours, allowing to considerably reduce its content. The problem of tannins is eliminated if the residue comes from a decaffeination process as the content of antimetabolites, around 0,4-1%, does not create problems for livestock.

As far as palatability is concerned, this is improved by adding compounds such as molasses which increase its approval rate.

Other technologies that aim the valorization of STL are the use as a natural and low-cost absorbent within a water treatment line and as a filler for heavy metals. Numerous studies demonstrate the effectiveness of waste in the absorption of Cr (VI) ions. The maximum activity is reached with a pH of the solution equal to 2 and a concentration of 0,8 g/L for a contact time of 180 minutes. Under these conditions, the removal of Cr ions reaches values of 99%. The kinetics of this adsorption is mathematically modeled with the Freundlich isotherm.

2.2 Survey of scientific literature

Nowadays, industries produce huge quantities of apparently useless by-products with big impacts from an economic and environmental point of view. According to FAO, 1,3 billion tons of food waste are produced each year for a total cost of USD 940 billion [29]. The enormous growth of these quantities and the strong attention paid by the circular economy to the issue of waste generation, together with the regulations, push industries towards a greater percentage of recycling of materials. All these actions lead to a very clear and precise scenario, characterized on one hand by the continuous increase in landfill costs and on the other by the need to valorise waste. Companies are therefore called upon to review the process management methods, with the main focus to starting from an intelligent and sustainable design that is able to foresee, for every single part of the product life cycle, the containment of waste. The term containment highlights the fact that, in most cases, their production is inevitable, therefore strategies are highlighted that allow the optimization of the supply chains.

The request to reuse the matrices labeled as waste progresses simultaneously with the search for innovative techniques, which make the exploitation of the resource feasible from an economic point of view. To face this new challenge, the scientific community is committed to researching possible ways to valorise waste. In this way the materials, which most of the time represent costs for industries, are converted into useful products such as chemicals, fuels or other energy sources. As can be seen from the inverted pyramid, the best option for valorising residues once generated is the possibility of *recycling* by extracting substances from plant by-products, which can be used as ingredients for functional foods,

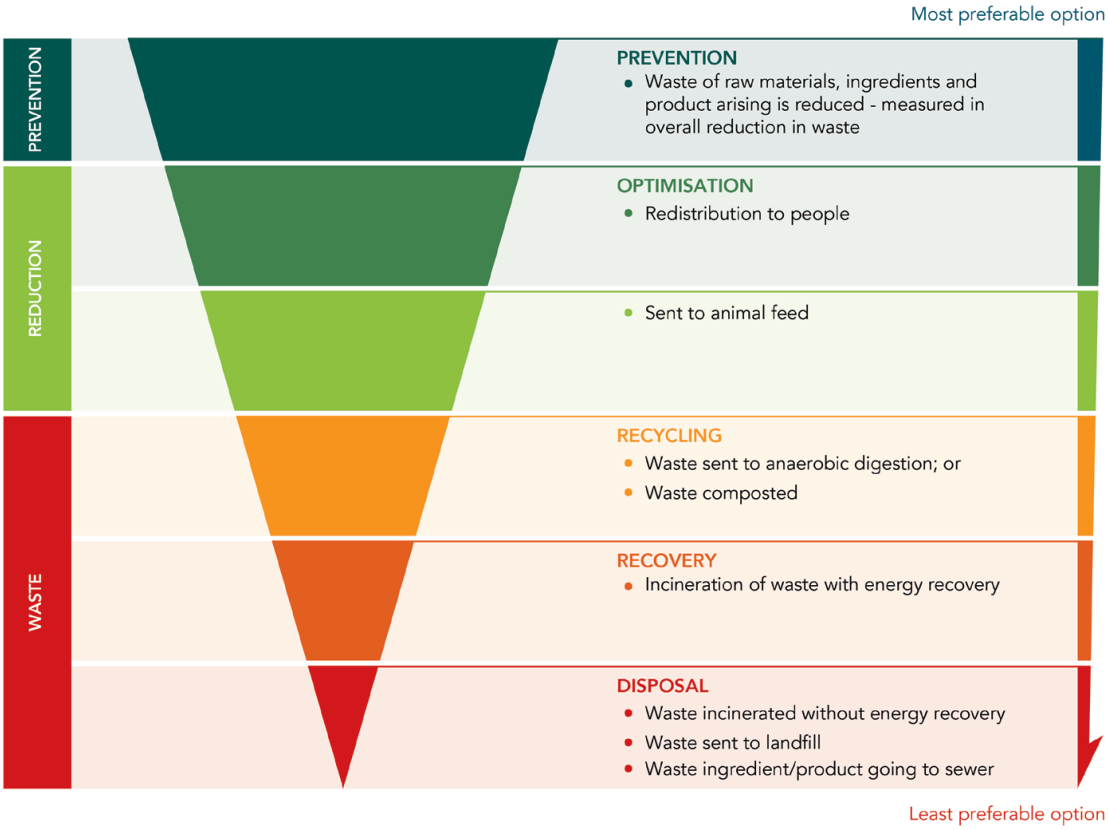


Figure 2.3: Hierarchy for food surplus and waste [30]

pharmacological or cosmetic compounds [30]. To do this, a set of techniques are exploited that can be divided into conventional and unconventional. Conventional ones are very popular for plant matrices in the industrial field, thanks to their ease implementation and their wide applicability.

The extraction efficiency depends on numerous chemical factors intrinsic in the by-product, such as composition, and physical factors of the matrix, like particle size. Furthermore, the characteristics of the solvent, ratio L/S, temperature of the sample and the time of extraction process are of fundamental importance.

Despite the continuous evolution of these techniques, in the last decade, conventional extraction methods (maceration or Soxhlet) are considered to have a high environmental impact; it must be take in mind that the so-called traditional systems have efficiencies that rarely go beyond 50% yield, furthermore requiring large quantities of solvent which are very often not compatible with environmental safety requirements. As for the "unconventional" extraction techniques, introduced relatively recently in the industrial field, these have numerous advantages such as reduction of solvent, the reduction of energy consumption, satisfaction of legal requirements in emissions, greater safety and control of the extraction technique, cost reduction and improvement of the quality and functionality of the entire process.

The main unconventional methods developed that have aroused particular interest in the last decade are:

- Negative pressure Extraction (NPE)
- Ultrasound Assisted Extraction (UAE)
- Supercritical Fluids Extraction (SFE)
- Microwave Assisted extraction (MAE)
- Accelerated Solvent Extraction (ASE)
- Extraction with Pulsed Electric Fields (PEF)

- Extraction by assisted Hydrodynamic Cavitation (HC)
- Rapid Solid-Liquid Extraction (RSLD)

2.2.1 Negative pressure Extraction (NPE)

Extraction through the application of negative pressures is an unconventional technology that uses the generation of cavitation to damage the plant matrix, facilitating the release of the analyte, and increasing the mass transfer of the system. NPC is classified as hydrodynamic cavitation as the phenomenon is generated mechanically.

2.2.2 Ultrasound Assisted Extraction (UAE)

The ultrasound-assisted extraction technique is based on the use of ultrasound, mechanical waves that belong to a wide spectrum of frequencies, which by convention begins at 20 kHz. As can be understood, these are frequencies that are above the audible spectrum. The operating principle exploits the application of ultrasound into the liquid, the waves generated propagate in the medium, creating a continuous succession of compression and decompression cycles. The very rapid sequence of cycles generates millions of micro bubbles, called cavities, which grow in volume with each cycle. The phenomenon is known as cavitation.

Analyzing the system at the level of the single cavity, after a certain number of cycles, bubble diameter reaches a critical resonant value at the same frequency as the ultrasounds that generated it. At this value, the cavity implodes, giving way to a microscopic area defined as a hotspot with temperatures of about 5.000 °C and pressures up to 2.000 atm. The enormous amount of energy developed generates a micro-jet of liquid that propagates at a speed around 280 m/s. These micro-jets of liquid, colliding with solid bodies, release all their energy, causing the surface break, allowing an easy release of the components with different intensity. A further intensification of the process due to the presence of micro-jets is to be attributed to the high turbulence generated with a consequent increase in the diffusion coefficient.

2.2.3 Supercritical Fluids Extraction (SFE)

The SFE uses a supercritical fluid, which makes the extraction process quick and efficient. According to the IUPAC definition, a supercritical fluid is any element, substance or mixture heated above the critical temperature (Tc) and pressurized above the critical pressure (Pc).

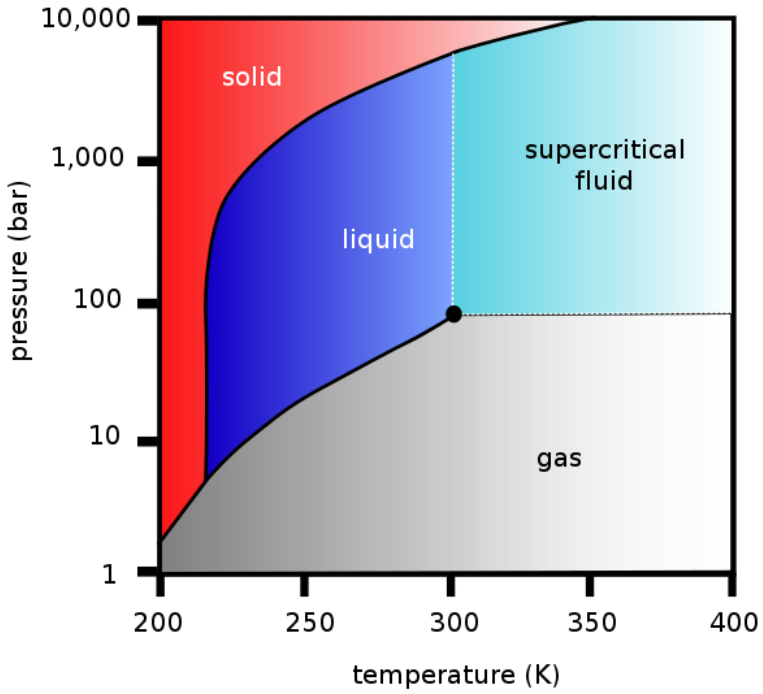


Figure 2.4: Phase diagram of CO_2

Practically speaking, supercritical CO_2 is used for most applications due to its high availability and non-toxicity, which is why it has been recognized as a GRAS (generally recognized as safe) process by the FDA (Food and Drug Administration). As anticipated, supercritical fluids have intermediate properties between those of liquid and those of gas; in particular they have a density similar to that of a liquid and a viscosity similar to that of gas. Since the solvatation power of fluid is directly related to its density, follows that, compared to a classic solvent extraction, extraction with a supercritical fluid of comparable solvating power (density) takes less time. Thanks to the lower viscosity, the supercritical fluid is also able to penetrate deeply into the sample matrix; therefore the mass transfer (diffusion) of the analyte from the matrix will be faster than that of the classical extraction with solvent. All this mean lower solvent consumption and, consequently, reduced costs compared to traditional liquid-liquid or Soxhlet extractions (also considering the costs related to the disposal of solvents). By appropriately choosing the supercritical fluid, the temperature and pressure conditions and the sample collection method, the extraction can be made highly selective with respect to the analyte of interest.

This means that the extracts obtained will have to undergo less intense separation and purification processes, unlike those obtained with organic solvents. Other advantages offered by this technique are the possibility of automation and applicability to the most varied sectors (polymers, food, pharmaceutical, environmental). It can therefore be said that SFE represents in all respects a valid non-conventional technology, as it limits the consumption of organic solvents, reduces analysis times and can be easily automated.

2.2.4 Microwave Assisted extraction (MAE)

Microwave-assisted extraction (MAE) is a rapid and efficient extraction technique based on the use of microwaves to heat the sample/solvent mixture in order to facilitate and speed up the extraction of the analyte. Unlike traditional heat sources, which act on sample surface, from which heat spreads to the inner layers of the body by conduction and convection, a microwave heat source acts on the entire volume (if the medium is homogeneous) or on localized heating centers, consisting of the polar molecules present in the product. Therefore, while with conventional heating some time is required to heat the vessel before the heat is transferred to the solution, microwaves directly heat the solution and the temperature gradient is kept minimum.

Heating can be carried out in open containers equipped with reflux refrigerant at atmospheric pressure or in closed containers under pressure. Using closed containers under pressure (pressurized microwave-assisted extraction, PMAE), the extraction can be carried out at temperatures above the boiling point of the solvent, further speeding up the process. The volumes of solvent used for extraction (typically 10-30 mL), as well as the extraction times (10-30 minutes), are significantly reduced compared to traditional techniques. In focused microwave-assisted extraction (FMAE) systems that work at atmospheric pressure, the microwaves are focused on the lower part of the container (where the sample/solvent mixture is located), thus allowing to reduce the applied powers and the dispersion of electromagnetic energy.

2.2.5 Accelerated Solvent Extraction (ASE)

Accelerated extraction with solvent or pressurized extraction, indicated with PSE or ASE, is a solid-liquid extraction technique. The ASE process is based on the use of solvent in sub-critical conditions, unlike the extraction with supercritical fluid, under pressure and at high temperatures to extract the analyte or analytes from the solid matrix in the liquid phase.

The increase in temperature, in fact, accelerates the extraction kinetics, while the high pressure keeps the solvent in the liquid state below the boiling point, thus allowing quick and safe extractions. The reduction in solvent quantity and in the extraction times is obtained by putting the solvent in direct contact with the sample within a confined and thermostated steel cell. The heart of the process inside the cell is carried out at temperatures between 50 and 200 °C, (on average at 100 °C) with residence times around 10 min to perform the static extraction under pressure (1.200-1.500 psi usually, with a maximum of 3.000 psi). Compared to traditional solid-liquid extraction techniques, this technique allows to reduce the amount of solvent needed, to reduce extraction times with a good predisposition to process automation. An advantage in the use of liquids in these physical conditions compared to supercritical fluids is determined by the fact that the first have a greater solvent strength and that, being already used in methods that involve extractions at atmospheric pressure, they do not require modifications or preliminary tests for the evaluation of extraction efficiency. The other advantage is represented by the fact that, using liquid solvents, there are no phase changes in the return of the system to atmospheric conditions and therefore no liquid or packed restrictors or traps are needed for the recovery of the analytes from the extract.

2.2.6 Extraction with Pulsed Electric Fields (PEF)

The pulsed electric field is an emerging technology in research and industrial application in food processing sector. It consists in subjecting the sample, immersed into the solvent, to a high pulsating electric field with intensity between 10-80 kV/cm. In particular, the pulsed electric field represents a non-thermal method applied mainly for the treatment of food for preservation purposes.

This system consists in the generation of a series of short bursts of electrical energy that lead to an increase in the permeability of the cell membrane or, even, to rupture by electroporation.

PEF is a promising "green" technology in food processing as it opens up a wide range of applications thanks to the phenomenon described.

The combination of PEF and diffusion extraction has been studied to improve the extraction of several compounds located within plant cells, such as dyes, polyphenols and other secondary metabolites. Furthermore, the pre-treatment with PEF, applied for example in winemaking before the fermentation phase, can improve the extraction of polyphenols from the grapes with a consequent variation in the organoleptic properties of the wine produced. In the industrial sector of extraction from fruit juices and vegetable oils, pretreatments with PEF, applied before the mechanical pressing of the fruits, lead to an increase in production yield, allowing the obtaining clearer extracts with a higher content in polyphenols without inducing negative organoleptic changes.

2.2.7 Rapid Solid-Liquid Extraction (RSLD)

The dynamic solid-liquid rapid extractor represents an innovative solid-liquid extraction technology that allows to exhaust in a short time, compared to other conventional extraction techniques, the solid matrices containing extractable substances in an organic or inorganic solvent and in their mixtures. The innovation of the extractor consists in the different extraction philosophy respect to the methods that aim to heat the extraction system to increase yield and accelerate extraction times; the Naviglio extractor is the equipment in which the operation is performed, the device performs the extraction at room or sub-ambient temperature and exploits an increase in pressure of the extracting liquid on the solid matrix to be extracted. The importance of extracting at low temperatures lies in the fact that in this way the thermal stress caused by thermolabile substances is avoided. Therefore, it is possible, for example, to avoid substantial changes to the composition of the substances contained in the plant matrices while preserving the biochemical activity of the compounds.

At the base of the extraction chambers (the two cylinders equipped with a mobile piston figure 2.5) [31] there are two porous membranes that let the liquid and the substances dissolved in it pass through, blocking the coarse particles of solid material. The two extraction chambers are connected via a duct onto which a valve is inserted which remains closed for the entire extraction time and is used only for the collection of the solvent.

The solid material to be extracted is placed in the extraction chambers which are then completely filled with the extracting solvent (organic or inorganic or their mixtures). When the pistons push at the same time, the system pressure increases "static phase"; when the pistons are moved from the equilibrium position, the "dynamics phase" begins, which is completed with the alternation of the thrusts of the two pistons.

This new extraction technology brings considerable innovations and advantages in obtaining quality extracts. First of all, it is not necessary to heat the extraction system as the action exerted is a mechanical type; current extraction techniques (percolation, Soxhlet, steam distillation, ultrasound) tend to increase the temperature to improve extraction efficiency, since they are based on diffusion and osmosis, both principles depend on temperature which in the case of thermolabile compounds, its increase contributes to their degradation.

In the Naviglio Extractor, being the extraction action a mechanical type, few extraction cycles are enough, about twenty which take about two hours, to bring completed exhaustion of any solid matrix that contains extractable material. Therefore, compared to maceration, which is an official extraction method in many processes, the operation is rapid and exhaustive at the same time. Furthermore, it is possible to carry out an aqueous extraction thanks to the reduced extraction times, which is impossible to achieve by maceration.

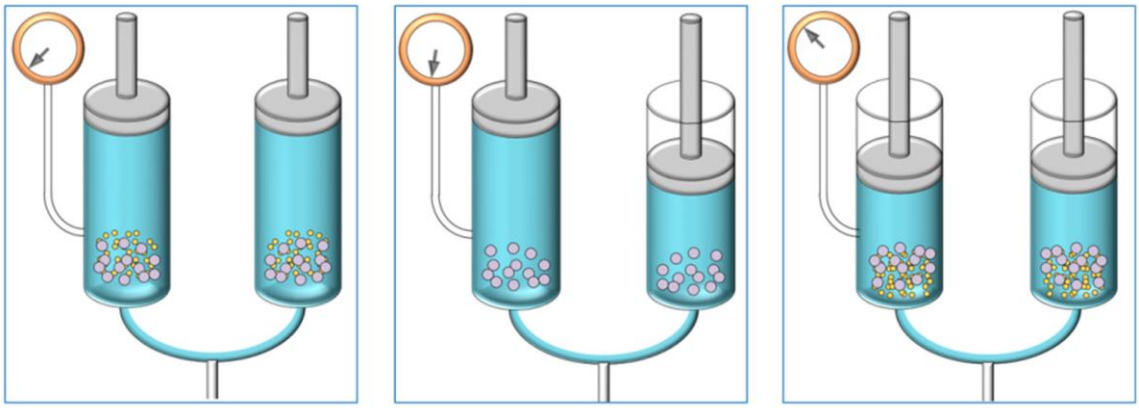


Figure 2.5: Schematic representation of the Naviglio extractor [31]

The Naviglio Extractor can be sized to different sizes, from industrial ones (100-1.000 L) to laboratory or housewives to satisfy the most limited production needs.

The results of an investigation within the scientific literature are summarized below, in which the main conditions on which the residue is subjected for the extraction of its components are reported.

Year	Authors	Title	Tecnology	Conditions
2010	Casas et al.	Extraction of resveratrol from the pomace of Palomino fino grapes by supercritical carbon dioxide.	SFE	100-400 bar/35-55 °C), and the addition of modifier (5% (v/v) of ethanol
2011	Liazid et al.	Microwave assisted extraction of anthocyanins from grape skins.	MAE	P 100-500 W, 50-100 °C, 5-20 min; solvent (50-80% methanol in water)
2014	Yu et al.	Study on extraction of polyphenol from grape peel microwave-assisted activity.	MAE	P 100-540 W, 3-10 min, 0-50, solvent (0-50% Ethanol in water)
2013	Bittar et al.	An innovative grape juice enriched in polyphenols by microwave-assisted extraction.	MAE	f 2.45 GHz, P 900 W, 20 min
2014	Rajha,Boussetta et al.	Effect of alternative physical pretreatments (pulsed electric field, high voltage electrical discharges and ultrasound) on the dead-end ultrafiltration of vine-shoot extracts.	UAE	f 24 kHz, P 400 W, 50 °C, 3 h diffusion (1.010-3.428 kJ/kg)
2013	Da Porto et al	Effect of the drying process on the intensification of phenolic compounds recovery from grape pomace using accelerated solvent extraction.	UAE	f 20 kHz, P 50-150 W, 30 °C, 30 min
2012	Casazza et al.	High-pressure high temperature extraction of phenolic compounds from grape skins.	HP	30-150 °C, 15-330 min
2011	Stavikova et al.	Antioxidant activity of grape skin aqueous extracts from pressurized hot water extraction combined with electron paramagnetic resonance spectroscopy.	ASE	150 bar, 40-120 °C
2013	Vergara-Salinas et al.	Effect of pressurized hot water extraction on antioxidants from grape pomace before and after enological fermentation.	ASE	103 bar, 50-200 _C, 5-30 min
2014	Rajha, Ziegler, et al.	Effect of the drying process on the intensification of phenolic compounds recovery from grape pomace using accelerated solvent extraction.	ASE	60-140 °C, % Ethanol/water (30:70; 70:30, v/v)

2015	Rajha, Chacar, et al.	b-Cyclodextrin-assisted extraction of polyphenols from vine shoot cultivars.	EAHS	beta-cyclodextrin (beta-CD) concentration (13.82-40 mg/ml), 33.18-66.82 °C, 0,30-6,19 h
2013	El Darra, Grimi, Maroun, et al.	Pulsed electric field, ultrasound, and thermal pretreatments for better phenolic extraction during red fermentation	PEF	0,8-5 kV/cm, 1-100 ms, 42-53 kJ/kg
2013	El Darra, Grimi, Vorobiev, Maroun, et al.	Extraction of polyphenols from red grape pomace assisted by pulsed ohmic heating.	PEF	5 kV/cm, 1 ms, 48 kJ/kg
2015	Brianceau et al.	Combined densification and pulsed electric field treatment for selective polyphenols recovery from fermented grape pomace.	PEF	1,2 kV/cm, 18 kJ/kg
2013	Delsart et al.	Effects of pulsed electric fields on Cabernet Sauvignon grape berries and on the characteristics of wines.	PEF	1) 0,7 kV/cm, 200 ms, 31 Wh/kg 2) 4 kV/cm, 1 ms, 4 Wh/kg
2012	Delsart et al.	Enhanced extraction of phenolic compounds from Merlot grapes by pulsed electric field treatment.	PEF	500-700 V/cm, and 40-100 ms
2015	Barba, Brianceau, et al.	Effect of alternative physical treatments (Ultrasounds, pulsed electric fields, and highvoltage electrical discharges) on selective recovery of bio-compounds from fermented grape pomace.	PEF	13,3 kV/cm, 0-564 kJ/kg
2014	Rajha, Boussetta, et al.	Effect of alternative physical pretreatments (pulsed electric field, high voltage electrical discharges and ultrasound) on the dead-end ultrafiltration of vine-shoot extracts.	PEF	13,3 kV/cm, 0-1.500 pulses, 50 °C, 50-762 kJ/kg, 3 h diffusion
2016	Mouratoglou et al.	Novel Glycerol-Based Natural Eutectic Mixtures and Their Efficiency in the Ultrasound-Assisted Extraction of Antioxidant Polyphenols from Agri-Food Waste Biomass	UAE	80 °C, 90min, aqueous solution of 10% by volume of glycerol:choline chloride 3:1 (molar ratio)
2018	Senrayan et al	A short extraction time of vegetable oil from Carica papaya L. seeds using continuous ultrasound acoustic cavitation: Analysis of fatty acid profile and thermal behavior	UAE	48 °C, 7 min, Hexane

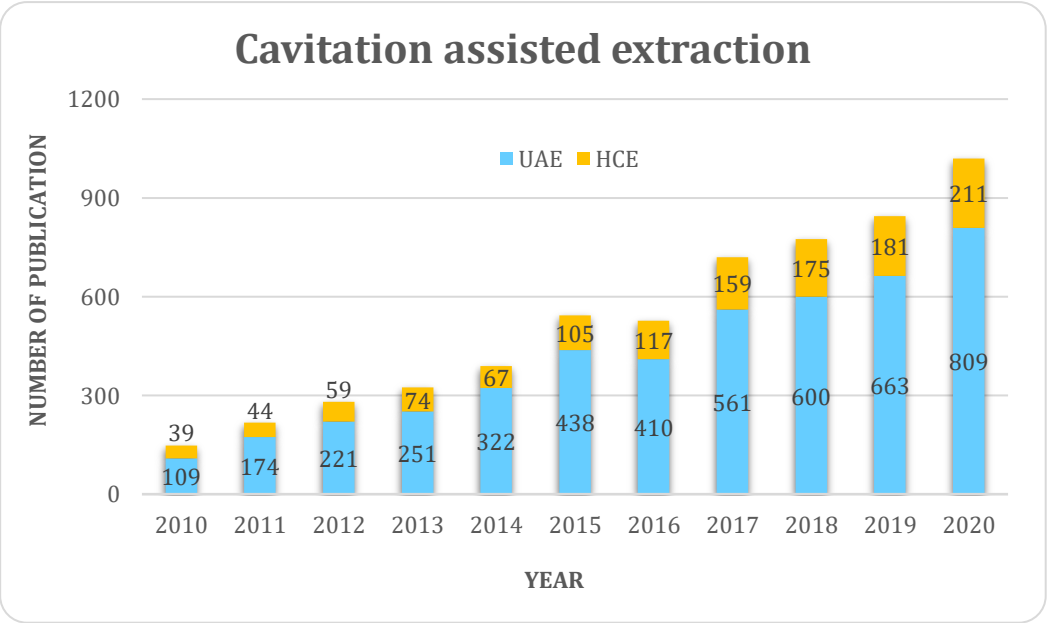
2011	Pan et al.	Continuous and pulsed ultrasound-assisted extractions of antioxidants from pomegranate peel.	UAE	25°C, 2-10-20-30-60-90min, water
2012	Galvan et al.	Ultrasound assisted extraction of polyphenols from black chokeberry	UAE	20-40-60-80 °C, up to 250 min, Ethanol at 50%
2010	Soria and Villamiel et al.	Effect of ultrasound on the technological properties and bioactivity of food	UAE	75 °C, 5 min, water
2015	Lee, I. et al.	Simultaneous treatment (cell disruption and lipid extraction) of wet microalgae using hydrodynamic cavitation for enhancing the lipid yield.	HCE	Cv: 1,17; 25,05 min
2018	Setyawan, M. et al.	Optimum Extraction of Algae-oil from Microalgae using Hydrodynamic Cavitation.	HCE	Cv: 0,126; 42 °C; 2 h
2017	Preece, K.E. et al.	Intensification of protein extraction from soybean processing materials using hydrodynamic cavitation.	HCE	Inlet pressure 100 MPa
2015	Tian, H. et al.	Negative-pressure cavitation extraction of secoisolariciresinol diglycoside from flaxseed cakes.	NPE	NP -0,04 MPa; 35 °C; 35 min; L/S: 13,16:1
2010	Zhang, D. et al.	Negative pressure cavitation extraction and antioxidant activity of genistein and genistin from the roots of pigeon pea [Cajanus cajan (L.) Millsp.].	NPE	NP -0,05 MPa; Room temp.; 45 min; L/S: 44:1
2011	Kong, Y. et al	Negative—Pressure cavitation extraction of cajaninstilbene acid and pinostrobin from pigeon pea [Cajanus cajan (L.) Millsp.] leaves and evaluation of antioxidant activity.	NPE	NP -0,075 MPa; 45 °C; 30 min; L/S: 30:1
2011	Dong, L.	Negative pressure cavitation accelerated processing for extraction of main bioactive flavonoids from Radix Scutellariae.	NPE	NP -0,07 MPa; Room temp.; 60 min; L/S: 40:1
2012	Dong, L. et al.	Application of cavitation system to accelerate the endogenous enzymatic hydrolysis of baicalin and wogonoside in Radix Scutellariae.	NPE	NP -0.07 MPa; 50 °C; 60 min; L/S: 20:1
2012	Mu, F. et al.	Negative-pressure cavitation extraction of four main vinca alkaloids from Catharanthusroseus leaves.	NPE	NP -0,075 MPa; 30 min; L/S: 20:1

2014	Luo, M. et al.	Optimization of enzyme-assisted negative pressure cavitation extraction of five main indole alkaloids from Catharanthus roseus leaves and its pilot-scale application.	NPE+Enz	NPC: NP -0.075 MPa; 30 min; L/S: 20:1. Enzyme: Incubation 35,87 °C; Incubation time 8.62 h; pH: 4,73
2012	Zhang, D. et al.	Enzyme pretreatment and negative pressure cavitation extraction of genistein and apigenin from the roots of Pigeon pea [Cajanus cajan (L.) Millsp.] and the evaluation of antioxidant activity.	NPE+Enz	NPC: NP -0,04 MPa; 30 °C; 20 min; L/S: 40:1. Enzyme: Incubation time 6 h; pH: 5
2013	Duan, M	Ionic liquid-based negative pressure cavitation-assisted extraction of three main flavonoids from the Pigeonpea roots and its pilot-scale application.	NPE	NP -0,07 MPa; 74 °C; 15 min; L/S: 20:1
2015	Qi, X. et al.	Green and efficient extraction of bioactive flavonoids from Equisetum palustre L. by deep eutectic solvents-based negative pressure cavitation method combined with macroporous resin enrichment.	NPE	NP -0,07 MPa; 60 °C; 20 min; L/S ratio: 25:1
2014	Jiao, J. et al.	A pilot-scale homogenization-assisted negative pressure cavitation extraction of Astragalus polysaccharides.	NPE	Homogenate time 70 s; NP -0,068; 64,8 °C; 53 min; L/S: 13.4
2015	Yao, X. et al	Negative pressure cavitation-microwave assisted preparation of extract of Pyrola incarnata Fisch. rich in hyperin, 2'-O-galloylhyperin and chimaphilin and evaluation of its antioxidant activity.	MWE	Microwave power 700 W; NP -0,05 MPa; 50 °C; 12 min; L/S: 30:1
2015	Duan, M. et al.	Homogenate-assisted negative pressure cavitation extraction of active compounds from Pyrola incarnata Fisch. and the extraction kinetics study.	NPE	Homogenate time 120 s; NP -0,05 MPa; 50 °C; 25 min; L/S: 30:1
2018	Wang, T. et al.	Ultrasound-negative pressure cavitation extraction of phenolic compounds from blueberry leaves and evaluation of its DPPH radical scavenging activity	NPE	NP -0,07 MPa; 50 °C; 15 min; L/S: 30:1

2018	Chen, C. et al.	Ultrasound-assisted extraction from defatted oat (Avena sativa L.) bran to simultaneously enhance phenolic compounds and b-Glucan contents: Compositional and kinetic studies.	UAE	f 40 kHz; P 200-600 W; 70 °C; 25 min
2016	He, B. et al.	Optimization of Ultrasound-Assisted Extraction of phenolic compounds and anthocyanins from blueberry (Vaccinium ashei) wine pomace.	UAE	P 400 W; 61.03 °C; 23.67 min ; L/S: 21,70:1
2016	Kazemi, M. et al.	Optimization of pulsed ultrasound-assisted technique for extraction of phenolics from pomegranate peel of Malas variety: Punicalagin and hydroxybenzoic acids.	UAE	f 24 kHz; I 105 W/cm2; 10 min; L/S: 70:1
2018	Nipornram, S. et al.	Optimization of low power ultrasound-assisted extraction of phenolic compounds from mandarin (Citrus reticulata Blanco cv. Sainampueng) peel.	UAE	f 38,5 kHz; P 56,71 W; 48 °C; 40 min
2017	Espada-Bellido, E. et al.	Optimization of the ultrasound-assisted extraction of anthocyanins and total phenolic compounds in mulberry (Morus nigra) pulp.	UAE	f 24 kHz; P 200 W; 64 °C; 10 min; L/S: 11:1,5; pH 7
2016	Zhao, Y. et al.	Extraction of Angelica sinensis polysaccharides using ultrasound-assisted way and its bioactivity.	UAE	P 180 W; 90 °C; 45 min; L/S: 7:1
2016	Zhu, W. et al.	Ultrasonic-assisted extraction, structure and antitumor activity of polysaccharide from Polygonum multiflorum.	UAE	P 140 W; 62 °C; 80 min; L/S: 20:1
2016	Olivera, C.F. et al.	Extraction of pectin from passion fruit peel assisted by ultrasound.	UAE	f 20 kHz; I 664 W/cm2; 85 °C; 10 min; L/S: 30:1; pH 2.
2018	Zhao, Y.	Ultrasound assisted extraction of polysaccharides from Lentinus edodes and its anti-hepatitis B activity in vitro.	UAE	P 290 W; 45 °C; 21 min; L/S: 20:1
2015	Rao, P.R. et al.	Mapping study of an ultrasonic bath for the extraction of andrographolide from Andrographis paniculata using ultrasound.	UAE	f 22 kHz; P 134 W; 40 °C; 10 min; L/S: 40:1
2017	Jang, S. et al.	Optimization of ultrasound-assisted extraction of glycyrrhizic acid fromlicorice using response surfacemethodology.	UAE	f 44 kHz; P 250 W; 69 °C; Extraction time 34 min.
2017	Juliano, P. et al.	Extraction of olive oil assisted by high-frequency ultrasound standing waves.	UAE	f 40 kHz and 585 kHz; P 242 W; 29 °C; 50 min.

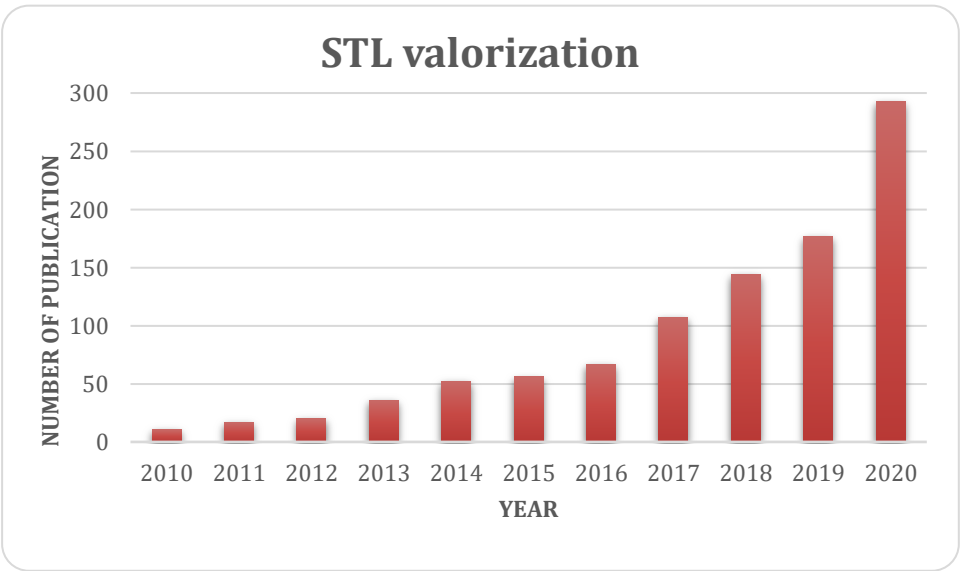
2017	Zhang, L. et al.	Study of ultrasonic cavitation during extraction of the peanut oil at varying frequencies.	UAE	f 40 kHz; Power density (W/L): 115; 60 min; L/S: 6:1
2016	Khoei, M. et al.	The ultrasound-assisted aqueous extraction of rice bran oil.	UAE	F 60 kHz; 45 °C; 70 min; pH 12
2017	Mnayer, D. et al.	Extraction of green absolute from thyme using ultrasound and sunflower oil.	UAE	f 20 kHz; P 98 W; 50 °C; 22 min; L/S: 10:1
2016	Liew, S.Q. et al.	Sequential ultrasound-microwave assisted acid extraction (UMAE) of pectin from pomelo peels.	MW+US	MW: P 643,44 W; Irradiation time 6,40 min. US: f 40 kHz; Sonication time 27,52 min. Solvent: water; pH 1,80.
2017	Lu, X. Et al.	Optimization of ultrasonic-microwave assisted extraction of oligosaccharides from lotus (Nelumbo nucifera Gaertn.) seeds.	MW+US	MW: P 250 W US: f 25 kHz; P 300.46 W; 5.42 min; L/S: 10:1; Solvent: water.
2015	Tchabo, W. et al.	Ultrasound-assisted enzymatic extraction (UAEE) of phytochemical compounds from mulberry (Morus nigra) must and optimization study using response surface methodology.	UAE+Enz.	US: f 34 kHz; P 60 W; 20 °C; Solvent: water. Enzyme: Enzyme concentration 0,010% (v/w); 12 min.
2018	Yang, Y. et al.	Efficient extraction of pectin from sisal waste by combined enzymatic and ultrasonic process.	UAE+Enz.	US: f 20 kHz; P 450W. Enzyme: Enzyme loading 88 U/g; 50 °C; 20 h; L/S: 15:1; pH 4.
2018	Goula, A.M. et al.	Ultrasound-Assisted Aqueous Enzymati Extraction of Oil from Pomegranate Seeds.	UAE+Enz.	US: f 20 kHz; P 130 W; 55 °C. Enzyme: Enzyme loading 2% w/w; 10 min; pH 5. L/S: 6:1 Solvent: Water.
2016	Dias, A.L. et al	Effect of ultrasound on the supercritical CO2 extraction of bioactive compounds from dedo de moca pepper (Capsicum baccatum L. var. pendulum).	UAE+SFE	Solvent flow rate 1,7569*10^4 kg/s; Pressure 20 MPa. US: P 800 W; 40 °C; 60 min.

The scientific domain, in these terms, proves to be particularly crowded. In particular, the technologies that exploit cavitation as a phenomenon capable of weakening the matrix and favoring the release of chemical components are of great interest. These are continuous or semi-continuous processes in loops that provide a consistent process intensification in line with the principles of "Green Extraction". As can be seen in the graph below, which shows the number of scientific articles relating to technologies that exploit assisted cavitation over the years, the interest aroused is growing thanks to the development of more performing equipment.



Graphic 2.2: Literature survey of cavitation assisted extraction tecnologies

Similarly, by carrying out a survey within the scientific literature, inserting "tea waste valorization" as keywords, it is shown that the by-product is continuously arousing a growing interest in the last decade. The reasons why more and more resources are being



Graphic 2.3: Literature survey of STL valorization

spent on the study of new technologies for the enhancement of STL are due to the policies that support the enhancement of any by-product before the final disposition, but also to the growing demand for what this matrix can still offer, such as polyphenols.

It should also be considered that in the last decade there has been an increase in the demand for sustainable tea products. This label is attributed to the product if the entire supply chain complies with the Voluntary Sustainability Standards (VSS) [15]. These standards are formulated to make the entire production chain sustainable, both from a social and environmental point of view.

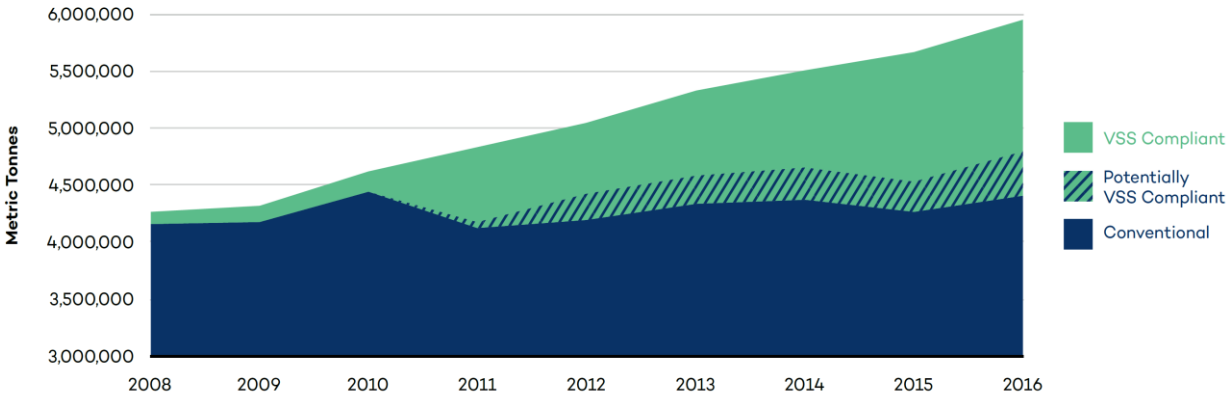
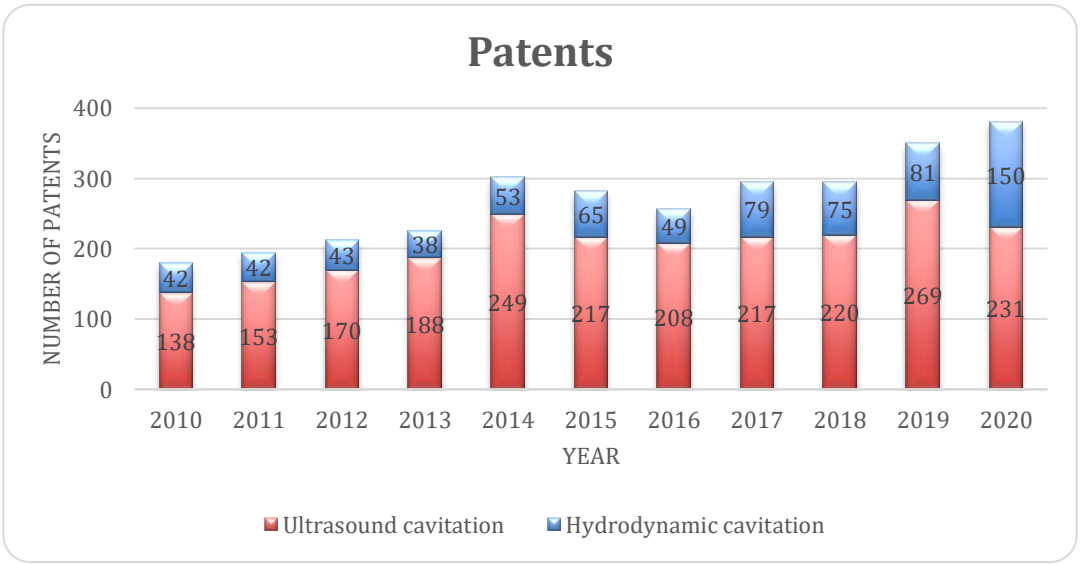


Figure 2.6: Global tea production trend [15]

Within these strategies, importance is also given to the methods of disposing of waste as otherwise they have a strong impact on the environment. Among these, the intensification processes clearly allows to substantially reduce the quantities that can no longer be exploited, at the same time creating further economic value in the supply chain.

2.3 Patent survey

The trend regarding the number of patents rconcerning the two cavitational extraction technologies is similar. As can be seen, the number of patents granted in 2020 is more than doubled compared to those granted at the beginning of the decade.



Graphic 2.4:Patent survey of cavitation assisted extraction tecnologies

Chapter 3

3 Fundamentals

3.1 Fundamentals of solid-liquid extraction with respect to vegetable matrixes

Solid-liquid extraction SLE also known as leaching, is one of the most widely used processes of chemical engineering: laboratory applications, industrial applications (such as pharmaceuticals, cosmetic and foods industry) and practical applications (cleaning). It is a crucial step, as it influences the final process products in quantitative and qualitative terms.

Dissolution is carried out to obtain a concentrated solution of a given compounds (solutesselectivaly extracted from the inner solid material).

The term SLE is attributed when the solutes physically interact with the matrix in which they are contained, unlike a simple dissolution. Furthermore, it is defined as such if the extraction of the various compounds does not allow the complete dissolution of the sample. Based on these considerations, the extraction of adsorted and/or entrapped or encapsulated compounds in solid matrices are included. Among these, from an industrial point of view, those plants that contain large quantities of specific compounds, such as polymers and various bioactive compounds, are of particular interest [32]. SLE kinetics are influenced by the rate of extraction of the soluble fraction into the solvent in which a sequence of phenomena are involved [33]:

- Diffusion of the solvent from the bulk to the suface of the solid through the layer limit;
- The solvent wetts and fills the solid microporosities creating a continous soaking phase (underflow);
- Dissolution of the solute compounds in the liquid solvent;
- Diffusion of the solute component outwards thanks to the concentration gradient;
- Diffusion of the solute through the boundary layer towards the bulk (overflow).

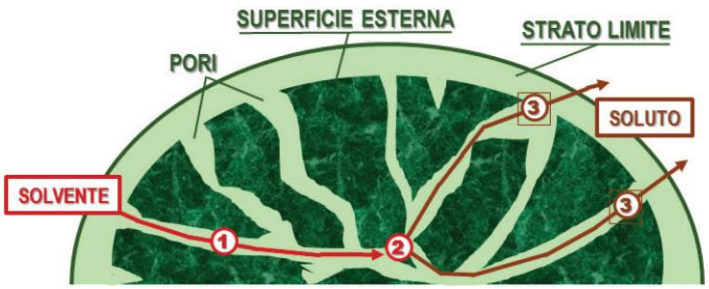


Figure 3.1: Schematic representation of the five solid-liquid extraction steps [33]

Diffusion stops when all the solute is dissolved and there is no concentration gradient within the solvent, which means true equilibrium is reached.

Diffusion mechanism have particular importance in extraction process, according to Fick's Law can be mathematically expressed (3.1):

$$\frac{dm_c}{dt} = \frac{D}{s} A(x_s - x) \quad (3.1)$$

Where:

m_c = mass of the solute c (kg);

t = time (s);

D = diffusivity coefficient (kg/(s*m));

s = thickness of the boundary layer (m);

A = surface through which diffusion occurs (m^2);

x_s-x = difference of the weight fraction of the solute c between the surface A and the point at s distance.

In way to achieve the best extraction conditios some factors can be optimized changing ones of the terms the appears into the equation:

by decreasing the "**particles size**" of the solid, the interfacial area increases and the diffusive paths inside the pores become shorter, therefore, the speed of diffusion increases; the raising the "**temperature**" of the system reduces the time needed to reach the equilibrium due to the increase in the diffusion coefficient as viscosity decreases (Fick's law); the increase of the "**affinity**" of the extraction liquid towards the compounds to be extracted increases the ability to create an intimate contact between the two phase. Enhance the "**mixing**" increase the turbolence of the system, decrease the thickness of the boudary layer and prevents sedimentation of the solid [33].

Over the years, importants changing have been done in the traditional extraction tecnologies improving the effectivnees.

In the field of solid-liquid extraction techniques, it is possible to distinguish four categories (table 3.1). In general, all four categories must be assigned to define a leaching system completely [34].

Category	**Operating cycle**	**Stream direction**	**Staging**	**Contact method**
Configuration	• Batch • Continuous • Multibatch intermittent	• Co-current • Countercurrent • Hybrid flow	• Single stage • Multiple-stage • Differential stage	• Sprayed percolation • Immersed percolation • Solid dispersion

Table 3: Categories of solid-liquid extraction

Recently, a great effort has been made on the sustainability of the processes by the scientific community with the aim of increasing the enhancement of plant matrices and food by-products. The results of this research have led to the implementation of new configurations and innovative methodologies (unconventional) that make it possible to reduce waste as much as possible, reduce the consumption of resources, process time, energy or external resources such as utilities. In the context of extraction, an important role is played the solvent which, in innovative technologies, is chosen not only by observing its extracting power but also its environmental impact.

To date, mainly laboratory scale rather than industrial scale, we find technologies that make use of supercritical fluids, enzymes, ultrasounds, microwaves, accelerated extractions and rapid solid-liquid extractions. The table summarizes the main characteristics of the main conventional and unconventional techniques [31].

Technique	Solvent	Particle size	Time	Yield	Quality extracted	Extract Stability	References
Squeezing	Not important	Not important	Minimum	High	Low	Low	[35][36][37] [38]
Maceration	Important	Important	Long	High	High	High	[39]
Decotion	Important	Important	Long	High	High	High	[40][41]
Percolation	Important	Important	Middle	Medium	Midium	Medium	[42]
Soxhelet	Important	Important	Long	High	Low	Low	[43][44]
SCD	Not important	Not important	Middle	Medium	Low	Low	[45]
MAE	Important	Not important	Middle	Medium	Low	Low	[6][8]
UAE	Important	Not important	Middle	Medium	High	High	[6][7]
SFE	Not important	Not important	Middle	High	Low	Low	[11][10]
ASE	Important	Not important	Minimum	High	Low	Low	[12]
RSLDE	Not important	Not important	Minimum	High	High	High	[13]

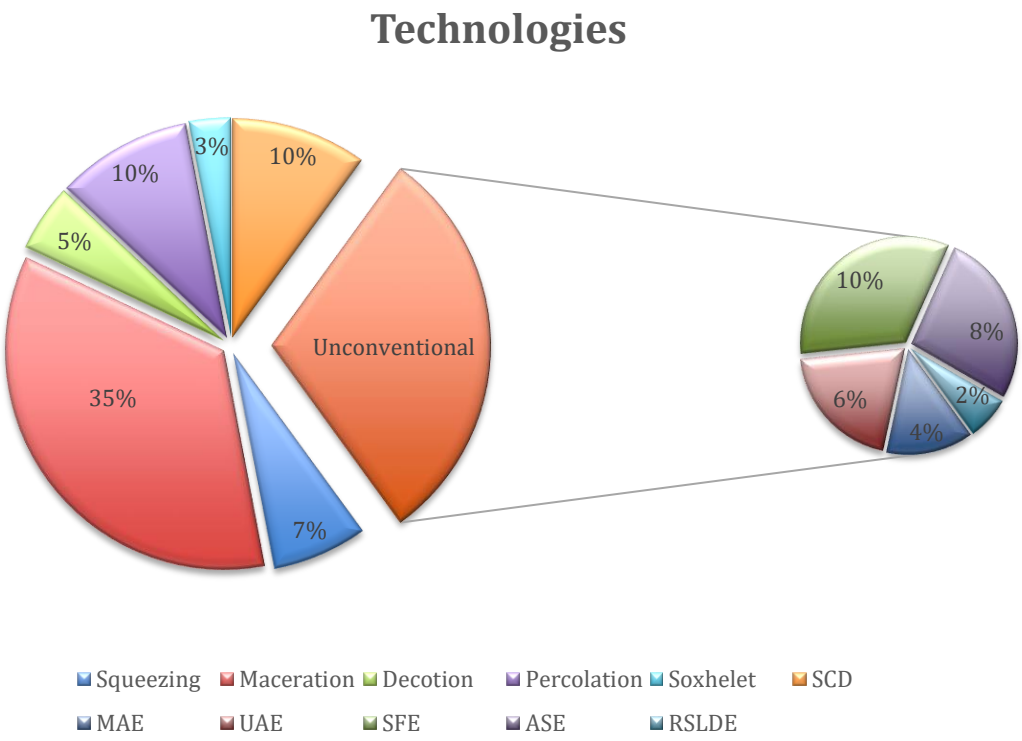
Table 4: Comparison between the main conventional and unconventional techniques

SCD: steam current distillation; MAE: microwave-assisted extraction; UAE: ultrasound assisted extraction; SFE: supercritical fluid extraction; ASE: accelerated solid-liquid extraction; RSLDE: rapid solid-liquid dynamic extraction.

Identifying the most suitable technology turns out to be a complicated evaluation. There is no single choice, but it depends on the priorities of the particular case. In fact, in some applications, more attention is paid to thermal stability rather than the quantity extracted. Furthermore, it should be taken in consideration that, despite some technologies being advantageous, their industrial scale up is critical.

For this reason, conventional techniques are still widespread in industry today.

The results of a quantitative survey in the scientific literature on the use of various extraction technologies are reported below (graphic 3.1).



Graphic 3.1: Technique diffusion in industrial scale

3.2 Fundamentals of liquid extract separation and purification techniques

By separation and purification, in chemistry, we mean all the techniques that allow the separation of substances into its components by removing impurities, thus modifying the relative quantity of components in the mixture.

Since ancient times, humans have put into practice rudimentary separation techniques, in particular to obtain metals and to obtain medicinal mixtures from plants. Initially, the progress and improvement of these techniques was mainly associated with practice, while following the industrial and technological revolution, the processes of separation and purification have attracted more attention and become indispensable. These processes are the basis for obtaining products with certain specifications in different sectors, for example

the oil industry, which focuses on the separation of crude oil in the different cuts to obtain fuels, the pharmaceutical, mining, food industry and many others.

In general, there are two reasons why we carry out separation processes. The first is to remove a component within a mixture, in this case the substance could be considered a contaminant or the component of main interest, so the process is called purification. The second is to modify the concentration of a mixture to allow the analysis of samples to be carried out within the limits of the devices.

The techniques of separation and purification can be classified into different categories according to the principles that are taken into consideration.

The figure 3.2 shows a classification scheme of the separation methods based on the various criteria considered.

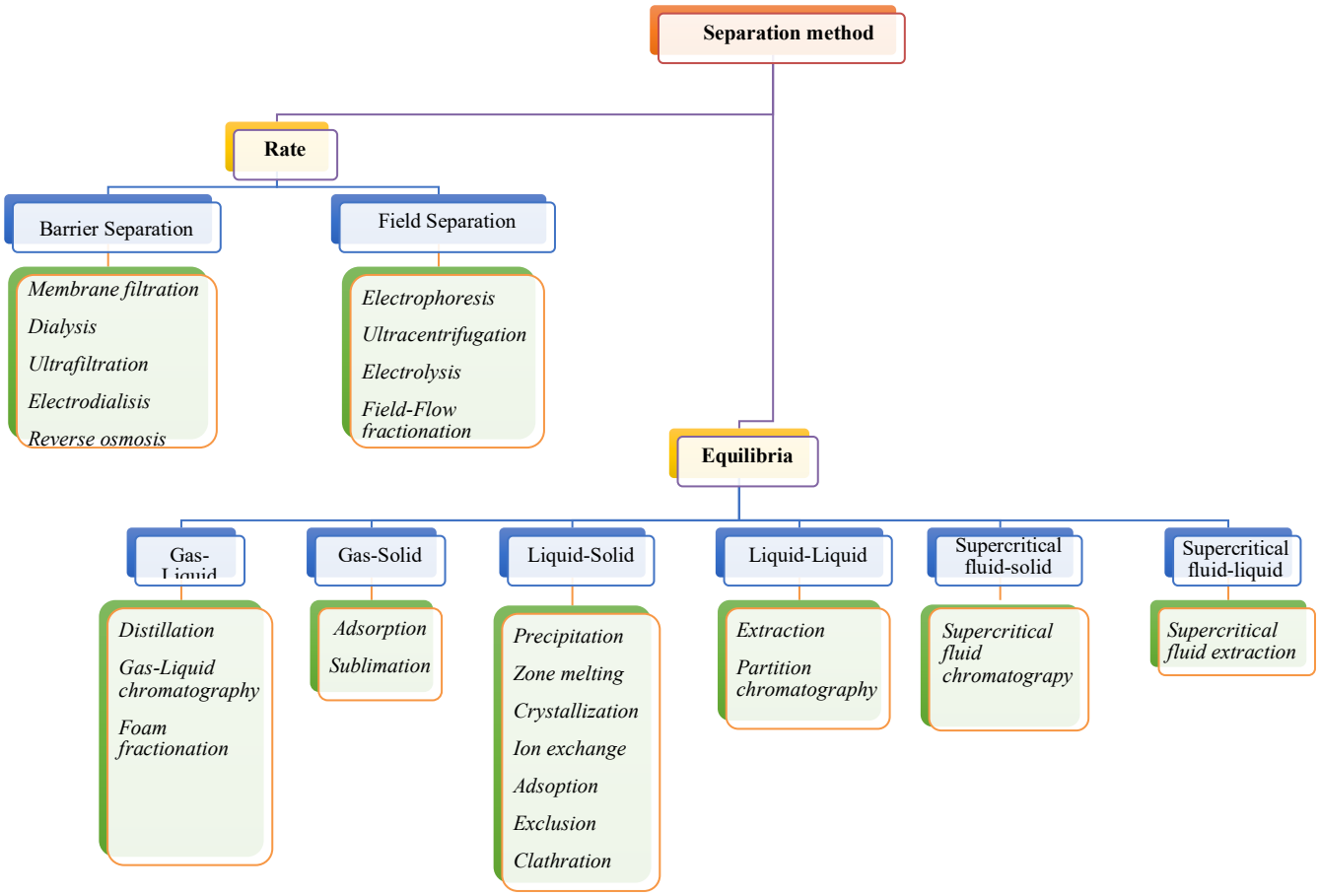


Figure 3.2: Scheamatic representation of separation method

A further classification could be made on the basis of the treated quantities, as some techniques are more suitable for laboratory scales, while others allow to manage industrial flows.

The methods based on equilibrium provide a ripartition of the component into two distinct phases, which are mutually immiscible. In this case, the component to be separated migrates, passing through the interface, from a phase in which with less affinity to another with greater affinity until equilibrium is reached.

The conditions of this equilibrium are described by the partition coefficient K expressed as:

$$K = \frac{Component\ concentration\ in\ phase\ A}{Component\ concentration\ in\ phase\ B}$$

The efficiency of this separation can therefore be evaluated a priori by considering the value assumed by the constant K. If the value of K >> 1 then the two phases taken into consideration allow the separation, otherwise if the value of K is close to unity the separation is not performing.

In some cases, when the separation is difficult because the coefficient assumes a value that does not allow to satisfy the predetermined target, the equilibrium step can be repeated several times. In this case the configuration assumed by the system is called multi-stage, unlike the previous one defined as single-stage. The number of transfer units required depends on the value of the transfer coefficient and the predetermined separation target. As can be understood, the multi-stage configuration requires more input work but the advantage of this, for the same amount of biomass, higher extraction yields are obtained compared to the single stage. Further research carried out on these configurations has made it possible to optimize the systems in terms of consumption of solvent and time. Nowadays, special equipment designs allow for automated separation to be conducted in multi-stage configurations with counter-current flows.

On the other hand, the processes that are based on the rate exploit the different kinetics of the phenomenon with which the components are separated. For example, the different diffusion speed of molecules within a porous system or the different migration speed of proteins in an electrophoretic separation. Being based on kinetics, these methods, unlike the equilibrium ones, are defined as time-dependent.

Of great importance, both for industries and for research, are the separation methods on a particle scale rather than at a molecular level. The purpose for which these techniques are implemented are essentially two:

- Removal of particles from gaseous or liquid streams;
- Separation of particles with different sizes.

Among the most important particle separation techniques we find filtration, centrifugation, precipitation, sedimentation, electrostatic separation, elutriation and particle electrophoresis.

Regarding the separation of compounds extracted from plant matrices, it must be taken into account that most of them have an organic nature. For this reason some of them are susceptible to high temperatures causing a loss of biochemical activity or in the worst case the complete degradation of the compounds. It is therefore necessary to choose the best separation technique that guarantees the preservation of the bioactive properties.

The main techniques applicable for the separation and purification of extracts are described below.

3.2.1 Principles of specific methods

3.2.1.1 Equilibrium method

3.2.1.1.1 Distillation

The distillation separation technique, known since ancient times, is based on the difference in the boiling point between the different components of the mixture. It consists in bringing the mixture to a boil condition, in this way the most volatile component is removed in the vapor phase and subsequently condensed.

Each pure liquid, above its surface, has a certain quantity of the component itself in the vapor phase, defined as vapor pressure. This physical characteristic depends on the temperature, in particular as the temperature increases, the pressure exerted by the vapor on the surface increases, as a greater amount of molecules passes to the vapor phase. When it reaches the pressure value of the surrounding environment, the liquid starts boiling. In the same way, the boiling point is reached for multi-component mixtures, in which the vapor phase contains molecules of each species that contribute to exerting the total vapor pressure. In general, the composition of the overlying vapor is different from that of the liquid as it is enriched with the low boiling component, thus allowing two or more components to be separated. This technique is based on a liquid-vapor equilibrium.

3.2.1.1.2 Chromatography

Chromatography is a separation process involving two phases, the stationary phase and the mobile phase. The stationary phase consists of a porous solid packed inside a capillary of different sizes. The mobile phase, on the other hand, is represented by the liquid that flows inside the column. In this case, the mixture to be separated is injected into the column and transported through the stationary phase by the mobile phase. As they flow through the packed medium, the various components are distributed along the path according to their affinity with the stationary phase, thus requiring different times to travel the entire length of the capillary tube. Molecules with greater affinity will have a greater interaction with the stationary surface thus determining a lower migration speed. The effectiveness and success of this technique depend on the choice of the two phases. In this case the type of equilibrium depends on the physical state of the stationary and mobile phase.

3.2.1.1.3 Exclusion and Clathration

Another feature exploited to separate different components is the size of the molecules. The systems used have the function of a molecular sieve. One example is size-exclusion chromatography in which larger molecules pass through the column with less time than small ones. This behavior is explained by the fact that the smaller molecules have the ability to penetrate inside the porosities of the stationary medium, lengthening the path and consequently the travel time.

Similarly, the clathration process has the size of the molecules as a principle of separation. In particular, the compound to be separated is included inside a cage formed by the host

molecules or by a network of host molecules. This technique is widely used in the oil industry.

3.2.1.1.4 Crystallization and precipitation

Crystallization is one of the oldest unitary operations known in the field of chemical engineering and allows to obtain a wide variety of materials whose applications mainly concern the pharmaceutical and food industries. This purification technique exploits the different hot and cold solubility of the compound under examination and of the impurities allowing to obtain a crystalline solid starting from a liquid or gaseous solution, in which solution is meant a system of two or more species that form a single homogeneous phase.

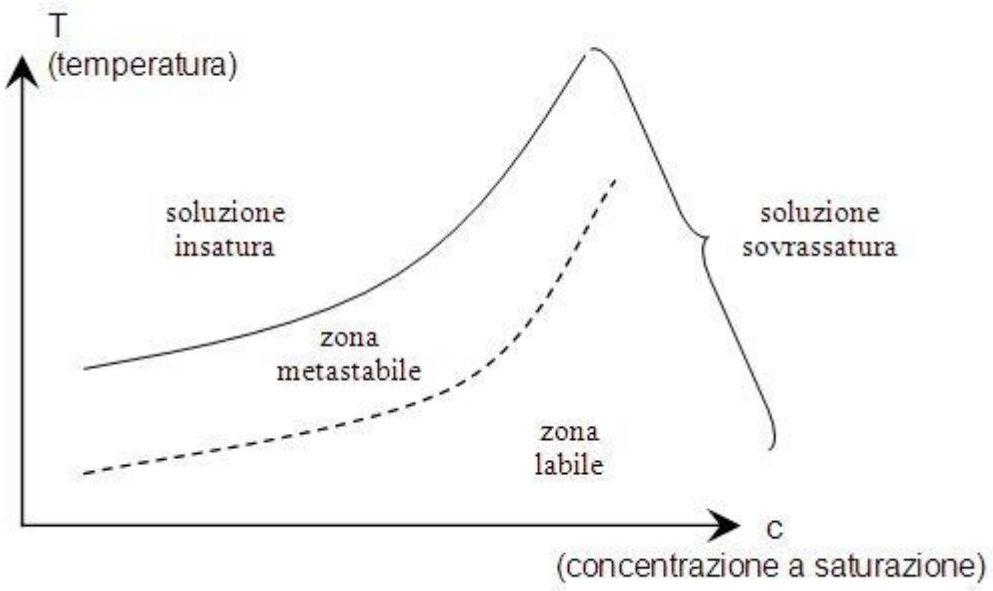


Figure 3.3: Solubility curve representation

The crystallization mechanism consists of two consecutive stages: nucleation and growth. The first is the stage of formation of a new solid phase while the second is that of crystal growth. Both nucleation and growth require a driving force which is represented by the supersaturation of the solution. A solution is defined saturated at a certain temperature when it reaches the conditions of thermodynamic equilibrium between the solute and the solvent, that is, when the solute is no longer able to dissolve in the solvent. Solubility capacity is the amount of solute required to reach the saturation conditions of a solution under certain conditions of temperature and pressure. Solubility strongly depends on temperature, but also on solvent type. In general, the solubility of a solute is represented through the solubility curve, a diagram (figure 3.3) that shows the concentration as a function of temperature. The solubility curve divides the concentration and temperature range into two distinct zones, one of stability (unsaturated solution) and one of instability (supersaturated solution).

By supersaturation we mean a condition of system instability. When the system is in an unstable condition it tends to re-establish the equilibrium conditions through the

crystallization of the solution after a certain period time, called the induction time to nucleation. It is therefore possible to define the supersaturation condition as metastable. The metastability field of the solution does not extend over the whole instability zone, but there is a supersaturation limit value beyond which the crystal formation is instantaneous.

In 1897 Ostwald introduced the terms "labile" and "metastable" to classify the different conditions of a supersaturated solution.

In particular he distinguished three areas:

1. Stable (unsaturated): crystallization is impossible.
2. Metastable (supersaturated): crystallization is unlikely unless there is a crystal already present in the solution.
3. Lable or unstable (supersaturated): spontaneous crystallization is probable, but not inevitable.

Supersaturation is the driving force of the crystallization process and is generally expressed in different ways.

Precipitation is sometimes distinguished from crystallization, as it involve the process in which an insoluble compound is formed within a solution through a chemical reaction. Sometimes to make the compound of interest insoluble it is necessary to add an external agent that modifies the properties of the system making it unstable.

3.2.1.2 Rate separations

3.2.1.2.1 Field separations

Electrophoresis is a separation technique based on electrokinetic phenomena in which colloidal particles or macromolecular ions with an electric charge move under the influence of an electric field, moving towards the cathode if they have a positive charge and towards the anode if they have a negative charge. The migration speed of the various particles depends on their charges and size. By exploiting this principle, it is possible to separate substances that are otherwise difficult to divide. Important applications of this technique are found in the biological field, for the separation of proteins, polysaccharides and nucleic acids. In the separation of proteins, the net surface charge is influenced by the pH thus determining the direction and speed of migration of the macromolecules. In the system that hosts the two electrodes, a saline solution is added, which propagates the current from one end to the other, and a gel that provides solid support to the samples to be separated. Without it, in fact, the molecules would diffuse into the liquid, making separation impractical.

3.2.1.2.2 Ultracentrifugation

A further exploited field force is the centrifugal one, to which the samples of different nature are subjected to separate the various components on the basis of a different density or molecular weight. The equipment used is the ultracentrifuge, a centrifuge at very high angular velocity (over 60.000 and, in special cases, even up to 500.000 revolutions per minute), in which accelerations up to over a million times the acceleration of gravity can be reached. During this operation, each molecular species moves through the density gradient at a speed that depends on its sedimentation coefficient and is located in a specific zone, or band, that can be easily separated from the others. Ultracetrifugation is particularly used for the separation of polymeric materials, such as proteins and nucleic acids.

3.2.1.2.3 Sedimentation

Process that exploits the action of a force (gravitational, centrifugal, electrical, etc.) allowing the movement of particles suspended in the liquid in the direction of the field. Specifically, the separation by gravity of solids suspended in liquids, allows to obtain a clarified liquid and a more concentrated suspension in solids (thickening).

3.2.1.3 Barrier Separations

3.2.1.3.1 Filtration

Widespread are the separation methods that are based on the selection of the molecules that cross a semipermeable barrier. In the physical-mechanical operation, the moving liquid, under the action of a pressure gradient, separates from the particles dispersed due to their retention by a porous filter medium in which the liquid is passed through. Also in this case the technique exploits the different size, shape or density of the particles which modifies their diffusion rate. This technique allows to manage different systems, liquid-gas, solid-liquid and solid-solid.

The degree of retention is changed by using membranes with different pore sizes. Based on this operating parameter of the membrane, the following are distinguished:

- Filtration
- Microfiltration (0,1-10 micrometer)
- Ultrafiltration (10-100 nanometer)
- Nanofiltration (1-10 nanometer)

Chapter 4

4 Evaluation of available experimental results

4.1 Description of experiments done and of experimental results obtained

The experimental campaign, carried out in the frame of Andritz TURBEX technology field testing, includes various tests aimed to determine the variables necessary for the design of the industrial extraction plant. In particular, several extraction tests were carried out to define the optimal conditions (S/L ratio, moisture content, rotor speed, etc.) in order to improve the extraction yields. The definition of the experimental activity derive from a careful analysis of the state of the art regarding the technology used, improving step by step after each analysis of the result. The work was carried out on a pilot scale plant, set up in the laboratory, consisting of an extraction section using a TURBEX EX-30 cavitational extractor coupled to peripheral equipment capable of managing the outlet flows to the extractor. In this specific case, the extractor was coupled to a centrifugal decanter followed by a screw press that allows you to remove the liquid soaked in the solid matrix at the outlet. The considerations associated with the industrial scale-up of the system, however, will be considered later, while in this chapter we will limit to describing only the activity carried out in the experimental tests.

The study was carried out in particular on the industrial production residue from TEA Garden in Malawi, analyzing the results obtained and validating the possible reuse of the waste matrix according to the principles of sustainability and circular economy. The biomass was previously characterized according to particle size and humidity [46]. The solid matrix is previously keept at low temperatures, until the moment of use to avoid deterioration.

The estimation of the diameter of the matrices took place through a screening process, a known quantity of sample was passed through sieves in series with pores of decreasing order of diameter. By weighing the fraction of solid that is retained by each level, an estimate of the weighted average size is obtained. From the analysis, the industrial production waste resulted in a similar appearance to a powder and with an average diameter of less than 200 μm.

Once the granulometry was defined, the moisture content and the organic material content of the matrix were characterized, using the weight-based thermo-gravimetric method, divided into two steps:

- Weighing the fresh sample
- Weighing of the sample after drying for 12 h at 100 °C.

In this way it is possible to evaluate the quantity of water that leaves the matrix and therefore its initial moisture content.

A similar procedure was carried out to determine the total organic material, drying in this case at temperature of 650 °C.

4.1.1 Polyphenol extraction

The extraction of polyphenols from the STL was performed using the unconventional extraction technique of hydrodynamic cavitation assisted by the TURBEX device.

In each extraction operation, 10 kg of STL matrix have been processed at an average temperature of 30 °C. A low temperature value was chosen so to maximise the effect of cavitation as well as to avoid unnecessary waste of energy for heating and thermal degradation of polyphenols.

As regards the configuration of the extraction steps, in the first instance it was assumed to carry out a first extraction using water as a solvent, with an L/S ratio of 14,5, and then proceed with the extraction of the polyphenols. This hypothesis has the aim of removing in advance the sugars still solubilized in the biomass to subsequently obtain an extract with a higher concentration of polyphenols, with a higher market value.

Analyzing the results obtained by applying this configuration, the system was found to be ineffective from the point of view of extractive yields. In fact, in the first extraction step, large quantities of polyphenols were lost with consequent excessive dilution of the polyphenolic extract obtained in the second step.

For this reason a single extraction step that used a hydroalcoholic solution EtOH/water at 60:40 (by volume) was chosen. This solvent allows to break the hydrogen bonds between polyphenols and biomass favoring their release.

Having identified the best configuration, the next goal was to optimize the fluid dynamic parameters (L/S) of the unit extraction operation. This type of analysis was done with a broader vision than taking into account only the single extraction yield target. In fact, high L/S values, despite exhausting the matrix, resulted in overly diluted streams which made the post-extraction phase of concentration expensive to the limit of impracticability.

The optimal L/S parameter, both from the extraction point of view and from the point of view of flow management in post processing, was 9.

During the experimentation, monitoring the parameter relating to the rotor rotation speed proved to be of particular importance. In fact, as the speed increases, the fluid dynamic regime becomes increasingly turbulent, with more relevant cavitational phenomena. This behavior could be thought to be an advantage in terms of extraction yield. The analysis on the samples, on the other hand, shows how the increase in the intensity of cavitational phenomena translates into a lower amount of total polyphenols content. The explanation of this behavior is to be found by analyzing at the molecular level what happens during the extraction phase. Cavitation, if pushed beyond a certain threshold, a formation of free radicals in the extractive medium occurs. As can be easily understood, these radicals in solution oxidize the extracted polyphenols, thus reducing their activity.

Analyzing the series of tests conducted with the TURBEX extractor, a rotor rotation of 900 rpm is efficient both in terms of extraction yield and in terms of biochemical activity and therefore of product quality.

At the end of each extraction, the solution was filtered to remove the possible presence of suspended solids. The liquid fraction is collected and destined for quantitative and qualitative analyzes.

4.1.1.1 Total Phenols Content quantification- TPC

The quantification of the total polyphenol content was carried out by the Folin-Ciocalteau method.

Using gallic acid as a standard, a calibration line was obtained that allows to correlate the absorbance of UV rays to the TPC (the measurement of which is obtained in equivalents of gallic acid or Gallic Acid Equivalent - GAE). The line was constructed by measuring the absorbance of samples with a known concentration of gallic acid, taking different volumes of the standard solution and bringing them to volume with deionized water. In the case of the determination of TPC for the STL extract, the standard solution is replaced with a solution of known concentration of the extract in deionized water, called stock solution. The sample preparation procedure is described below:

Stock solution preparation: A quantity of extract, obtained from the previous drying step, is weighed and it is solubilized in a known volume of water so that there are no suspended particles. The concentration of the stock solution must be such that the UV absorbance of the most concentrated sample does not go beyond the limits of the previously constructed calibration line.

Samples preparation: The samples to be analyzed are prepared by adding the following reagents to the stock solution:

1. Deionized water
2. Na_2CO_3 in aqueous solution at 10% w/w
3. Dimethyl sulfoxide (DMSO) in aqueous solution at 50% v/v
4. Folin-Ciocalteu reagent (solution of phosphomolybdate and phosphotungstate) in aqueous solution at 50% v/v

After the addition of these reagents, the samples are shaken vigorously and left for 25 minutes to complete the reaction. The reaction between the phenols present in the extract and the reagents causes a change in the color of the solution. The more pronounced the color intensity, the greater the presence of polyphenols in the sample and therefore the UV absorbance will also be higher.

The polyphenol content is then determined using a colorimetric quantification at a wavelength equal to 725 nm, using a UV-Vis spectrophotometer. The results were interpreted by comparing the absorbances recorded with a previously prepared calibration line, based on the absorbances of gallic acid.

The calculations required to obtain the final TPC are shown below:

The μg/mL of gallic acid equivalents (GAE) contained in the stock solution are calculated. Having said q and m respectively the slope and the intercept with the x axis of the calibration line, q is subtracted from the absorbance obtained from the sample of stock solution only, and the result is divided by m.

$$GAE = \frac{ABS - q}{m}$$

Once the GAE has been obtained, the total polyphenol content is calculated by dividing the GAE by the concentration of solid extract present in the stock solution.

$$TPC = \frac{GAE}{Concentration\ of\ solid\ extract}$$

4.1.1.2 Qualitative and quantitative analyzes

HPLC

The extracted samples were also characterized by an HPLC analysis in order to obtain all the information necessary for the identification of the single component in the samples and the relative quantities.

4.1.1.3 Results

The analyzes described were also made for the SPT waste before subjected it to the extraction step in order to be able to carry out performance evaluations on objective data. The table 4.1 shows the characterization of the polyphenolic mix with the quantities referring to the gram (on a dry basis) of STL.

SPENT BLACK TEA LEAVES **before extraction process**	
Components	Content [mg/g *dry basis*]
EpiGalloCatechin (EGC)	0,4
Catechin	0,3
EpiGalloCatechin 3-O-Gallate (EGCG)	9,7
EpiCatechin (EC)	3,2
GalloCatechin 3-O-Gallate (GCG)	1,3
EpiGalloCatechin 3-O-MetilGallate (EGCMG)	0,5
EpiCatechin 3-O-Gallate (ECG)	10,21
TOTAL CATECHINS (TC)	**25,61**

CAFFEIN	**32,25**

Gallic Acid	**2,92**
P-coumaric acid	0,23
Chlorogenic Acid	0,53
Quercetin	0,86
Caffeic Acid	5,73

Sinapic Acid	0,59
TOTAL PHENOLIC ACIDS	**10,86**
Theaflavin	**0,71**

Table 4.1: Polyphenol characterization of STP (before extraction)

The following table 4.2 shows the results of the analyzes carried out on the polyphenolic extract with the relative yields of the extraction calculated on the basis of the starting feedstock.

Components	**Content [mg/g *dry basis*]**	**Yield [%]**
EpiGalloCatechin (EGC)	1,78	61,4%
Catechin	1,56	71,8%
EpiGalloCatechin 3-O-Gallate (EGCG)	48,9	69,6%
EpiCatechin (EC)	12,8	55,2%
GalloCatechin 3-O-Gallate (GCG)	6,75	71,7%
EpiGalloCatechin 3-O-MetilGallate (EGCMG)	2,31	63,8%
EpiCatechin 3-O-Gallate (ECG)	51,64	69,8%
TOTAL CATECHINS (TC)	**125,74**	**67,8%**
CAFFEIN	**121**	**51,8%**
Gallic Acid	**15,45**	**73,0%**
P-coumaric acid	1,23	73,8%
Chlorogenic Acid	2,88	75,0%
Quercetin	4,54	72,9%
Caffeic Acid	28,12	67,7%
Sinapic Acid	3,41	79,8%
TOTAL PHENOLIC ACIDS	**55,63**	**70,7%**
Theaflavin	**4,46**	**86,7%**

Table 4.2:Polyphenol characterization of the extract product and yield extraction

Once the first extraction step is completed, the matrix still has a significant amount of high added value components such as proteins and dietary fiber, which is why the post-extraction residue was used as feedstock for the second extraction step.

4.1.2 Protein and dietary fiber extraction

The second extraction step was performed in the same TURBEX extractor always connected to the peripheral equipment that allows managing the outgoing streams.

In order to extract these macromolecules from the matrix it is essential to go through the hydrolysis of the hydrogen bonds that keep them trapped.

With a view to a more sustainable process, trying to reduce the possible amount of solvent consumed, it was decided to carry out the hydrolysis operation before the extraction phase. In particular, the exhausted biomass of the polyphenol fraction (36% solids) was maintained in batch conditions in contact with an 8M alkaline solution of potassium hydroxide.

The alkaline soaking was done by adding the basic solution with a L/S ratio of 3,5 to the solid biomass, obtaining a mixture with the characteristics of a paste.

After 20 minutes, the hydrolysis action is completed and the mixture can be considered ready for the second extraction step.

This extraction was carried out using water as a solvent at temperature of 30 °C with a L/S ratio of 7,5.

In analogy to the considerations made previously, the reduced value of extractive liquid used facilitates the subsequent phases of separation and concentration of components of interest. In fact, systems that are too diluted make the precipitation phases of both proteins and dietary fibers difficult.

4.1.2.1 Protein precipitation

At this point, having obtained the extract rich in proteins and DF, attention was focused on the precipitation of the extract in order to perform the characterization analyzes. This operation was carried out in two steps in order to separate the solubilized compounds and obtain final extracts with a higher purity.

The liquid extract then immediately underwent a pH shifting up to a value of 3, with the addition of hydrochloric acid at 37% w, and then left to rest. The variation of the pH of the liquid system leads to the reaching of the isoelectric point of the proteins, which induces the formation of agglomerates with larger dimensions causing a subsequent precipitation.

Carrying out these phases numerous times, during the experimental work, it was acquired the awareness that the precipitation of proteins was favored at low temperatures (15 °C), also improving the morphology of the agglomerate.

After a time of 20 minutes the precipitate was centrifuged to recover the protein solid separated from the supernatant.

4.1.2.2 Total protein content quantification

The characterization of the product obtained was made using the Kjeldahl method which consists of five phases schematized in the figure.

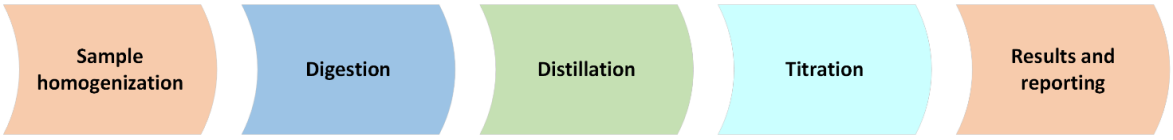


Figure 4.1: Kjeldahl method steps

The main phases of the analysis for determining the protein content, more precisely nitrogen, consist of digestion, distillation and titration.

Digestion: Organically bound nitrogen is transformed into ammonium ions with the use of concentrated sulfuric acid. Kjeldahl catalyzed tablets increase the boiling point of the acid thanks to the sulfur salts and accelerate the process.

Distillation: The mixture obtained with digestion is alkalized with sodium hydroxide before distillation to release ammonia. Ammonia is steam-distilled in a receiving solution containing a known amount of previously standardized strong acid.

Titratione: The pH of the target acid solution increases with the addition of ammonia. The nitrogen and protein content is then determined indirectly by calculating the excess acid through back titration.

The results obtained through this methodology show that the total protein content is 32% within the final product.

4.1.2.3 Dietary fiber precipitation.

The supernatant, once the proteins were separated, was recovered as it was destined for the next step of precipitation of the dietary fiber.

The protein precipitation operation was carried out by alcoholizing the supernatant with 96% ethanol in a ratio of 1:0,85 between supernatant and ethanol, maintaining the temperature at 5 °C to make the aggregation conditions more favorable.

4.2 Interpretation of experimental results

Below is a schematic representation of the experimental activity with the values of the extraction yields of the steps involved.

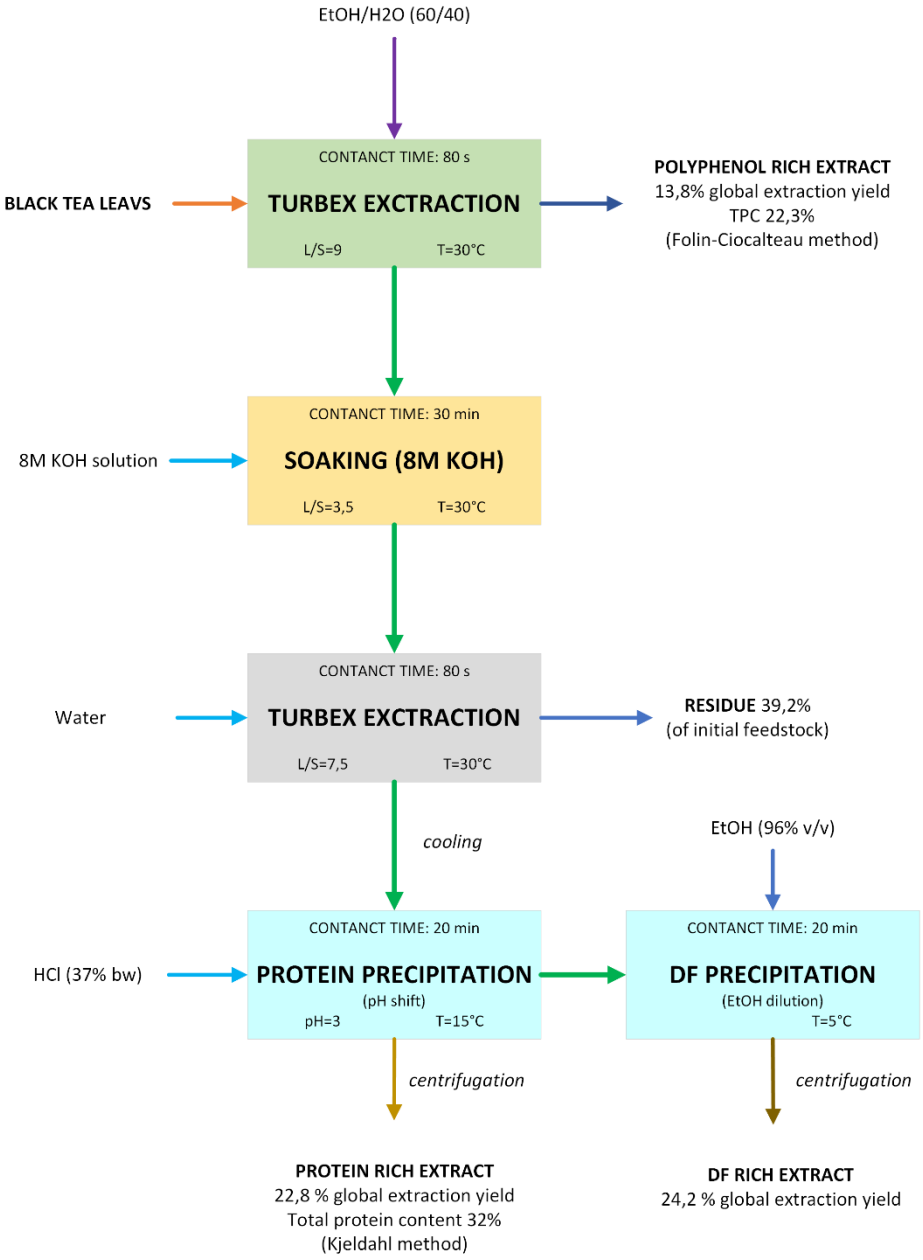


Figure 4.2 Flow sheme of experimental activity with yield extraction

For the validation of the extractive effectiveness of the TURBEX system on this matrix, a comparative study was carried out with conventional methods, taking into account the total polyphenol content as the main key parameter.

Analyzing the scientific literature, conventional extractions lead to extracts with a polyphenol content with maximum values not exceeding 15% [46] using 50:50 EtOH/water as solvent.

For an overall assessment of cavitational extraction technology, it is essential to have a broader view, which goes beyond the analysis of extraction yields. In fact, in the scientific literature, works that make it possible to reach a polyphenolic content over 10% are carried out in much more expensive conditions. The operating temperatures have values between 60 and 80 °C with residence times of not less than 45 min.

The results obtained are shown, in terms of extraction efficiency, in line with those obtained with ultrasound technologies in which the overall yields are estimated at around 56%.

As shown in the table (4.2), the extraction is extremely efficient for some compounds, for example theaflavin with yields over 85%.

Chapter 5

5 TURBEX solid-liquid extractor

5.1 Introduction on Turbex extractor

From the literature, it emerges that, among the innovative and emerging process intensification techniques, the most promising for the extraction of microcomponents with high nutraceutical value, as in the case of tea industry residues, appears to be extraction assisted by controlled cavitation or "CAE" (Cavitation Assisted Extraction).

The possibility that the technique offers to significantly increase the recovery of natural components, improve extractive yields with a minimum product degradation, reducing also process time and temperature, makes the advantageous to perfome extractions at room temperature. These considerations can be particularly appreciated in the food sector, considering that many products of this industry can be vulnerable to high temperatures and sensitive to physical and chemical changes. Phenolic compounds, for example, usually degrade at temperatures above 70 °C, which is why the optimal operating range for their extraction is between 20 °C and 50 °C [47].

The CAE extraction plants also offer the advantage, much appreciated by the industry, of requiring simple and practical equipment, which allows a rapid start-up and an increase in production, reducing costs at the same time thanks to the elimination of many steps of process.

The term “cavitation” indicates the liquid-vapor phase transition, in isothermal conditions, caused by pressure reduction up to the value of the vapor pressure of the liquid phase.

The cavitation phenomenon may be undesirable due to the temperatures and pressures that are created in the solution. However, if it is controlled, it can be exploited advantage to the process carried out. Cavitation is generated when, at the working temperature, the local pressure of the liquid reaches a level below its own vapor pressure with a rapid creation of bubbles and subsequent implosion [48].

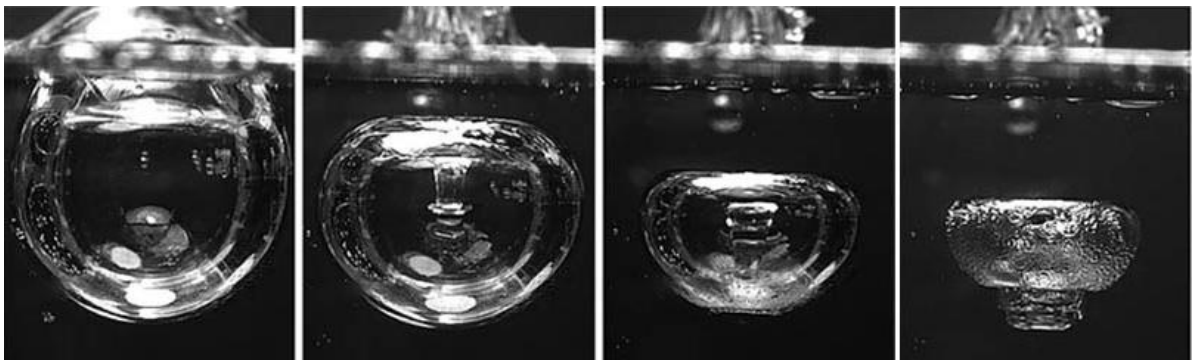


Figure 5.1: Buble formation and implosion [48]

Controlled cavitation generated industrially can be classified in [49]:

5.1.1 Ultrasound Cavitation

When ultrasounds are applied to a continuous fluid, they produce nearly sinusoidal pressure waves, which induce vapor bubbles if the local pressure drops below the vapor pressure.

The first part of the wave is of tension, which generates a series of bubbles (for water and aqueous solutions, with a radius generally between 10 and 200 microns), while the second part, which follows immediately, is of compression , which collapses the bubbles created [50].

Ultrasound method uses frequencies beyond the human audible, lower than microwaves (around 20 kHz) [51]. The sound waves cause a succession of compressions (high pressure) and rarefactions (low pressure) in the medium, thus generating voids, the cavitational bubbles.

Once generated, they increase their size during the rarefaction phases up to their critical size and decrease it during the compression cycles.

Ultrasounds therefore exploit mechanical vibrations transmitted to the liquid with ultrasonic frequencies [52], generating implosion bubbles of different sizes and consequent jet streams, which transfer energy to the system favoring mass transport.

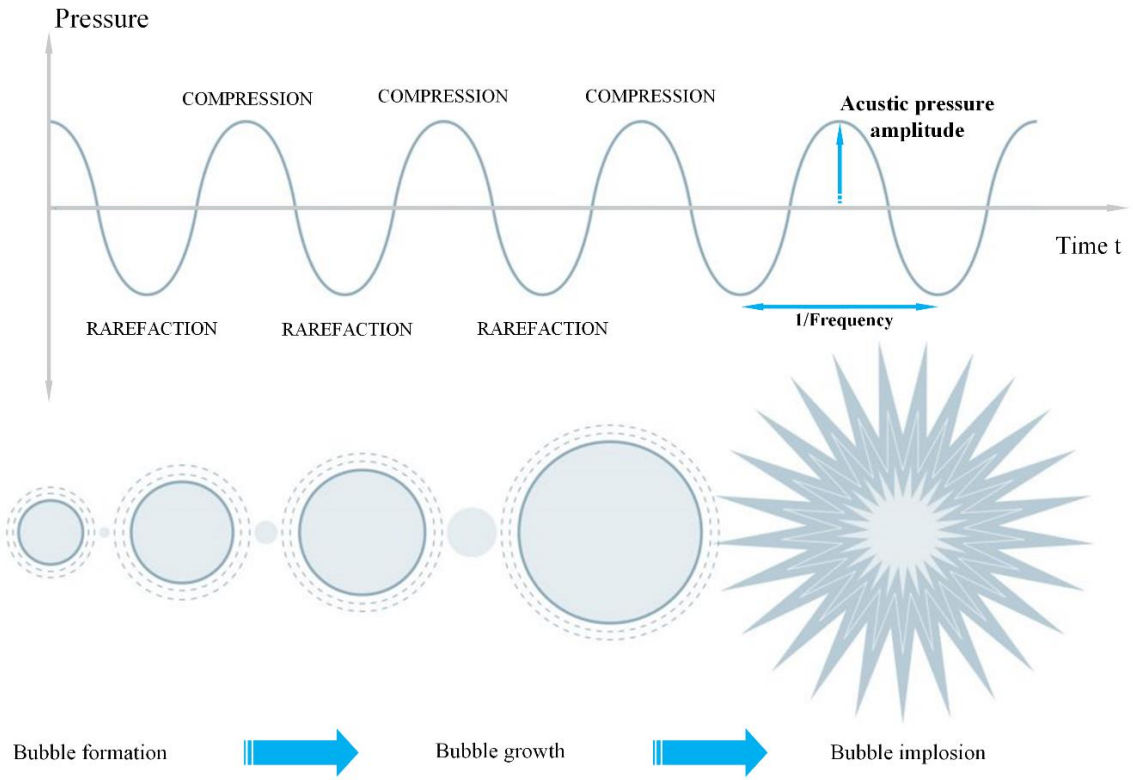


Figure 5.2: Schematic representation of the acoustic cavitation mechanism [52]

5.1.2 Hydrodynamic Cavitation

Hydrodynamic cavitation is generated by the passage of a liquid through constrictions such as perforated plates or throttling valves. When the liquid passes through the impediment, its speed increases with a consequent reduction of pressure. If the geometric configuration is sufficient to bring the pressure decrease below the threshold value (normally coinciding with the vapor pressure of the medium used, at the operating temperature), cavitation occurs. Once the pressure returns to normal value, the micro-bubbles collapse, releasing high amounts of energy around them. The intensity of the pressure drop, and therefore of the energy generated, depends mostly on the geometry of the constraint imposed on the system.

The asymmetrical implosions of the bubbles, the high pressures and temperatures, result in high shear stresses generating micro-jets in the liquid. In this way, maceration and rupture of the cell wall by micro-jets directed on the surface of the solid is obtained, also considerably increasing the mass transfer. Controlling cavitation means controlling the dynamics of the steam bubbles that are created, and causing dynamic implosion in a confined region at higher pressure, punctually focusing intense energies to physically damage the plant structures, leading to a better penetration of the solvent in the matrix and a simpler release of the interest components.

The presence of hot spots dispersed in mass at room temperature, allows to obtain the aforementioned effects avoiding, at the same time, the overall temperature increase of the system, reducing thermal degradation in the process. The use of this unconventional method for the extraction of natural products and plant compounds is therefore of particular interest.

In the case of hydrodynamic cavitation, controlled cavitation is generated by cavitational elements or hydrodynamic screw drivers of the "rotor-stator" type, in which the rotor element imposes on the fluid a speed such as to generate cavitation.

The solid matrix that contains the compounds to be extracted is then subjected to the action of various phenomena, pressure and temperature shocks, shear stresses and turbulence, which break it up, making the compounds to be extracted more accessible.

The cavitational extractor also performs a microscopic mixing, which eliminates solid agglomerates, making the matrix more accessible for extraction, thus minimizing treatment time. Therefore, by feeding a solid matrix dispersion in a liquid phase to a cavitational extractor, a disintegration effect of the matrix is guaranteed, with the associated generation of interfacial area and an increase in the volume of the porosity of the matrix itself. Then a micro-mixing effect of the matrix with the liquid phase of extraction is obtained which, in a continuous process, guarantees the optimization of the extraction yield.

Both the cavitation generated by ultrasounds and the hydrodynamic cavitation allow to obtain significantly higher yields (i.e. of the order of magnitude of +20 compared to the traditional extraction technique), in considerably shorter times (ie approximately ≤75% compared to the traditional extraction technique), working at much lower process temperatures than the traditional extraction technique (i.e. ambient temperature or slightly higher than ambient temperature, against the boiling temperature of the solvent of the traditional technique) and, for these reasons, according to the studies carried out so far, it could turn out to be an idea of radical innovation with the potential to become a "disruptive technology" in the context of the exploitation of waste from the agri-food chain.

5.2 Solid-liquid extraction performance of TURBEX EX30 extractor

Among the extraction systems that take advantage of the possibility of generating cavitation in a controlled way, we find the TURBEX EX 30 hydrodynamic extractor, through which the experimental tests of this thesis were carried out.

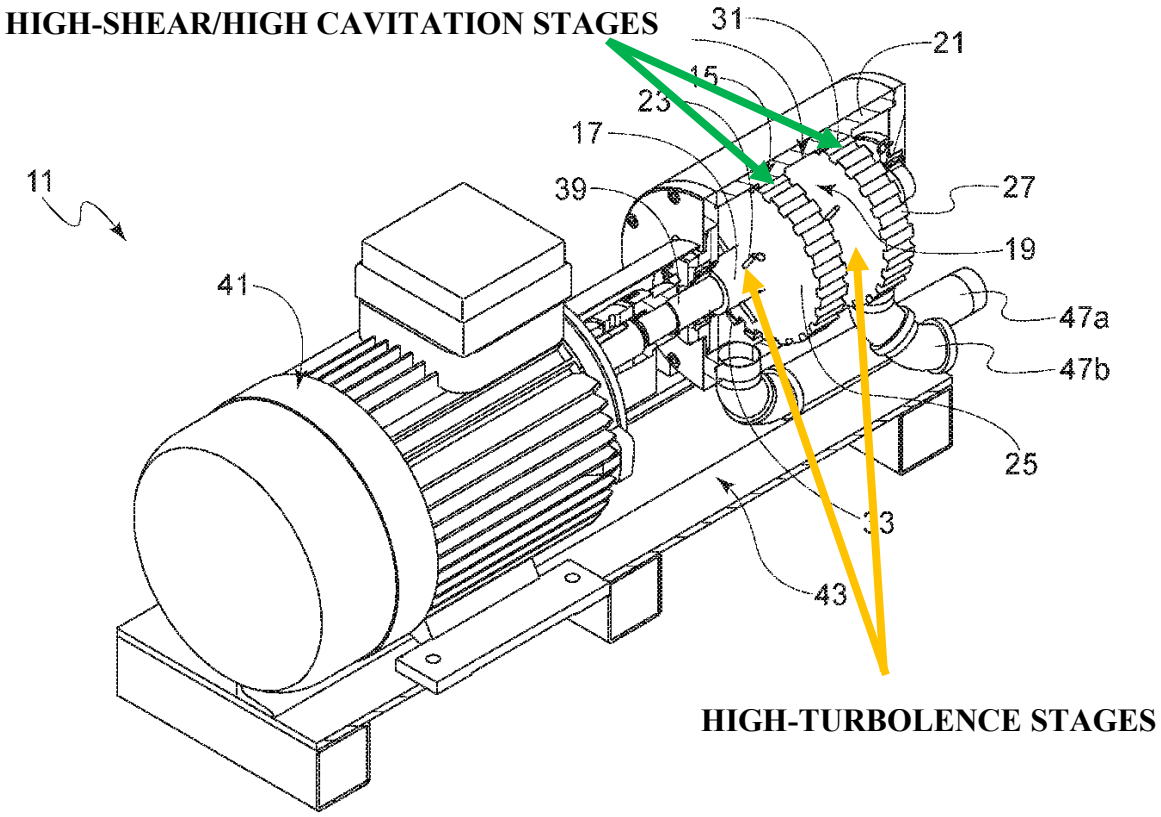


Figure 5.3: TURBEX representation [53]

The technology is described in the patent WO 2018/146647 [53] in which the ability to improve the aspects related to extraction is highlighted. In particular, the phase contact and the transfer of properties favored by the high turbulence and high-shear stress caused by the cavitation phenomenon. The configuration also allows to manage multiphase flows: gas-liquid, solid-liquid, liquid-liquid, gas-solid-liquid.

The TURBEX EX30 prototype represents a unique technology of its kind. This multistage device uses in a combined way the three process intensification techniques aimed at generating interfacial area and exchange area, which are high turbulence, high shear stress and hydrodynamic cavitation.

The design, in order to carry out its function, provides at least one internal zone, which is defined stage, with high mixing due to turbulence (TB) and another stage with high-shear stresses in which the cavitational phenomena are confined (TG/TH). Specifically, the TURBEX EX30 multi-stage prototype with which the experimental tests were carried out has a configuration TB-TG/HC-TB-TG/HC-TB-TG/HC-TB.

The cavitational phenomena are achieved with a multirotor-multistator configuration, in which one or more disks with a defined geometry are connected to same motor shaft. The

rotation of the disks inside a confined chamber, generate friction with the liquid contained and thus creating cavitation.

The turbulence inside the high mixing chamber is guaranteed by the presence of a pin placed radially on the shaft. The high relative sliding speeds between the phases are generated by the particular geometry of the external surface of the rotor, and of the stator that encloses it. These are specifically toothed surfaces.

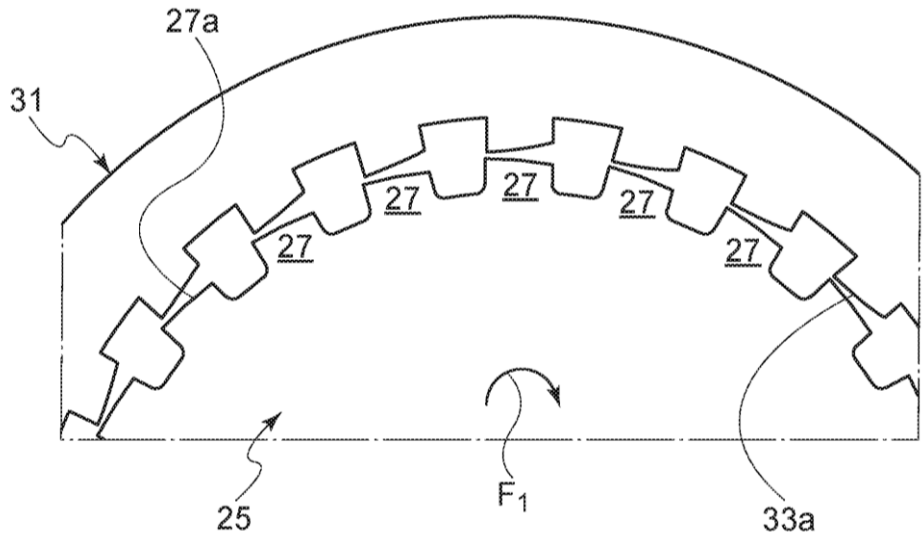


Figure 5.4: Stator-rotor surface profile [53]

The design of the tooth profile has also been designed in such a way as to maximize the efficiency of the overall system. In fact, the invention provides a parabolic profile as the flow lines of the liquid. In this way the possible dissipations that would be caused with the passage in the separation zone defined as "vena contracta" are reduced.

These internal dissipations, if not limited, affect the performance of the machine as they would be converted into thermal energy, thus causing an excessive increase in temperature.

Another important aspect, determined by the particular design of the tooth, is the ability to ensure the unidirectionality of the flows, which would otherwise be subject to back-diffusion phenomena.

The invention has the ability to manage both equicurrent and countercurrent flows according to specific needs. Once the adequate system has been defined, the equipment is feeded through the lights placed in the mixing stages, in particular in the first and last if the configuration chosen is the countercurrent one as in our case.

Surely the main advantage of the invention is the ability to combine the internal phenomena that allow to increase the factors that govern the transport of property.

Specifically, looking at the generic transport relationship defined as:

$$F_p = A * K * \nabla$$

Where:

F_p= flow property;

A=specific area;

K=diffusion coefficient;

∇= true driving force;

The analyzed invention allows to increase the coefficient A through the generation of new interphase contact surfaces thanks to the high-shear stress and cavitation efforts.

The operation of the equipment subjects the phases to extreme conditions at a punctual level. These are reached at the points where the bubbles implode. Collapse usually occurs in conditions close to adiabaticity, thanks to the conversion into thermal energy (heat) of the kinetic energy. The phenomenon generates very high temperatures and pressures, reaching up to 2.000 K and 2.000 bar at the moment of the implosion. This sudden increase in temperature and pressure leads to the formation of hot-spots, which are used to accelerate the reactivity within the system or to exert physical effects on a matrix within the medium.

The fluid also, in areas with a restricted section, for example near the overlap of the stator-rotor teeth, reaches speeds of the order of 750 m/s [53].

The intimate contact that is created in the high turbulence zone increases the diffusive phenomena that are included in the K coefficient within the equation. In addition, last but not least, the TURBEX prototype is an intensified, innovative system, able to manage the flow of solid and liquid in countercurrent (i.e. solid matrix fed in the 1st zone TB and liquid extracting fed in the last zone TB). In a counter-current configuration, the system with 3 physical rotor/stator stages has experimentally demonstrated the ability to perform up to 15 theoretical equilibrium stages (figure 5.5), thus allowing the perfect exhaustion of the extracted matrices, as well as the minimization of the liquid phase of flow rate.

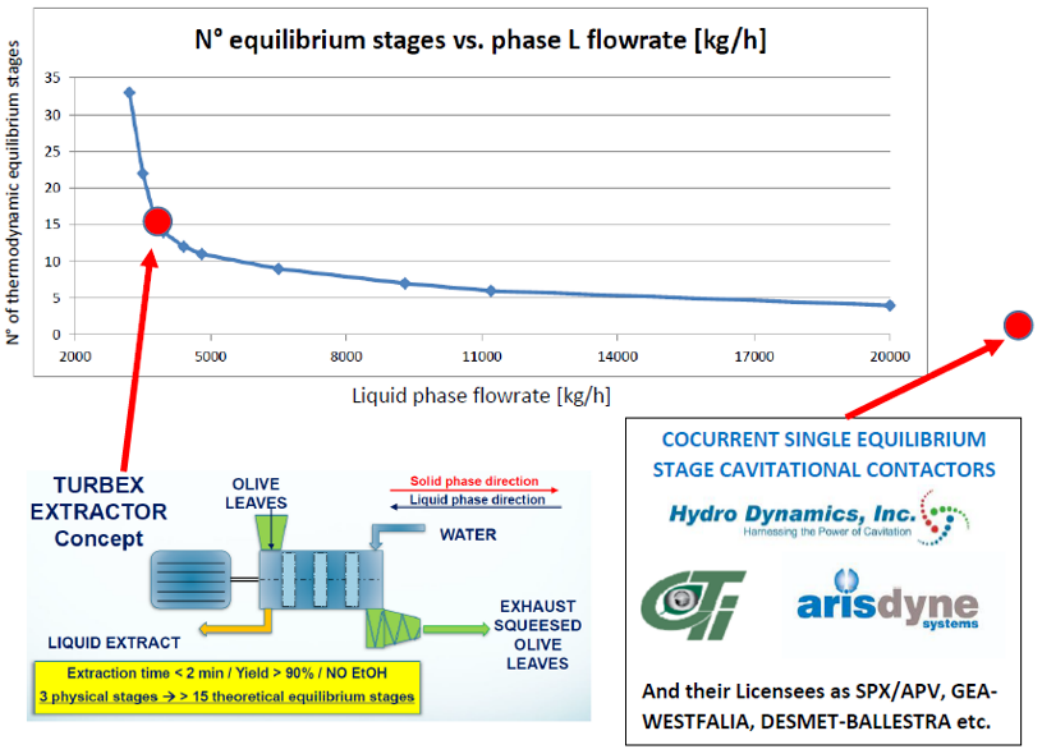


Figure 5.5: Results of comparative analysis between the number of equilibrium stages performed by the TURBEX and the other cavitational extractor varying the liquid phase flowrate (Courtesy to Giuliano Cavaglià)

On the market it is possible find other systems that allow to improve extraction efficiency by exploiting assisted hydrodynamic cavitation. The table compares the main characteristic aspects of the extractors.

ELEMENT OF COMPARISON	**EQUIPMENT**			
	CAVITUNE	***CFC REACTOR*** arisdyne systems	***SPR REACTOR*** Hydro Dynamics, Inc.	***TURBEX***
Phase contact mechanism	CAVITATION	CAVITATION	CAVITATION	SEQUENCE OF **TURBOLENCE CAVITATION SHEAR** STAGES
Static/Dynamic	STATIC	STATIC	DYNAMIC	DYNAMIC
Phase feeding	UNIQUE feed port	UNIQUE feed port	UNIQUE feed port	**SEPARATE** feed port
Operating mode	COCURRENT only	COCURRENT only	COCURRENT only	COCURRENT or **COUNTERCORRENT**
N° of cavitational events per pass through	150-500	100-400	20.000-30.000	**100.000-150.000** (3 rotor TURBEX)
Cavitation zone/ equipment crosssection	100%	100%	50-75%	**100%**
Single cavitation event intensity	5	5	3	5
Gas-Liquid operations	YES	YES	YES	YES
Liquid-Liquid operation	YES	YES	YES	YES
Solid-Liquid operations	Solid < 5 % Size < 200 µm	Solid < 5 % Size < 200 µm	Solid < 15 % Size < 1-2 µm	Solid < **25 %** Size < **5 µm**
Gas-Solid-Liquid operations	Solid < 5 % Size < 200 µm	Solid < 5 % Size < 200 µm	Solid < 15 % Size < 1-2 µm	Solid < **25 %** Size < **5 µm**
Mass transfer operations N° of equilibrium stages	1 (only COCURRENT)	1 (only COCURRENT)	1 (only COCURRENT)	**15** (3 rotot TURBEX COUNTERCURRENT)
Solid_liquid extraction yield achievable	Around 50%	Around 50%	50-60%	**>90%**
Turbolence interphase area generation	Limited	Limited	Negligible	**YES** Dedicated turbolent steges
High shear interphase area generation	Moderate	Moderate	Negligible	**YES** Dedicated high shear steges
Turbolence boost on mass transfer coefficient	Limited	Limited	Negligible	**YES** Dedicated turbolent steges
High shear boost on mass transfer coefficient	Moderate	Moderate	Negligible	**YES** Dedicated high shear steges

Tabella 5: Comparison between TURBEX and other rotor-stator cavitational extractors (Courtesy to Giuliano Cavaglià)

As can be easily seen, the TURBEX prototype today represents an advanced technology, able to manage solid and liquid flows in countercurrent fed separately. This configuration therefore allows to perform a higher number of theoretical equilibrium stages than competing systems.

The TURBEX system developed for experimentation is designed to process up to 150 kg (on a dry basis) of solid. The system consists of peripheral equipments that allow the management of outlet flows. The figure shows the prototype used in the experimental phase developed from the collaboration of the inventor Giuliano Cavaglià with the Adritz group.

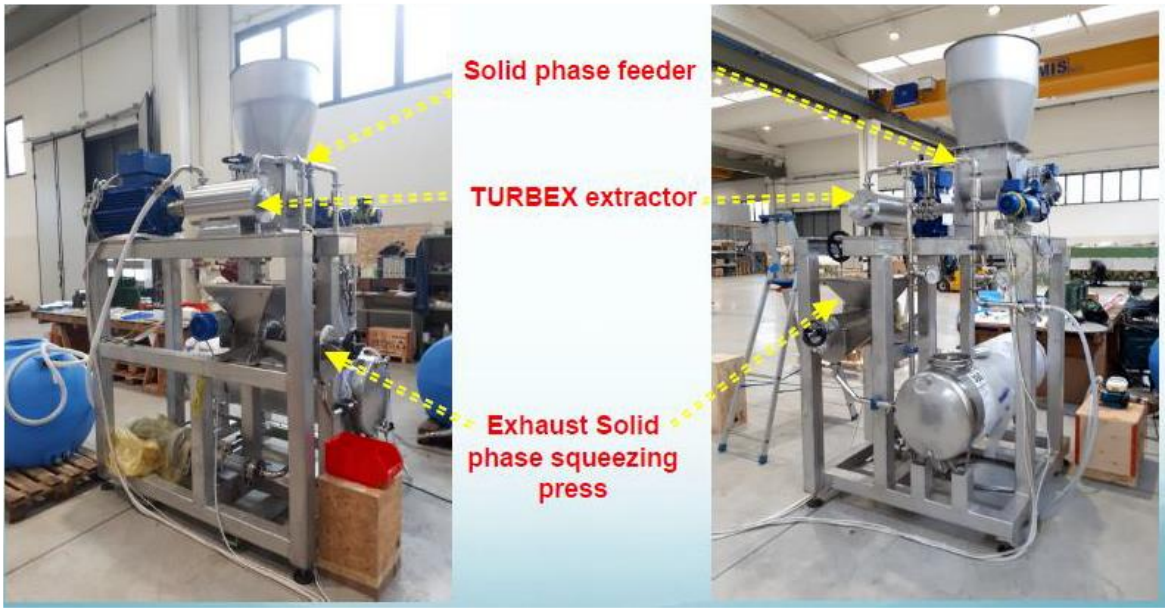


Figure 5.6: View of the TURBEX EX30 Prototype extraction unit. (Courtesy to Giuliano Cavaglià)

The whole system consists of a hopper in which the solid (previously soaked) is placed to be fed to the extractor via a screw feeder. The outgoing liquid stream containing the extract is filtered before being collected inside the drum.

The solid output stream needs more attention for its management. This in fact is first sent to a centrifugal decanter and then to a screw press to recover the soaked liquid.

All the theoretical explanations that justify the high performance of this extractor have been confirmed during the various experimental tests conducted to date on different plant matrices, thus proving to be a technology that can be adapted to the valorization of any type of waste from the food industry.

The results obtained experimentally demonstrate the high extraction efficiency of TURBEX equipment (up to 90%) with lower L/S ratios with residence times of the order of minutes. All this, in an industrial context, has the additional advantage of reducing investment and management costs by increasing profitability.

Chapter 6

6 Definition of a Turbex based spent tea leaves valorization process

6.1 6.1.1 Process Description and flow diagram

6.1.1 Targets

Starting from the results of the experimental tests performed on STL with TURBEX EX 30 prototype, it has been designed a process suitable to valorise tea industry byproducts/wastes, through a sequence of solid-liquid extraction steps, aimed to recover nutraceutically valuable components, such as polyphenols, proteins and dietary fibers. The following chapter explores the design of the entire system in its main components. The project, as regards the extraction section, is based on the data obtained during the experimental tests, adapting them to use at an industrial level by making an appropriate scale-up. The products of our interest are a mix of polyphenols, proteins and dietary fibers, which not only if not enhanced represent a loss due to the added value linked to beneficial activities but represent a risk factor for the environment, given their antioxidant activity, and inhibitory of bacterial activity. With a view to a green process, a lower consumption of solvent was opted for, making it possible to reduce the costs of both post-treatment of waste water and purification of the final product. Not less important is the competitiveness of the process from an industrial point of view, which is why it was decided to focus on technology with assisted cavitation extraction, which leads to significant increases in the final yields obtained.

6.1.2 Matrix characterization

The matrix that has been chosen to use as feedstock for the design of the plant is presented as industrial waste, with an average size of less than 200 μm. The chemical composition of the matrix, which is the same as entering the drying section of the plant, is visible in the table.

Feedstock composition		
Components	**%w HB**	**%w DM**
Water	70,00%	-
Polyphenols	1,50%	5,0%
Proteins	4,20%	14,0%
NDF extractable	10,50%	35,0%
NDF	11,70%	39,0%
Ash	1,20%	4,0%
Water sol. Carbohydrate (WSC)	0,90%	3,0%

Total	100,00%	100,0%

Table 6.1: STL feedstock composition

6.1.3 Plant Overview

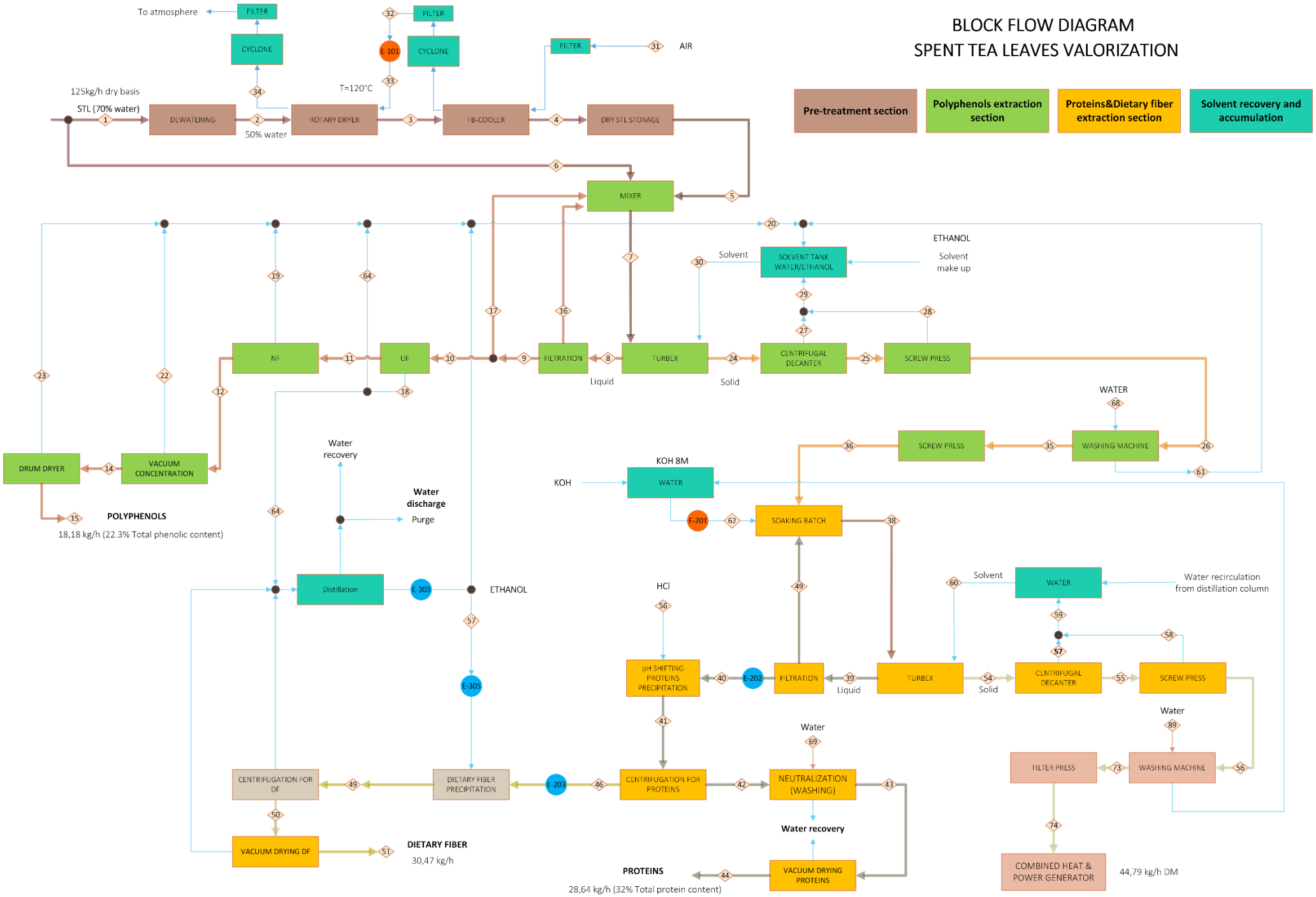
The plant is located in India in the Assam region, famous for the impressive production of Indian black tea, a drink characterized by a strong and spicy flavor. It was assumed that a door-to-door industrial plant had to be built with respect to a drink tea production plant, capable of treating an amount equal to 1.000 tons/y (on a dry basis) with a turndow ratio between 60% and 110% of the nominal capacity. The production of drink tea does not feature seasonal processing, so it is reasonable to assume that the plant will operate throughout the year. Despite this, it has been assumed that the production of the drink and therefore the corresponding production of the STL varies according to seasonality. Considering this variation, a drying section of the matrix was therefore provided to avoid any decomposition phenomena, since it is still organic material. The characteristics of the system are then shown in the table. The plant therefore works for a total of 8.000 hours per year, thus producing a post-drying flow rate of *125* kg/h of STL.

Supply type	**Spent Tea Leaves (STL)**	
Plant nominal capacity	1.000	ton/year (DB)
Plant operation period	8.000	hours
Nominal hourly feeding	125	kg/h
Hourly feeding MAX	137,5	kg/h
Hourly feeding MIN	75	kg/h
Turndown Ratio MAX	0,6	
Turndown Ratio MIN	1,1	

Table 6.2: STL valorization plant characteristics

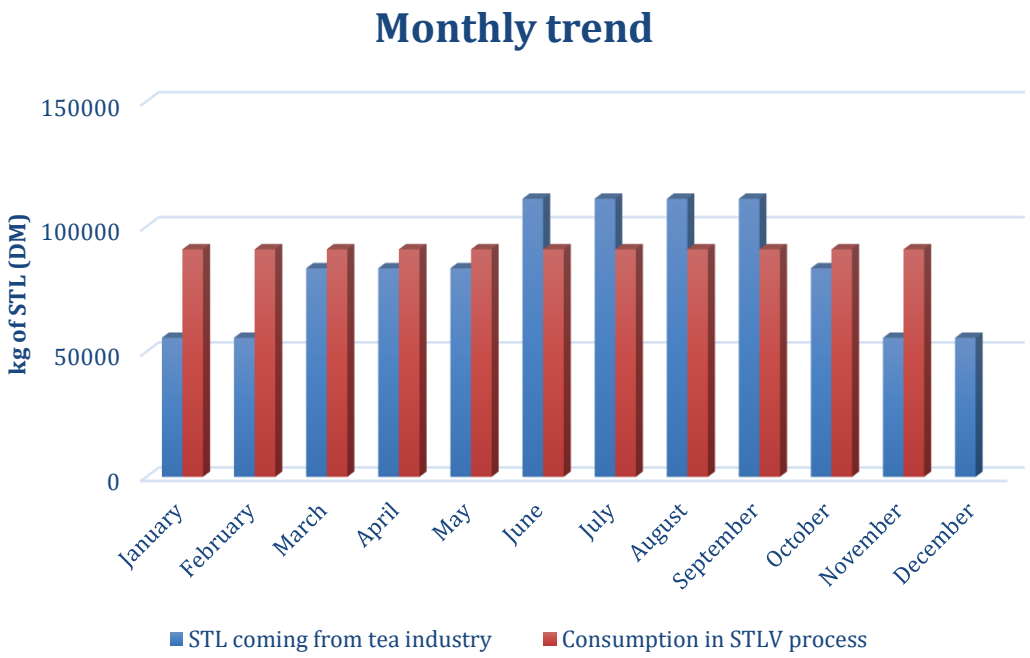
The process can ideally be divided into four fundamental sections:

- Pretreatment and storage section
- Polyphenol extraction section
- Protein and dietary fiber extraction section
- Solvent recovery section.


BLOCK FLOW DIAGRAM
SPENT TEA LEAVES VALORIZATION
Pre-treatment section
Polyphenols extraction section
Proteins&Dietary fiber extraction section
Solvent recovery and accumulation
To atmosphere
FILTER
CYCLONE
E-101
AIR
125kg/h dry basis
STL (70% water)
T=120°C
DEWATERING
ROTARY DRYER
FB-COOLER
DRY STL STORAGE
50% water
MIXER
ETHANOL
Solvent
SOLVENT TANK WATER/ETHANOL
Solvent make up
NF
UF
FILTRATION
TURBEX
CENTRIFUGAL DECANTER
SCREW PRESS
Liquid
Solid
WATER
WASHING MACHINE
DRUM DRYER
VACUUM CONCENTRATION
POLYPHENOLS
18,18 kg/h (22.3% Total phenolic content)
Water recovery
Water discharge
Purge
KOH 8M
KOH
SOAKING BATCH
Distillation
ETHANOL
HCl
pH SHIFTING PROTEINS PRECIPITATION
Water recirculation from distillation column
CENTRIFUGATION FOR DF
DIETARY FIBER PRECIPITATION
CENTRIFUGATION FOR PROTEINS
NEUTRALIZATION (WASHING)
Water recovery
VACUUM DRYING DF
DIETARY FIBER
30,47 kg/h
PROTEINS
28,64 kg/h (32% Total protein content)
VACUUM DRYING PROTEINS
FILTER PRESS
COMBINED HEAT & POWER GENERATOR
44,79 kg/h DM

6.1.3.1 Pretreatment section

In this section, the STL is dried by reducing the water activity to a value such that no degradation phenomena occur. In fact, the input matrix has a moisture content of 70% (on a wet basis) and in order to reduce it, two steps must be used. The first consists of a mechanical dewatering. This equipment allows to obtain a stream with a moisture content of 50% which is manageable by the following equipment. The further removal of the water content takes place through a rotaty dryer. The drying process is performed using hot air at an inlet temperature of 120 °C and air outlet temperature around 50 °C. The residue with a lower moisture content of 6% can now be stored after being cooled using a fluidized solid cooler. Once the drying phase is completed, the STL, ready for the subsequent phases, is stored inside the silo. It should be noted that the pre-treatment section is mainly used in the summer months, when the daily production is much higher than the annual average.



The graph 6.1 shows the monthly flow of STL arriving from the door-to-door ready to drink tea plant in blue, while the biomass consumption in nominal conditions is in red.

6.1.3.2 Polyphenol extraction section

TURBEX EX30 solid-liquid cavitational extractor is the key equipment of this plant section. Its design and scale-up has been made so that it reflects the parameters defined as optimal in the laboratory, that is, by exploiting the phenomenon of cavitation generated in a hydrodynamic way to weaken the cell wall of the matrix, and extract the *target components*.

As fluid dynamic parameters for the sizing of the plant at an industrial level, those recorded during the experimental tests in the pilot plant were used, thus defining temperature, residence time and L/S ratio.

The solid stream arriving, partly from the drying section and partly from the door-to-door ready to drink tea plant, is sent to a mixer in which it is added to the exhausted solvent stream, in this way the solid/liquid contact is maximized and allows to maintain the countercurrent fluid dynamics conditions. The stream in the slurry phase, exiting the mixer, is sent to the actual extraction section through a screw feeder. As anticipated, the extraction is carried out using a TURBEX EX30 hydrodynamic cavitational extractor in which thermodynamic equilibrium is reached, recovering the polyphenolic component of interest in the liquid phase.

The solvent used in this first step is a hydroalcoholic solution (ethanol/water 60:40 by volume) at room temperature. The use of this solution is not selective for the polyphenolic portion only, in fact the analyzes carried out on the extract confirm the presence of sugars and proteins. The operating parameters that allow an optimized extraction yield by almost completely exhausting the matrix, provide a L/S ratio of 9 with a residence time of 80 s. The outgoing liquid stream, previously filtered to remove possible traces of solids, is conducted towards the concentration section suitable for the separation of the phase extracted from the solvent.

The extract in solution in fact, must be concentrated in order to recover the solvent and to be able to arrive at a final product with a moisture content that allows storage without loss of quality.

The pretreatment and concentration operations were not done experimentally, therefore the design was done by analyzing the scientific literature.

The stream rich in polyphenols is sent to a concentration step with ultrafiltration and nano-filtration. The use of the two separation sets has the advantage of concentrating the polyphenols in the final product as the solubilized sugars remain in the permeate. This results in an increase in the economic value of the product. Downstream of the two steps, the retained stream is concentrated up to a solids content of 17%. However, being still far from the solid content value that can be managed by a drum-dryer, we opted for a further concentration using two multiple effect evaporators.

These evaporators work under vacuum at low temperature so to reduce the risk of polyphenol degradation. The concentrated liquid extract obtained with the vacuum evaporation phase has a dry residue content of approx 30% by weight.

The next step of concentration involves the use of a vacuum drum dryer, thus obtaining a product with quality that meets the sales requirements.

Polyphenols powder	
Water	0,9%
Polyphenols	**22,4%**
Proteins	17,4%
NDF extract. (fiber)	32,9%
NDF	26,3%
Ash	0,0%
WSC	0,1%

Table 6.3: Polyphenol rich extract composition

The table 6.3 shows the chemical composition of the final product rich in polyphenols which has the characteristics of a powder.

As for the solid phase leaving the TURBEX, this is sent to a centrifugal separator followed by a screw press as it is still soaked in the liquid to be enhanced. In this way the first extraction stage can be considered concluded. The liquid phase leaving the two dewatering equipment is collected inside the liquid extractant recyclig drum e thereafter it is immediately reinjected in the fresh liquid extractant feeding line.

The exhaust solid phase leaving the said screw press is further washed with water so to recover ethanol and subsequently dewatered up to a dry residue content of about 36% by weight, prior to be sent to the second extraction step.

6.1.3.3 Protein and dietary fiber extraction section

At this point of the process STL's composition is lignocellulosic and contains a high percentage of proteins and soluble dietary fiber.

The second stage is performed in a similar way to the previous one from a process point of view. The only differences are the operating parameters and the nature of the solvent as the nature of the components of interest is different. Within the scientific literature there are several studies concerning the extraction of proteins and DF from plant matrices.

For this particular process, following the results obtained from the experimental tests, it was decided to first carry out an alkaline hydrolysis and then the extraction using water at room temperature as the only solvent. The strategy used, unlike the works reported in the literature in which the entire extraction is performed with an alkaline solvent, involves a previous soaking with an alkaline solution inside the mixer. This phase has the purpose of breaking the hydrogen bonds between vegetable proteins and lignin, for this reason it is necessary to ensure a sufficient residence time, keeping the solid matrix in contact with a potassium hydroxide solution.

This operating mode allows to obtain a high extraction yield while reducing the amount of KOH. Specifically, the soaking is carried out at room temperature by adding the matrix (at 36% solids), arriving from the first stage, with a solution of KOH 8M in a ratio of 3,5 between liquid solution and solid, for a residence time of 30 minutes. The paste obtained in the mixer is then sent to the second extraction step performed by TURBEX. As anticipated, the extractive solvent consists of water with an L/S ratio equal to 7,5 on a dry basis.

At this point the liquid stream, rich in protein extracts and soluble fibers, previously filtered, is cooled down to 15 °C.

The strategy of separation and concentration of proteins and dietary fibers is different from that previously seen with polyphenols due to the different nature of the compounds.

The first step for the recovery of the compounds extracted from the solvent involves the precipitation of the proteins shifting the pH at value equal to 3 by adding HCl (36% bw). The low pH of the stream allows the isoelectric point of the proteins to be reached with consequent less interaction with the system, thus inducing precipitation. To obtain a high efficiency of the precipitation phase it is necessary to guarantee a residence time of 20 minutes, this allows to improve the morphology of the precipitate. The subsequent separation is carried out through a centrifugal decanter, obtaining on one side a stream rich in proteins with 30% solids and on the other a supernatant.

The protein slurry continues drying using a vacuum drum dryer with which it is possible to obtain the final protein powder product ready for sale. The table shows the chemical composition of the extract with a protein content of 32%.

Proteins powder	
Water	2,0%
Polyphenols	3,6%
Proteins	**32,6%**
NDF extract. (fiber)	33,7%
NDF	25,8%
Ash	0,0%
WSC	1,3%

Table 6.4: Protein rich extract composition

The supernatant, still rich in exploitable fibers, is further cooled to 5 °C and subsequently added to ethanol (96%), also previously conditioned, in a ratio of 1:0,85 supernatant: EtOH. The addition of the alcoholic solution, less polar than water, decreases the screening effect of the medium and when its content is sufficiently high the interaction between the phosphate groups become so strong to the point of forming stable bonds, inducing precipitation.

The low temperature proves to be a fundamental parameter in obtaining a better morphology of the precipitate itself. By analyzing in more detail the scientific literature regarding the ethanolic precipitation of vegetable fibers, a better separation performance in an acid environment is evident, which is why it was decided not to neutralize the supernatant.

Similarly, as done for proteins, after a time of 20 minutes, the subsequent separation of the dietary fibers is carried out in a centrifugal decanter and subsequently dried inside the vacuum drum dryer, obtaining a tea leaf flour with proven prebiotic and immunomodulatory functions.

Dietary Fiber powder	
Water	0,5%
Polyphenols	0,0%
Proteins	0,0%
NDF extract. (fiber)	**54,0%**
NDF	**45,0%**
Ash	0,0%
WSC	0,0%

Table 6.5: Dietary fiber powder extract composition

6.1.3.4 Solvent recovery section

The solutions separated by the various concentration steps are accumulated and sent to a distillation column for the recovery of the solvent. In particular, the distillation column allows to recover the quantity of ethanol used in the first extraction step and during the DFs precipitation. This operation is of fundamental importance as it allows to reduce both operating costs and lower environmental impact. The water extracted from the bottom of the column, in part, is purged in order to avoid the accumulation of dissolved compounds.

Supply		
Wet STL Feedstock	3.333,3	ton/y
Dry STL Feedstock	1.000	ton/y
Product		
Polyphenols powder *(total polyphenols content 22%)*	145	ton/y
Proteins powder *(total proteins content 32%)*	230	ton/y
Dietary Fiber powder	244	ton/y
Residue		
Lignocellulosic feedstock	354	ton/y
Destination	Heat&Power valorization	

Table 6.6: STL valorization plant characteristics

6.2 Utilities and reactants consumption

The low temperatures with which the extraction operations are carried out, together with the efficiency of the separation steps allow to reduce the specific consumption of the utilities within the plant.

The table 6.7 shows the final values. We then proceed with the calculation of the specific consumption of utilities.

Heat&Power consumption						
Utility	Duty		Quantity		Specific consumption	
CW	1.675	kW_t	52	m^3/h	0,7	$m^3_{CW}/kg_{Product}$
LPS	1.800	kW_t	3,3	ton/h	43	$kg_{LPS}/kg_{Product}$
Electrical	95	kW_e	-	-	1,3	$kWh/kg_{Product}$

Table 6.7: Heat and power consumption in STL valorization plant

In the same way, the consumption of the reactants used within the process is evaluated. As you can see, the consumption of acid and base are higher than alcohol due to the greater difficulty in recovery.

Reactants consumption				
	Quantity		Specific consumption	
HCl (37% w/w)	240	kg/h	3,2	$kg/kg_{Product}$
KOH	150	kg/h	2	$kg/kg_{Product}$
EtOH (96% w/w)	4	kg/h	0,05	$kg/kg_{Product}$

Table 6.8: Reactants consumption in STL valorization plant

Reactants		
Chloridric acid (37% w/w)	1900	ton/y
Potassium Hydroxide	1200	ton/y
Ethanol (96% w/w)	32	ton/y

Table 6.9: Yearly reactants consumption in STL valorization plant

6.3 Design basis

In this section the design criteria will be described thoroughly for all the principal pieces of equipment used inside the plant. These devices have been designed for the maximum required capacity, which corresponds to 110% of the nominal capacity.

The plant can be divided into four main sections:

- pre-treatment section;
- polyphenols extraction and concentration section;
- protein & dietary fiber extraction and concentration section;
- solvent recovery section.

Such a plant has been developed starting from experimental works and its aim is to valorize wastes spent tea leaves in order to create compounds with high added value.

6.3.1 Utilities characteristics

In order to complete the various functional operations, it is necessary to use the utilities available in the system. The table 6.10 shows the characteristics of those used for the design calculations.

Utility conditions			
Cooling Water			
	Temperature (IN)	20	°C
	Temperature (OUT)	40	°C
	Pressure	1	atm
River Water			
	Temperature	15	°C
	Pressure	1	atm
Ethylene glicol with water			
	Temperature	-10	°C
Low pressure steam			
	Temperature	158	°C
	Pressure	0,5	MPa g.
Electric Energy LT		415 Volt (+/-10%) -3 Ph- 50 +/- 0,5 Hz;	

Table 6.10: Utilities characteristics in STL plant valorization

6.3.2 Pre-treatment section

The first section of the plant involves a pre-treatment section where STL is brought to conditions where it can be easily stored and handled. In particular, moisture content must be reduced in order for it to be sent to the extraction section without degradation issue.

Storage tanks

In this plant there are two STL storage tanks: one is the first piece of equipment found on site and it is used for the storage of wet STL TK-101, while the second storage silo can be found after the fluidized bed cooler and it contains the dried biomass SILO DRY STL.

The wet storage silo has a residence time of 12 hours. This short hold-up period does not allow the formation of bacteria and therefore the biomass properties are intact and the biomass is not degraded. For this reason the wet storage vessel is preferred over the underground one. The conformation is vertical and the total calculated capacity is 10 cubic metres.

As far as the dry storage tank is concerned instead, this problem is no longer of importance since moisture content has been brought down to 6%.

The required volume must guarantee the possibility of storing the matrix during the summer months. This is necessary because a portion of the spent tea leaves arriving from the door-to-door ready to drink plant is not processed directly as it is higher than the manageable average. For this reason, a number of silos equal to 2 each with a volume of 55 m^3 is required.

This tanks are placed above ground and the geometry is vertical.

Screw Press (SP-101)

After the wet storage tank is located the screw press dewatering machine. The screw press is the first step of moisture removal. In this first step moisture content is reduced to 50% in weight, which is a tolerable percentage for the rotary dryer to work with.

The characteristics of the equipment were evaluated considering the input stream, identifying the appropriate model from the commercial standards. A similar approach was followed for the SP-102, SP-201 and SP-202.

Rotary dryer (RD-101)

The rotary dryer is a technology widely known and used in industrial drying processes, for this reason it represents an effective way to reduce humidity from the STL. The moisture content at the outlet of the dryer is 6%. The solid is brought to the inlet thanks to a belt conveyor from the dewatering.

The equipment uses air as a drying fluid, previously used as a coolant in the fluidized bed cooler. Knowing the physical characteristics of the incoming air, it is possible to establish the quantity required to reduce the humidity value. An air temperature not exceeding 120 °C was decided as a process parameter in order to reduce degradation phenomena on the matrix.

The dryer consists of a rotating steel drum with four openings. Two for the entry and exit of the product being processed and two for the entry and exit of the working fluid (hot air) necessary to perform the drying process. Inside the rotating drum, the product comes into

direct contact with the air in a counter-current flow. The operation, carried out continuously, guarantees a stable final product over time.

Fluidized bed cooler (FBC-101)

The dried STL reaches a temperature of 70 degrees at the output of the rotating drum and for this reason it is necessary to cool down the matrix before it can be stored inside the silo. The lowering of temperature is achieved by using a fluidized bed cooler into which air is blown from below at room temperature (about 25 °C). Also in this configuration there is a direct contact between the cooling fluid and the solid matrix which is why a high heat transfer coefficient is obtained.

At the end of the operation, the solid matrix at 30 °C is in the conditions to be sent to the storage silos with the aid of screw conveyor.

Cyclones (CY-101-CY-102)

There are two cyclones in the facility, both of which have been designed as tangential enter separation cyclones. For the design of the cyclones the method used has been taken from the book "Perry's Chemical Engineers' Handbook". The design considers the fluid's inlet velocity and its volume flowrate, and by combining these parameters with the geometry of the cyclone, provides with the possibility of sizing the device. Both cyclones found on site deal with a gas phase, and therefore their inlet velocity in this case has been set at 18 m/s.

The loss of pressure inside the cyclone has been evaluated, too. Pressure drops are a function of the fluid's inlet velocity, and they have a behaviour that tends to increase with the increase of velocity.

6.3.3 Polyphenols extraction and concentration section

The STL arriving from the drink tea plant and part of the stabilized one are taken to the first extraction step by means of belt conveyor T-102 and screw conveyors T-104.

This step has the main objective of extracting the polyphenolic content from the matrix using the unconventional technology of assisted cavitational extraction performed through the use of the TURBEX hydrodynamic cavitator EX-101, EX-201.

In order to efficiently conduct the extraction process, we opted for the use of an extractor capable of handling a flow rate of 200 kg/h of STL on dry basis. The geometric characteristics are similar to those of the equipment used during the experimental work. In particular, it is characterized by a single central rotor which guarantees the rotation of the two toothed wheels that delimit the three physical stages.

The process parameters reported above do not allow for selective extraction of the polyphenolic content. For this reason, easily extractable sugars are dissolved in the extracted stream.

The liquid extract leaving the turbex is collected in the accumulation drum D-101 and then pumped to the next steps.

The design of the extractor described in this section is similar to that used in the section for extracting proteins and dietary fiber EX-201.

Ultrafiltration membranes (UF-201 A/B)

The extract is sent to a buffer tank before the section involving membranes. Membranes are placed in parallel to allow the regeneration, so that when one is in regeneration the other one can be used to maintain the process continuous.

The first stage is a set of ultrafiltration membranes, working at 5 atm which allows to remove 78% of the solvent in a single step.

Ultrafiltration membranes have been designed starting from the permeate flux, initially set at 10 $l/m^2/h$. This value, together with the yield of separation, is used to calculate the total area. As regards ultrafiltration, they are tubular membranes in particular the model utilized is the Industrial Ultrafiltration series from GK. Having all these details enables to calculate the total amount of area required. In particular, for this section, 2 modules are required to perform the separation with a total operating area of 46,4 m^2.

Permeate flux decreases with time, hence separation performances tend to follow the same pattern. In particular, permeate flux tends to decrease until it reaches a stationary value. By performing a linearization of this curve and fixing a percentage of flux after which regeneration starts, it is possible to extract the operating time by linear interpolation. The slope of the straight line represents the fouling index (0,0147 in this case). The percentage of flux after which regeneration starts is set at 20% of the initial value. By following this path, the estimated operating time for ultrafiltration membranes is 150 minutes. After this time, fouling becomes too strong and the regeneration process takes place. This process involves different solvents treating the membranes for different periods of time. The details of the cleaning process are underlined in the table 6.11 below.

Regeneration solvent	**Time (min)**
Process water	10
NaOH 0,5 M	40
Process water rinse	10
Nitric acid 0,5%	40
Process water rinse	10
Total regeneration time	**110**

Table 6.11: Regeneration condition U-F membranes

Since the estimated operating time for the membranes is 150 minutes and the regeneration process occurs in 110 minutes, the amount of membranes must be doubled so that if one section is following regeneration, the other one is operative and the continuity of the process is guaranteed.

The permeate stream is composed of water and ethanol for a combined 99%, and the remaining part is made of reducing sugars present in cellulose and part of the polyphenols that are lost in the stream. The retentate, which now contains a higher percentage of polyphenols, is still not pure enough because a high fraction of solvent is still present. This stream is sent to an intermediate buffer tank operating at 4 atm.

Nanofiltration membranes (NF-101)

As discussed in the previous section, a further step of solvent removal must be provided to the stream. This second stage of separation involves nanofiltration membranes. The stream at the outlet of buffer D-104 is pumped up to 15 atm to enter the membrane section.

Nanofiltration membranes are characterised for their extremely high rejection to the solute, 98% for the polyphenols.

The model used for this operation is the Industrial Nanofiltration series DL8040C50, characterized by an approximate molecular weight cut-off of 150-300 Dalton for uncharged organic molecules. The average permeate flux for these membranes is 31 m^3/day and an active area of 27,9 m^2 per module. These data are allow to set up a similar calculation to the previous one to estimate the actual number of membranes and the permeate flux. Specifically, the number of membranes needed is 1, with an initial permeate flux of 1,02 l/m^2/h. Fouling and regeneration have to be evaluated in this scenario as well, and the results are shown in the following table 6.12.

Regeneration solvent	**Time (min)**
Process water	10
NaOH 0,5 M	20
Process water rinse	10
Nitric acid 0,5%	20
Process water rinse	10
Total regeneration time	**70**

Table 6.12: Regeneration condition N-F membranes

In this case, the linearization of the permeate flux's curve shows a fouling index equal to 0,0025 and, following the same hypothesis used for ultrafiltration, it is possible to calculate the operating time, which is 600 minutes. Since the total regeneration time in this case is much lower, the total number of membranes must not be doubled.

The fact of having oversized the membrane allows to manage the stream variation through a buffer tank placed before and after the membrane.

The permeate stream follows the same path of the ultrafiltration stream. In fact, the permeate is mixed with ultrafiltration's permeate pumped to the solvent recovery section in the buffer tank-D-302.

The retentate enters the intermediate tank, D-104.

Evaporators for polyphenols (EV-201 and EV-202)

The retentate coming from the tank D-105 is sent to a series of two co-current evaporators: EV-101 and EV-102. The first evaporator works at 0,5 atm whereas the second one operates at 0,3 atm.

EV-101 was designed starting from the required specific regarding the concentration of solute at the solid outlet of the first evaporator: 0,22. Mass balances were set up according to Kern's methodology, and the biphasic equilibrium mixture diagram enabled to extract the boiling point of the mixture and its equilibrium composition. This information supplies with the possibility of calculating the equipment's outlet conditions in terms of temperature and mass composition, and the inlet flowrate of low pressure steam entering the evaporator. On top of that, the exchange area was calculated by using a fouling factor equal to 0,001 and overall heat exchange coefficient obtained from Kernel book. As a result, the estimated area of the first evaporator is 0,41 square metres. The temperature of the two outlet streams are at same temperature, 66 °C, which is the boiling point of the solvent in these conditions. These two streams are fed to the second evaporator.

The second evaporator, EV-102, is designed in a similar way. The heating means is the vapour stream fed from the first evaporator at 0,5 atm of pressure containing water and ethanol.

The estimated concentration of solute at the outlet is now raised to 0,3. The same hypothesis and calculations have been performed for this evaporator and the result are in accordance to the required specifics. Going deeper into the details, the final required exchange surface for the second effect is 1,475 m^2 with a operating temperature of 55,6 °C, which corresponds to the solvent's boiling point at 0,3 atm of pressure.

Considering the whole system the total efficiency of the two evaporators is 3,11 kg of evaporated solvent per kg of inlet steam.

The heating medium of the second effect, once condensed and further cooled in the HE-102 heat exchanger, is used as a motor fluid in the ejector which guarantees the operation of the plant in vacuum conditions.

The streams moving away through the two effects being sufficiently concentrated of ethanol are stored inside the solvent storage tank D-106 in order to be reintegrated in the process.

This method allows to obtain a slurry with a solid concentration of 30% in weight. Unfortunately it is not enough to obtain a marketable product, since the stream still contains a high percentage of solvent. For this reason one last stage is necessary for the purification of polyphenols.

Drum dryer for polyphenols (DD-101)

The last stage of purification involves a vaccum drum dryer. The dryer used is an ANDRITZ Model T Double Drum Dryer. Specifics regarding this piece of equipment were found on the Handbook of Industrial Drying.

Considering the heat necessary to remove the vapors from the incoming stream and evaluating the appropriate value of the global exchange coefficient, it is possible to calculate the minimum area necessary to perform the operation. For the final choice of the dimensions of the dryer it is essential to consider that the area useful for drying is represented by the portion included in a rotation of 300° of the single roller.

The peculiarity of this equipment lies in providing heat indirectly, furthermore it was decided to carry out the vacuum drying step with the double advantage of maintaining a low temperature as much as possible and to be able to recover the solvent still containing ethanol.

The low temperatures along the entire line makes it possible to preserve the chemical activity of the polyphenols, thus being able to put on the market a product that meets quality standards.

This data has been utilised to calculate the required flowrate of low pressure steam to guarantee such performances and, by combining the mass balances with the specific evaporation rate, the overall exchange surface has been successfully calculated.

The same model of drum dryer with the same specifications can also be found elsewhere in the plant. Specifically: DD-201 and DD-202 follow the same sizing rules as DD-101.

Residue extraction with water (W-201)

The residue from the polyphenols extraction (EX-101) still contains 28% of ethanol which has to be recovered and reintegrated. The solid is then sent to the washer, the extractor model selected is the Kennedy one.

The solvent used for this separation is process water entering at room temperature.

The system has been dimensioned to reduce the quantity of ethanol to 1%, to obtain this result with a counter-current flow an L/S ratio of 1,05 is required.

The recovered extract is then pumped to the storage tank of the hydroalcoholic solvent D-106.

The solid, purified from the presence of ethanol, is concentrated again, inside the SP-201 screw press, to eliminate excess water, obtaining a stream of 36% solids.

Water-ethanol storage vessel (D-105)

This tank contains the solvent used for the extraction of polyphenols in EX-101. Inside this vessel there needs to be a settled ratio of 60% volume of ethanol.

The tank must be designed, just like all other tanks, to keep the full quantity of solvent inside it for a given residence time. In this particular case, full residence time is four hour that result in a required volume of 5 cubic metres. The capacity of the tank calculated with this procedure is the increased by a security factor which corresponds to an additional 20%. The selected vessel, from commercial standard, to guarantee such conditions is a vertical vessel with a nominal capacity of 7,5 m^3 and the temperature inside the tank is 30 °C.

6.3.4 Protein & dietary fiber extraction and concentration section

The third section of the plant involves the separation of proteins and dietary fiber from the biomass, using, in this case, pure water as a solvent.

Since the first extraction follow a similar path, the equipment utilised has been designed with the same hypothesis for each extraction.

The release and extraction of the components of interest in this step is facilitated through a peventive hydrolysis in an alkaline environment. In particular, the solid stream after washing and squeezing is added to an 8 M solution of potassium hydroxide inside the mixer in a ratio of 3,5 L/S (on a dry basis).

6.3.4.1 Mixer MX-201

The alkali solution is pumped from its tank D-205 to a mixer MX-201 where it enters in contact with the biomass. To ensure efficient contact between the tea leaf residue and the alkaline solution, it was decided to soak in batch conditions. For this reason buffer D-201 has been placed upstream, whose sizing allows to accumulate the feed during the soaking time.

This mixer is characterized by a conical bottom which facilitates the unloading, by gravity, of the post soaking paste inside the hopper which feeds the screw feeder SF-201.

Disc stack centrifuge (DS-201-DS-202)

The centrifuge is used because the flowrate that is being treated is too high to use a regular static decanter in the precipitation of proteins and dietary fibers. This piece of equipment concentrates the solid removing part of the solvent, the method implemented is the Coulson and Richardson one. From correlations taken from this source it has been possible to evaluate σ. This parameter allows to evaluate, together with various parameters such as the efficiency, the settling velocity and the rotational velocity.

Proteins stream neutralization (W-202)

The separated solid stream of the centrifuge, rich in protein content, carries with it a portion of acid used for the pH variation and subsequent precipitation. For this reason, before sending the stream to the drum dryer for final drying, it is washed with water using a washer similar to the one previously described (W-201). This washer uses an L/S ratio of 0,99 allowing to reduce the acid content below 1%.

Heat exchangers

The procedure followed for the design of these exchangers is the Kern method, where the shell side and tube side are designed starting from a hypothesised overall heat exchange coefficient and, consequently, an estimated exchange surface. By using the fluid's properties for both shell side and tubes side the Reynolds number and the mass velocity are established. These coefficients represent a starting point for the evaluation of the heat coefficient.

The evaluation of the number of tubes is made possible by setting up a reverse calculation to obtain the actual values for the exchanger, such as required clean heat coefficient, actual number of tubes and required exchange surface. When evaluating the dirty overall heat exchange coefficient, it must be taken into consideration the fouling factor, which varies depending on the fluid passing through the tubes and the shell.

The heat coefficient obtained in this way must not be higher than the estimated one because that would mean the heat exchange surface is not high enough to assure the necessary exchange of heat, and this coefficient is then put back into the calculation to verify the actual required area for the coefficient and to see whether the set value of tubes is enough.

The Kern method also allows to estimate the pressure drops inside the exchanger. The distinction between the sides is that in the tubes side not only must distributed pressure

drops be evaluated, but also localised pressure drops need to be looked at, whilst the latter are not present in the shell side.

Pumps

Pumps were chosen taking into account the flowrates and the hydraulic heads to be supplied.

Belt conveyor

Belt conveyor has been designed to transport the inlet solid STL from different equipment.

This transport system, which manages a humid matrix, allows to reduce any problems of destruction differently from screw conveyors, used for biomass with a low moisture content.

Knowing the mass flowrate of STL to be moved, the distance between the two equipment (which needs to have an inclination of less than 45° according to the slope angle) and speed belt (0,1 m/s) we can chose the belt width from standard commercial availability. Five rolls, with diameter of 70 cm, ensure the correct sustain during transport.

Buffer Tank

The buffer tanks are necessary for the continuouty of the entire process. All these tanks are sized considering the liquid volume and a void fraction over the liquid level of 0,2. For all the buffers is chosen a vertical arrangement.

The minimum volume required is evaluated in order to accommodate two batch discharges from the mixers, ensuring the liquid head for the discharge in the main process stream through control valves.

The buffers have also been arranged upstream of the nano and ultra filtration system in order to easily allow cleaning operations.

Buffer tanks are constructed in stainless steel AISI 316.

6.3.5 Solvent recovery section

Ethanol separation column (T-301)

As seen, ethanol plays a fundamental role in the success of the entire process. The streams that leave the various unit operations are recovered, partly inside the collection drum D-105, the content of which is fed directly into the process and the remaining part in the D-302 tank. This drum has the purpose of accumulating the hydroalcoholic solution to be fed into the distillation column to remove the excess water accumulated in the various operations. For this purpose the sieve-trayed distillation column C-301 was dimensioned.

The column is equipped with 19 stages where the inlet is fed at stage 8. Furthermore, the molar distillate to feed ratio is 0,48 and the molar reflux ratio is set to 3,55. The column works at atmospheric pressure and the feed enters the column with a temperature of 70°C.

By imposing a specific of 0,60 metres of tray spacing, the results obtained from the simulation show that the column is 18,5 m tall and has a diameter of 2,9 m. The separation of ethanol in the distillate is 99,5 % of the initial amount.

Part of the stream exiting from the bottom of the column, containing water and dissolved solids, is purged to avoid their accumulation within the process.

Residue washing with water (W-301)

The solid residue, now exhausted of its components in the various extraction steps, is destined for further valorisation for the production of thermal and electrical energy. Before being able to allocate the exhausted biomass to the following combustion steps, it is preferable to reduce the quantity of dissolved salts in the water content soaked in the matrix. For this reason, a washer similar to those previously arranged in the plant was used with a L/S ratio of 1,05.

Filter press (PF-001)

This equipment is necessary to reduce the water content of the exhausted biomass in order to exploit it for a subsequent production of thermal and electrical energy. It has been chosen a filter press because it has good performances in water removal and it is a well-established technology. The minimum dryness required is 0,58 (it needs experimental validation), chamber thickness is 25 mm and the cycle time is 48 min. From these data, knowing the volumetric flowrate of slurry it is possible to calculate the total volume of the filter press and the number of plates needed. It is assumed an expandability of 10% and the total number of membrane plates are 18. It is chosen an automatic filter press to reduce the cycle time and from catalogue the equipment that best fits the specifications is the filter press with membrane plates of size 630x630 mm. The calculation of the ancillary equipment requirements is done to maintain the same separation performances of another technical inquiry but scaled according to the different flowrate of slurry to be treated. The filtration membranes are polymeric and the structure has a 316 stainless coating to increase corrosion resistance.

Storage silo-PPs, silo-proteins and silo DFs

Solids are stored in vertical silos with hopper bases. The hoppers have a discharge angle of 60° (vs vertical) which is higher than the repose angle of all solids. For the calculation of bulk solid volume a minimal void fraction of 0,4 is considered.

Product storage tanks are arranged in parallel configuration to ensure that one storage section is filling, another is under quality control and the last one is discharging. The switch between these tanks is done with solenoid valves.

6.4 6.1.4 Equipment list

TAG	DESCRIPTION	DETAILS	*SPC N°*
PRE-TREATMENTS SECTION			
P-101	Blower	INLET PRESSURE **1** bar OUTLET PRESSURE **3** bar INLET TEMPERATURE **25** °C TYPE **Centrifugal** MODEL **Maffei lateral channel blower SM7 (50 Hz)** FLOWRATE **(nom) 607,95** m^3/h	
P-101	Blower	INLET PRESSURE **1** bar OUTLET PRESSURE **3** bar INLET TEMPERATURE **40** °C TYPE **Centrifugal** MODEL **Maffei lateral channel blower SM7 (50 Hz)** FLOWRATE **(nom) 607,95** m3/h	
CY-101	Cyclone	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **40** °C TYPE **Conical cyclone** MATERIAL **AISI 304** FLOWRATE **(nom) 604** m^3/h DIAMETER **109** mm OUTLET DIAMETER **109** mm INTERNAL DIAMETER **219** mm PRESSURE DROP **850** Pa	
CY-102	Cyclone	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **50** °C TYPE **Conical cyclone** MATERIAL **AISI 304** FLOWRATE **(nom) 604** m^3/h INLET DIAMETER **109** mm OUTLET DIAMETER **109** mm INTERNAL DIAMETER **219** mm PRESSURE DROP **850** Pa	
E-101	Air heater	OPERATING PRESSURE (shel side) **1,5** bar OPERATING PRESSURE (tubes side) **1,5** bar INLET TEMPERATURE (shell side) **158,00** °C OUTLET TEMPERATURE (shell side) **158,00** °C INLET TEMPERATURE (tubes side) **40,00** °C OUTLET TEMPERATURE (tubes side) **120,00** °C TYPE **Shell&Tubes** FLOWRATE (tube side) **(nom) 4820** kg/h FLOWRATE (shell side) **(nom) 12** kg/h EXCHANGE AREA **0,6** m^2 TUBES NUMBER **398** TUBES LENGTH **365** mm TUBES INNER DIAMETER **2,21** mm NUMBER OF PASSES **2**	

		DUTY **19** kW	
E-102	Coaxial heat exchanger	OPERATING PRESSURE (shel side) **1** bar OPERATING PRESSURE (tubes side) **1** bar INLET TEMPERATURE (in side) **65,00** °C OUTLET TEMPERATURE (in side) **30,00** °C INLET TEMPERATURE (out side) **10,00** °C OUTLET TEMPERATURE (out side) **20,00** °C TYPE **Coaxial tube** FLOWRATE (in side) **(nom)** **26,6** kg/h FLOWRATE (out side) **(nom)** **31,1** kg/h EXCHANGE AREA **0,05** m^2 TUBES NUMBER **-** TUBES LENGTH **2377,5** mm NUMBER OF PASSES **-** DUTY **0,4** kW	
E-103	Vapor drum dryer condenser	OPERATING PRESSURE (shel side) **1** bar OPERATING PRESSURE (tubes side) **1** bar INLET TEMPERATURE (shell side) **45,00** °C OUTLET TEMPERATURE (shell side) **45,00** °C INLET TEMPERATURE (tubes side) **20,00** °C OUTLET TEMPERATURE (tubes side) **40,00** °C TYPE **Shell&Tubes** FLOWRATE (tube side) **(nom)** **41,80** kg/h FLOWRATE (shell side) **(nom)** **494,4** kg/h EXCHANGE AREA **0,7** m^2 TUBES NUMBER **20** TUBES LENGTH **1463** mm TUBES INNER DIAMETER **11,4** mm NUMBER OF PASSES 1**2** DUTY **11,5** kW	
RD-101	Rotary dryer	OPERATIVE PRESSURE **1** bar FEED TEMPERATURE **25-70** °C AIR TEMPERATURE **120-50** °C TYPE **Agitator rotary dryer** FEED FLOWRATE **(nom)** **55,6** kg/h AIR FLOWRATE **(min)** **386** m^3/h **(nom)** **607** m^3/h WATER REMOVED **26** kg/h DUTY **1,3** kW	
FBC-101	Fluidized Bed Cooler	OPERATING PRESSURE **1** bar INLET TEMPERATURE **25** °C OUTLET TEMPERATURE **40** °C UTILITY **Air** TYPE **Fluidized bed** FLOWRATE **(nom)** **607** m^3/h	
T-101	Dry STL belt conveyor	TYPE **belt conveyor** CAPACITY **30** kg/h LENGTH **30000** mm BELT SPEED **0,01** m/s BELT WDTH **50** mm BELT ROLL DIAMETER **700** mm NUMBER OF ROLL **5**	

		POWER	**0,1**	kW	
T-102	Wet STL belt conveyor	TYPE CAPACITY LENGTH BELT SPEED BELT WDTH BELT ROLL DIAMETER NUMBER OF ROLL POWER	**belt conveyor** **350** **10000** **0,1** **200** **700** **5** **0,1**	 kg/h mm m/s mm mm kW	
T-103	STL screw conveyor	TYPE CAPACITY	**screw feeder** **50**	 kg/h	
TK-101	Wet STL storage tank	OPERATIVE PRESSURE OPERATIVE TEMPERATURE TYPE VOLUME INTERNAL DIAMETER MATERIAL	**1** **25** **Underground tank** **10** **3000** **Carbon Steel**	bar °C m^3 mm 	
F-101	Filter air	OPERATIVE PRESSURE OPERATIVE TEMPERATURE	**1** **25**	bar °C	
F-102	Sleeve filter	OPERATIVE PRESSURE OPERATIVE TEMPERATURE	**1** **40**	bar °C	
F-103	Sleeve filter	OPERATIVE PRESSURE OPERATIVE TEMPERATURE	**1** **50**	bar °C	
RV-101	Rotary valve				
RV-102	Rotary valve				
RV-103	Rotary valve				
RV-104	Rotary valve				
SILO DRY STL A/B	Dry STL storage silo	OPERATIVE PRESSURE OPERATIVE TEMPERATURE TYPE VOLUME INTERNAL DIAMETER BODY HEIGHT MATERIAL	**1** **25** **Alimatic Silo Type NL 2461** **55** **2400** **10000** **AISI 316**	bar °C m^3 mm mm 	
SP-101	Screw press	MODEL CAPACITY POWER FEED SCREEW DIA. FEED SCREW PITCH FEED SCREEW ROT. SPEED PRESS SCREW DIA. DIMENSION	**TZ180** **500** **3** **180** **100** **15** **190** **1700*500*800**	 kg/h kW mm mm rpm mm mm	

POLYPHENOLS EXTRACTION SECTION			
DD-101	Polyphenols rotary drum dryer	OPERATIVE PRESSURE **0,1** atm FEED TEMPERATURE **55** °C TYPE **Double drum dryer** MODEL **Model T** MATERIAL **AISI 304** FEED FLOWRATE **(nom)** **60** kg/h LPS FLOWRATE **(nom)** **0.12** kg/s DRYING AREA **3,1** m^2 HEIGHT **1700** mm LENGTH **1900** mm WIDTH **2300** mm DRUM DIAMETER **500** mm DRUM LENGHT **1000** mm DUTY **24,64** kW INSTALLED POWER **7,5** kW	
EV-101	Ethanol evaporator	OPERATIVE PRESSURE **0.5** bar OPERATIVE TEMPERATURE **66** °C TYPE **Short vertical tubes** EXCHANGE AREA **0.931** m^2 N° OF TUBES **47** TUBE INTERNAL DIAMETER **12.7** mm TUBE LENGTH **500** mm FEED FLOWRATE **(nom)** **0,113** m^3/h LPS FLOWRATE **(nom)** **17,05** kg/h HEAT DUTY **9,89** kW MATERIAL **AISI 304**	
EV-102	Ethanol evaporator	OPERATIVE PRESSURE **0,3** bar OPERATIVE TEMPERATURE **55,6** °C TYPE **Short vertical tubes** EXCHANGE AREA **3,35** m^2 N° OF TUBES **81** TUBE INTERNAL DIAMETER **26,6** mm TUBE LENGTH **500** mm FEED FLOWRATE **(nom)** **0,086** m^3/h HEAT DUTY **8,84** kW MATERIAL **AISI 304**	
EX-101	Polyphenols extractor	OPERATIVE PRESSURE **1** bar FEED TEMPERATURE **25** °C SOLVENT TEMPERATURE **30** °C TYPE **TURBEX Hydrodinamic cavitator** FEED FLOWRATE **(nom)** **125** kg/h **(max)** **200** kg/h SOLVENT/FEED RATIO **9**($kg/kg_{dry\ bases}$) RESIDENCE TIME **80** se STAGE **3** ROT. SPEED **900** rpm POWER REQUIRED **8** kW	
DC-101	Centrifugal decanter	SOLID CAPACITY **500** kg/h INSTALLED POWER **20** kW EFFICIENCY **45%**	

SP-102	Screw press	MODEL **TZ180** CAPACITY **500** kg/h POWER **3** kW FEED SCREEW DIA. **180** mm FEED SCREW PITCH **100** mm FEED SCREEW ROT. SPEED **15** rpm PRESS SCREW DIA. **190** mm DIMENSION **1700*500*800** mm	
S-101	Ejector		
F-104	Filter	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **25** °C	
NF-101	Polyphenols nanofiltration membrane	TRANSMEMBRANE PRESSURE **15** bar TEMPERATURE **25** °C TYPE **Spiral membrane** MODEL **DL8040C50** FEED FLOWRATE **(nom)** **0,22** m3/h CUT-OFF **450** Da TOTAL AREA **27,9** m^2 WORKING TIME **600** min REGENERATION TIME **70** min	
MX-101	Humidificatio n mixer	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **25** °C TYPE **Vertical Mixer** VOLUME **0,2** m^3 RESIDENCE TIME **20** min	
G-101	Ultrafiltration pump	TYPE **Centrifugal** ELECTRIC CONSUMPTION **4,80** kW PUMP EFFICIENCY **0,85**	
G-102	Pump	TYPE **Centrifugal** ELECTRIC CONSUMPTION **2,7** kW PUMP EFFICIENCY **0,85**	
G-103	Pump	TYPE **Centrifugal** PUMP EFFICIENCY **0 ,85**	
G-104	Pump	TYPE **Centrifugal** PUMP EFFICIENCY **0,85**	
G-105	Pump	TYPE **Centrifugal** PUMP EFFICIENCY **0,85**	
G-106	Progressing cavity pump	TYPE **Progressing Cavity** PUMP EFFICIENCY **0,85**	
G-107	Progressing cavity pump	TYPE **Progressing Cavity** PUMP EFFICIENCY **0,85**	
SF-101	Screw feeder to polyphenols extractor	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **25** °C FLOWRATE **(nom)** **388,2** kg/h	

D-101	Polyphenols extract buffer	OPERATIVE PRESSURE OPERATIVE TEMPERATURE TYPE VOLUME INTERNAL DIAMETER HEIGHT		**1** **25** **Vertical tank** **2** **1100** **2000**	bar °C m^3 mm mm	
D-103	Polyphenols nanofiltration buffer tank	OPERATIVE PRESSURE OPERATIVE TEMPERATURE TYPE VOLUME INTERNAL DIAMETER HEIGHT MATERIAL		**1** **25** **Vertical tank** **2** **1100** **2000** **Carbon Steel**	bar °C m^3 mm mm 	
D-102	Polyphenols ultrafiltration buffer tank	OPERATIVE PRESSURE OPERATIVE TEMPERATURE TYPE VOLUME INTERNAL DIAMETER HEIGHT MATERIAL		**1** **25** **Vertical tank** **1** **900** **1500** **Carbon Steel**	bar °C m^3 mm mm 	
D-104	Multiple effect buffer tank	OPERATIVE PRESSURE OPERATIVE TEMPERATURE TYPE VOLUME INTERNAL DIAMETER HEIGHT MATERIAL		**1** **25** **Vertical tank** **1** **900** **1500** **Carbon Steel**	bar °C m^3 mm mm 	
D-105	Ethanol/water storage tank	OPERATIVE PRESSURE OPERATIVE TEMPERATURE TYPE VOLUME INTERNAL DIAMETER HEIGHT MATERIAL		**1** **25** **Vertical tank** **7,5** **1600** **3500** **Carbon Steel**	bar °C m^3 mm mm 	
UF-101 A/B	Polyphenols ultrafiltration membrane	TRANSMEMBRANE PRESSURE TEMPERATURE TYPE MODEL FEED FLOWRATE CUT-OFF TOTAL AREA WORKING TIME REGENERATION TIME	**(nom)**	**5** **25** **Spiral membrane** **GK8040F50** **0,74** **2000** **46,4** **150** **110**	bar °C m^3/h Da m^2 min min	

PROTEINS AND DIETARY FIBER EXTRACTION SECTION			
DS-201	Proteins Centrifuge	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **15** °C TYPE **Disks centrifuge** FLOWRATE **(nom) 1,38** m^3/h DISKS SLOPE **45°**	
DS-202	Dietary fiber Centrifuge	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **5** °C TYPE **Disks centrifuge** FLOWRATE **(nom) 2,42** m^3/h DISKS SLOPE **45°**	
D-201	Buffer tank	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **25** °C TYPE **Vertical tank** VOLUME **1** m^3 INTERNAL DIAMETER **900** mm HEIGHT **1500** mm MATERIAL **Carbon Steel**	
D-202	Proteins&DF extract buffer	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **25** °C TYPE **Vertical tank** VOLUME **3** m^3 INTERNAL DIAMETER **1200** mm HEIGHT **2500** mm MATERIAL **Carbon Steel**	
D-203	Buffer proteins precipitation	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **25** °C TYPE **Vertical tank** VOLUME **2** m^3 INTERNAL DIAMETER **1100** mm HEIGHT **2000** mm MATERIAL **Carbon Steel**	
D-204	Buffer dietary fiber precipitation	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **25** °C TYPE **Vertical tank** VOLUME **3** m^3 INTERNAL DIAMETER **1200** mm HEIGHT **2500** mm MATERIAL **Carbon Steel**	
D-205	Alkaline solution storage tank	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **25** °C TYPE **Vertical tank** VOLUME **1** m^3 INTERNAL DIAMETER **900** mm HEIGHT **1500** mm MATERIAL **Carbon Steel**	

D-206	Water storage tank	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **25** °C TYPE **Vertical tank** VOLUME **3** m^3 INTERNAL DIAMETER **1200** mm HEIGHT **2500** mm MATERIAL **Carbon Steel**	
E-201	Vapor drum dryer condenser	OPERATING PRESSURE (shel side) **1** bar OPERATING PRESSURE (tubes side) **1** bar INLET TEMPERATURE (shell side) **5,00** °C OUTLET TEMPERATURE (shell side) **10,00** °C INLET TEMPERATURE (tubes side) **25,00** °C OUTLET TEMPERATURE (tubes side) **15,00** °C TYPE **Shell&Tubes** FLOWRATE (tube side) **(nom)** **1060** kg/h FLOWRATE (shell side) **(nom)** **781** kg/h EXCHANGE AREA **0,75** m^2 TUBES NUMBER **20** TUBES LENGTH **914** mm TUBES INNER DIAMETER **12,2** mm NUMBER OF PASSES 1**2** DUTY **4,54** kW	
E-202	Vapor drum dryer condenser	OPERATING PRESSURE (shel side) **1** bar OPERATING PRESSURE (tubes side) **1** bar INLET TEMPERATURE (shell side) **-10,00** °C OUTLET TEMPERATURE (shell side) **1,00** °C INLET TEMPERATURE (tubes side) **15,00** °C OUTLET TEMPERATURE (tubes side) **5,00** °C TYPE **Shell&Tubes** FLOWRATE (tube side) **(nom)** **1130** kg/h FLOWRATE (shell side) **(nom)** **511** kg/h EXCHANGE AREA **0,66** m^2 TUBES NUMBER **20** TUBES LENGTH **713** mm TUBES INNER DIAMETER **12,2** mm NUMBER OF PASSES 1**2** DUTY **5,1** kW	
E-203	Vapor drum dryer condenser	OPERATING PRESSURE (shel side) **1** bar OPERATING PRESSURE (tubes side) **1** bar INLET TEMPERATURE (shell side) **65,00** °C OUTLET TEMPERATURE (shell side) **65,00** °C INLET TEMPERATURE (tubes side) **20,00** °C OUTLET TEMPERATURE (tubes side) **40,00** °C TYPE **Shell&Tubes** FLOWRATE (tube side) **(nom)** **63,60** kg/h FLOWRATE (shell side) **(nom)** **1300** kg/h EXCHANGE AREA **0,84** m^2 TUBES NUMBER **20** TUBES LENGTH **1463** mm TUBES INNER DIAMETER **11,4** mm NUMBER OF PASSES **6** DUTY **30,2** kW	

MX-201	Alkaline soaking mixer	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **25** °C TYPE **Vertical Mixer** VOLUME **1** m^3 MIXER HEIGHT **900** mm MIXER DIAMETER **1500** mm RESIDENCE TIME **30** min	
MX-202	pH shifting mixing and protein precipitation	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **25** °C TYPE **Vertical Mixer** VOLUME **1** m^3 MIXER HEIGHT **900** mm MIXER DIAMETER **1500** mm RESIDENCE TIME **20** min	
MX-203	Ethanol mixing and dietary fiber precipitation	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **25** °C TYPE **Vertical Mixer** VOLUME **2** m^3 MIXER HEIGHT **1100** mm MIXER DIAMETER **2500** mm RESIDENCE TIME **20** min	
EX-201	Proteins&DF extractor	OPERATIVE PRESSURE **1** bar FEED TEMPERATURE **25** °C SOLVENT TEMPERATURE **30** °C TYPE **TURBEX Hydrodinamic cavitator** FEED FLOWRATE **(nom) 125** kg/h **(max) 200** kg/h SOLVENT/FEED RATIO **7,5**($kg/kg_{dry\ bases}$) RESIDENCE TIME **80** sec STAGE **3** ROT. SPEED **900** rpm POWER REQUIRED **8** kW	
G-201	Progressing cavity pump	OPERATIVE TEMPERATURE **25,00** °C TYPE **Progressing Cavity** FLOWRATE **9,16** m^3/h PUMP EFFICIENCY **0,85**	
G-202	Pump	TYPE **Centrifugal** PUMP EFFICIENCY **0,85**	
G-203	Pump	TYPE **Centrifugal** PUMP EFFICIENCY **0,85**	
G-204	Pump	TYPE **Centrifugal** PUMP EFFICIENCY **0,85**	
G-205	Pump	TYPE **Centrifugal** PUMP EFFICIENCY **0,85**	
G-206	Pump	TYPE **Centrifugal** PUMP EFFICIENCY **0,85**	
G-207	Progressing cavity pump	TYPE **Progressing Cavity** PUMP EFFICIENCY **0,85**	

G-208	Progressing cavity pump	TYPE **Progressing Cavity** PUMP EFFICIENCY **0,85**	
DC-201	Centrifugal decanter	SOLID CAPACITY **500** kg/h INSTALLED POWER **20** kW EFFICIENCY **45%**	
SF-201	Screw feeder to polyphenols extractor	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **25** °C FLOWRATE **(nom)** **630** kg/h	
SP-201	Screw press	MODEL **TZ180** CAPACITY **500** kg/h POWER **3** kW FEED SCREEW DIA. **180** mm FEED SCREW PITCH **100** mm FEED SCREEW ROT. SPEED **15** rpm PRESS SCREW DIA. **190** mm DIMENSION **1700*500*800** mm	
SP-201	Screw press	MODEL **TZ180** CAPACITY **500** kg/h POWER **3** kW FEED SCREEW DIA. **180** mm FEED SCREW PITCH **100** mm FEED SCREEW ROT. SPEED **15** rpm PRESS SCREW DIA. **190** mm DIMENSION **1700*500*800** mm	
DD-201	Proteins rotary drum dryer	OPERATIVE PRESSURE **0,1** atm FEED TEMPERATURE **45,9** °C TYPE **Double drum dryer** MODEL **Model T** MATERIAL **AISI 304** FEED FLOWRATE **(nom)** **110,5** kg/h LPS FLOWRATE **(nom)** **0,024** kg/s DRYING AREA **3,1** m^2 HEIGHT **1700** mm LENGTH **1900** mm WIDTH **2300** mm DRUM DIAMETER **500** mm DRUM LENGHT **1000** mm DUTY **50,95** kW INSTALLED POWER **7,5** kW	
DD-202	Dietary fiber rotary drum dryer	OPERATIVE PRESSURE **0,3** atm FEED TEMPERATURE **65** °C TYPE **Double drum dryer** MODEL **Model T** MATERIAL **AISI 304** FEED FLOWRATE **(nom)** **94.1** kg/h LPS FLOWRATE **(nom)** **0.01** kg/s DRYING AREA **3,1** m^2 HEIGHT **1700** mm LENGTH **1900** mm WIDTH **2300** mm DRUM DIAMETER **500** mm DRUM LENGHT **1000** mm DUTY **21,56** kW	

		INSTALLED POWER **7,5** kW	
W-201	Solid washer with water	OPERATIVE PRESSURE **1** bar FEED TEMPERATURE **25** °C SOLVENT TEMPERATURE **25** °C TYPE **Kennedy** FEED FLOWRATE **(nom)** **276** kg/h SOLVENT/FEED RATIO **1,05** (kg/kg)	
W-202	Proteins washer with water	OPERATIVE PRESSURE **1** bar FEED TEMPERATURE **5** °C SOLVENT TEMPERATURE **30** °C TYPE **Kennedy** FEED FLOWRATE **(nom)** **95** kg/h SOLVENT/FEED RATIO **0,99** (kg/kg)	

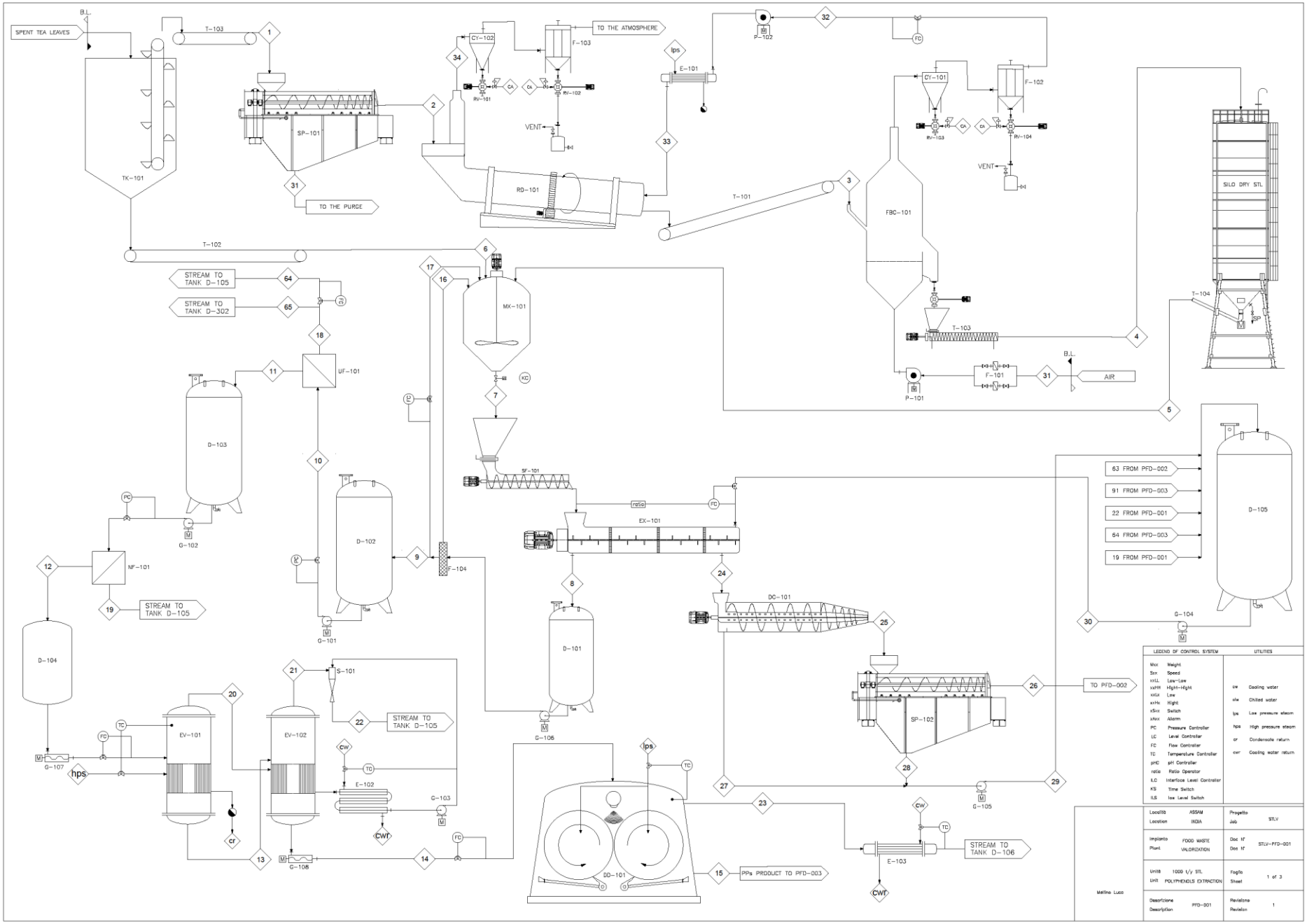
SOLVENTS RECOVERY SECTION			
E-301	Column condenser	OPERATING PRESSURE (shell side) **1** bar OPERATING PRESSURE (tubes side) **1** bar INLET TEMPERATURE (shell side) **15,00** °C OUTLET TEMPERATURE (shell side) **50,00** °C INLET TEMPERATURE (tubes side) **78,00** °C OUTLET TEMPERATURE (tubes side) **78,00** °C TYPE **Shell&Tubes** FLOWRATE (tube side) **(nom)** **38** m^3/h FLOWRATE (fin side) **(nom)** **12** m^3/h EXCHANGE AREA **40** m^2 TUBES NUMBER **370** TUBES LENGTH **2,19** mm TUBES INNER DIAMETER **15,7** mm NUMBER OF PASSES 4 DUTY **1556,5** kW	
E-302	E-302 reboiler	OPERATING PRESSURE (tube side) **1** bar OPERATING PRESSURE (shell side) **1** bar INLET TEMPERATURE (tube side) **158,00** °C OUTLET TEMPERATURE (tube side) **158,00** °C INLET TEMPERATURE (shell side) **100,00** °C OUTLET TEMPERATURE (shell side) **100,00** °C TYPE **Kettle reboiler** FLOWRATE (tube side) **(nom)** **2790,45** kg/h FLOWRATE (shell side) **(nom)** **4100** kg/h EXCHANGE AREA **30,35** m^2 TUBES NUMBER **252** TUBES LENGTH **3657** mm TUBES ID **16** mm SHELL ID **1397** mm TUBE PASSES **2** SHELL PASSES **1** DUTY **1620** kW	
E-303	Vapor drum dryer condenser	OPERATING PRESSURE (shel side) **1** bar OPERATING PRESSURE (tubes side) **1** bar INLET TEMPERATURE (shell side) **10,00** °C OUTLET TEMPERATURE (shell side) **15,00** °C INLET TEMPERATURE (tubes side) **75,00** °C OUTLET TEMPERATURE (tubes side) **25,00** °C TYPE **Shell&Tubes** FLOWRATE (tube side) **(nom)** **1280** kg/h FLOWRATE (shell side) **(nom)** **10000** kg/h EXCHANGE AREA **4,2** m^2 TUBES NUMBER **42** TUBES LENGTH **2194** mm TUBES INNER DIAMETER **12,2** mm NUMBER OF PASSES **6** DUTY **58,42** kW	
E-304	Vapor drum dryer condenser	OPERATING PRESSURE (shel side) **1,5** bar OPERATING PRESSURE (tubes side) **1** bar INLET TEMPERATURE (shell side) **158,00** °C OUTLET TEMPERATURE (shell side) **158,00** °C INLET TEMPERATURE (tubes side) **10,00** °C OUTLET TEMPERATURE (tubes side) **70,00** °C	

		TYPE **Shell&Tubes** FLOWRATE (tube side) **(nom)** **4820** kg/h FLOWRATE (shell side) **(nom)** **285.9** kg/h EXCHANGE AREA **2,7** m^2 TUBES NUMBER **32** TUBES LENGTH **1828** mm TUBES INNER DIAMETER **15,7** mm NUMBER OF PASSES **4** DUTY **165** kW	
E-305	Vapor drum dryer condenser	OPERATING PRESSURE (shel side) **1** bar OPERATING PRESSURE (tubes side) **1** bar INLET TEMPERATURE (shell side) **-10,00** °C OUTLET TEMPERATURE (shell side) **1,00** °C INLET TEMPERATURE (tubes side) **25,00** °C OUTLET TEMPERATURE (tubes side) **5,00** °C TYPE **Shell&Tubes** FLOWRATE (tube side) **(nom)** **1080** kg/h FLOWRATE (shell side) **(nom)** **576** kg/h EXCHANGE AREA **0,74** m^2 TUBES NUMBER **20** TUBES LENGTH **731** mm TUBES INNER DIAMETER **12,2** mm NUMBER OF PASSES 1**2** DUTY **5,75** kW	
C-301	Water-ethanol distillation column	OPERATIVE PRESSURE **1** bar TOP TEMPERATURE **78,76** °C BOTTOM TEMPERATURE **100** °C TYPE **Distillation column sieve trays** FEED FLOWRATE **(nom)** **2850** kg/h D:F RATIO **0,48** STAGES NUMBER **19** FEED STAGE **9** TRAY TYPE **SIEVE** TRAY SPACING **0,609** m COLUMN HEIGHT **18,5** m COLUMN DIAMETER **2,90** m CONDENSER **Total condenser** CONDENSER DUTY **1556,5** kW REBOILER **Kettle reboiler** REBOILER DUTY **1620** kW	
SILO-PPs	Polyphenols powder storage silo	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **25** °C TYPE **Alimatic Silo Type NL 2461** VOLUME **7** m^3 INTERNAL DIAMETER **400** mm BODY HEIGHT **5400** mm MATERIAL **AISI 316**	
SILO-Proteinss	Proteins powder storage silo	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **10** °C TYPE **Type CB-16-4-8** VOLUME **10** m^3 INTERNAL DIAMETER **400** mm BODY HEIGHT **6650** mm MATERIAL **AISI 316**	

SILO-DF	Dietary fiber powder storage silo	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **10** °C TYPE **Type CB-16-4-8** VOLUME **10** m^3 INTERNAL DIAMETER **400** mm BODY HEIGHT **6650** mm MATERIAL **AISI 316**	
D-301	Buffer tank residual	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **25** °C TYPE **Vertical tank** VOLUME **1** m^3 INTERNAL DIAMETER **900** mm HEIGHT **1500** mm MATERIAL **Carbon Steel**	
D-302	Buffer tank column distillation	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **25** °C TYPE **Vertical tank** VOLUME **3** m^3 INTERNAL DIAMETER **1200** mm HEIGHT **2500** mm MATERIAL **Carbon Steel**	
D-303	Buffer tank filter press	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **25** °C TYPE **Vertical tank** VOLUME **1** m^3 INTERNAL DIAMETER **900** mm HEIGHT **1500** mm MATERIAL **Carbon Steel**	
D-304	Ethanol storage tank	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **25** °C TYPE **Vertical Tank** VOLUME **3** m^3 INTERNAL DIAMETER **1200** mm HEIGHT **2500** mm MATERIAL **Carbon Steel**	
FP-301	Residue filter press	VOLUME **0,145** m^3 NUMBER OF CHAMBER **15** TYPE **Side beam filter press ME model 630** WIDTH **2800** mm LENGHT **2000** mm FILTERING AREA **0,4** m^2 CHAMBER THICKNESS **25** mm CHAMBER VOLUME **0,01** m^3	
G-301	Pump	TYPE **Centrifugal** PUMP EFFICIENCY **0,85**	
G-302	Pump	TYPE **Centrifugal** PUMP EFFICIENCY **0,85**	
G-303	Pump	TYPE **Centrifugal** PUMP EFFICIENCY **0,85**	

G-304	Progressing cavity pump	TYPE **Progressing Cavity** PUMP EFFICIENCY **0,85**	
G-305	Volumetric Pump	TYPE **Volumetric** PUMP EFFICIENCY **0,85**	
W-301	Solid washer with water	OPERATIVE PRESSURE **1** bar FEED TEMPERATURE **25** °C SOLVENT TEMPERATURE **25** °C TYPE **Kennedy** FEED FLOWRATE **(nom)** **125** kg/h SOLVENT/FEED RATIO **1,01** (kg/kg)	
D-305	Chlorhydric Acid storage tank	OPERATIVE PRESSURE **1** bar OPERATIVE TEMPERATURE **25** °C TYPE **Vertical tank** VOLUME **1** m^3 INTERNAL DIAMETER **900** mm HEIGHT **1100** mm MATERIAL **Carbon Steel**	

6.5 Preliminary P&Id



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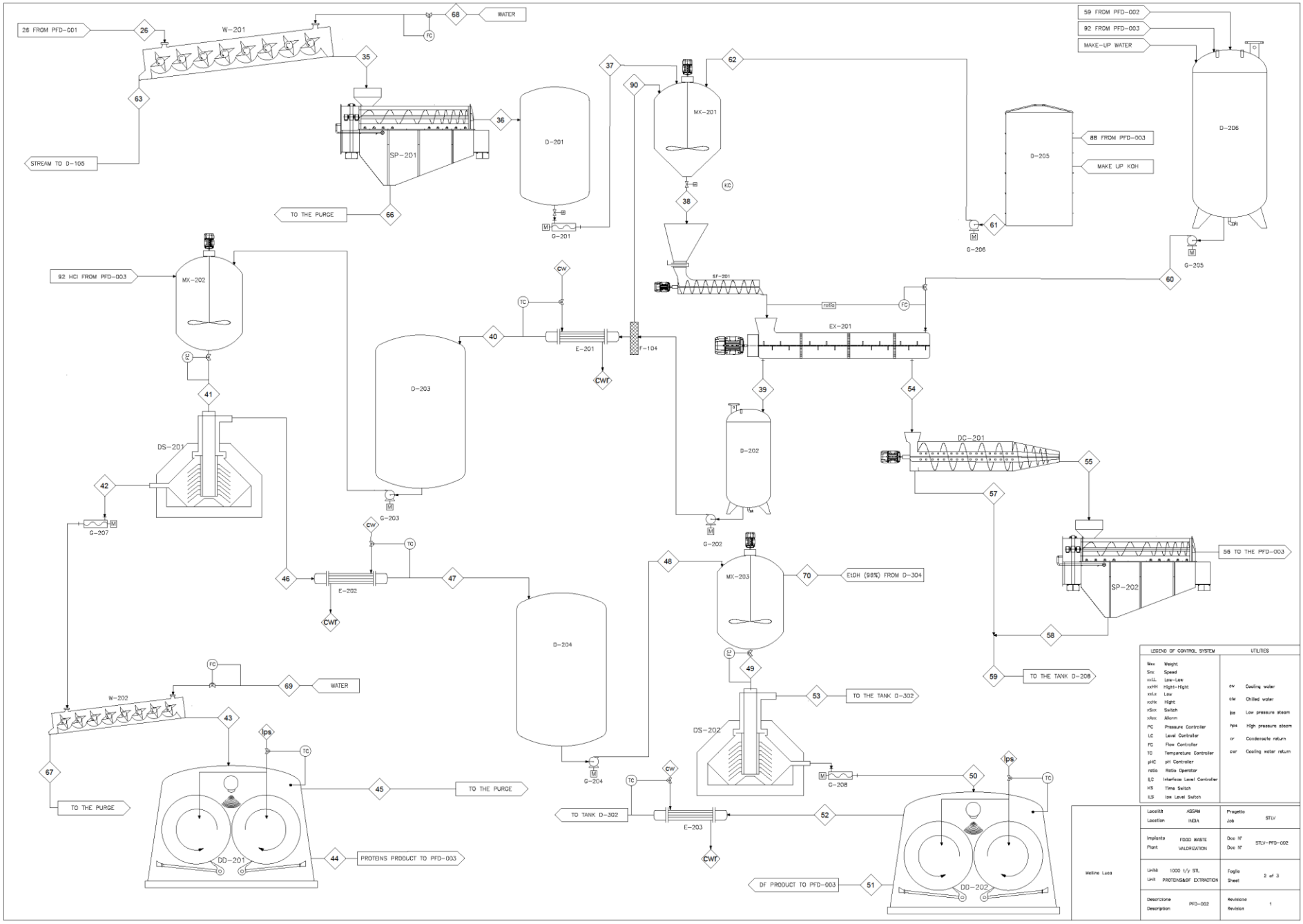

LEGEND OF CONTROL SYSTEM		UTILITIES	
Wxx	Weight		
Snx	Speed		
xxLL	Low-Low		
xxHH	Hight-Hight	cw	Cooling water
xxLx	Low	chw	Chilled water
xxHx	Hight	lps	Low pressure steam
xSxx	Switch	hps	High pressure steam
xAxx	Allarm	cr	Condensate return
PC	Pressure Controller	cwr	Cooling water return
LC	Level Controller		
FC	Flow Controller		
TC	Temperature Controller		
pHC	pH Controller		
ratio	Ratio Operator		
ILC	Interface Level Controller		
KS	Time Switch		
ILS	low Level Switch		

Località / Location	KERAM INDIA	Progetto / Job	STLV
Impianto / Plant	FOOD WASTE VALORIZATION	Doc N° / Doc N°	STLV-PFD-002
Unità / Unit	1000 t/y STL PROTEINS&DF EXTRACTION	Foglio / Sheet	3 of 3
Descrizione / Description	PFD-002	Revisione / Revision	1

Matteo Luca

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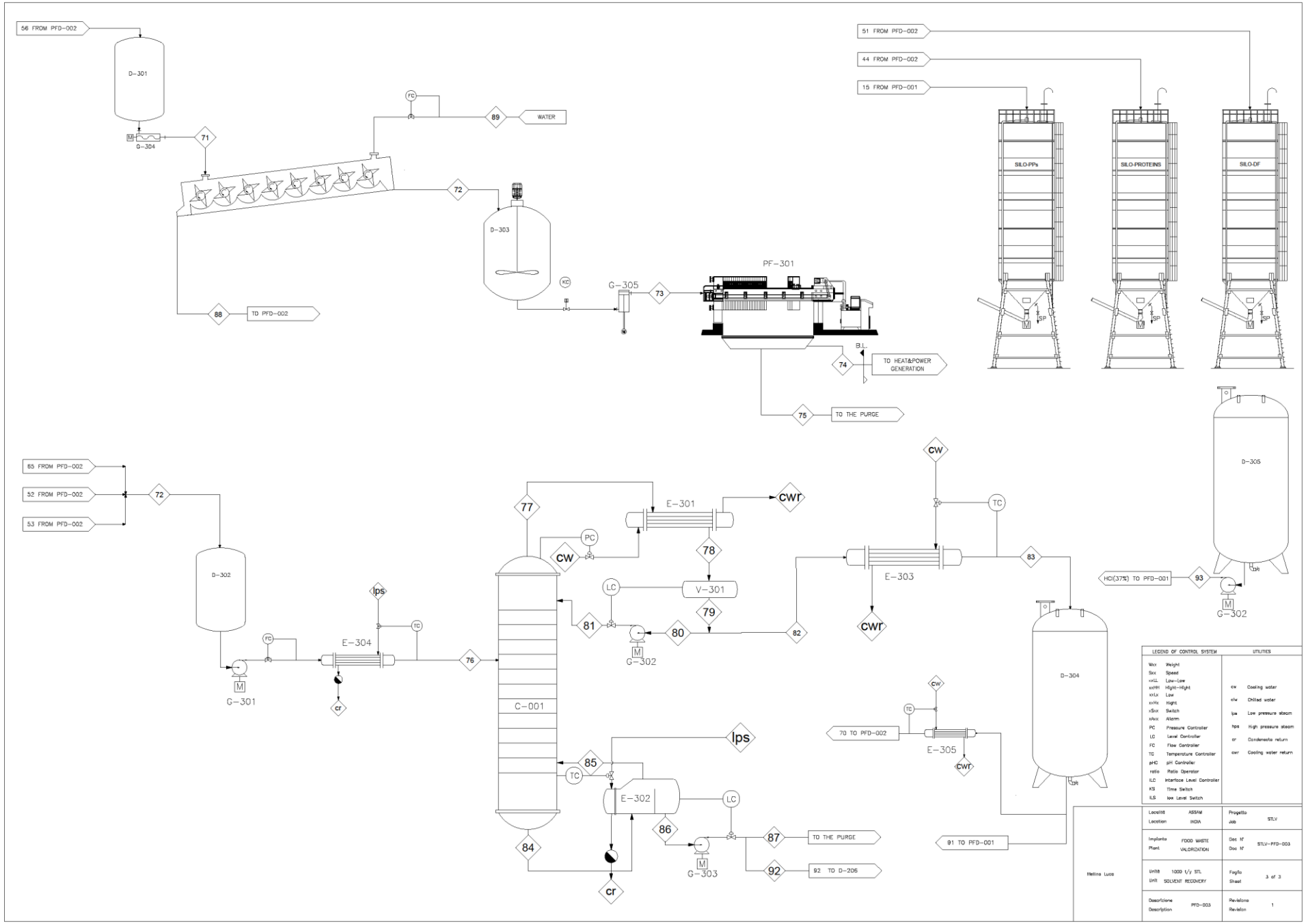

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6.6 Preliminary variable cost estimate

Based on the results obtained from heat and mass balances, it is possible to make a preliminary estimate of variable cost (table 6.13) of the designed plant.

The estimate includes both the management costs associated with the use of the various reagents and that of the utilities, essential for the success of the unit operations.

As anticipated, the reported values represent a first economic estimate, as they do not include a possible optimization through energy integration.

Not less important is the fact that this estimate does not include the economic value of the residue leaving the last extraction step, which is energetically enhanced.

Utility	*Costs per year*
CW	30.000€
LPS	20.000 €
HPS	- €
Electricity	50.000 €
Total	100.000 €

Table 6.13: Preliminary estimation of utilities cost per year

Reactants	**Cost per year**
Chloridric acid (37% w/w)	450.000 €
Potassium Hydroxide	1.400.000 €
Ethanol (96% w/w)	440.000 €
Tot.	2.290.00 €

Table 6.14: Preliminary estimation of reactants cost per year

6.7 Preliminary revenue estimate

The preliminary estimate of the incomes due to the sales of solid extracts was made considering the market values (table 6.15) of products with similar characteristics, in terms of chemical-physical characteristics.

Components	**Price (€/kg)**
Polyphenols rich extract (*)	45
Proteins	2,6
Dietary Fibes	4,5

Table 6.15: Market value (potential end-users evaluation)

(*) polyphenols rich extract with total polyphenol content of 22%

Product	Income per year
Polyphenols rich extract (powder)	6.550.000 €
Proteins rich extract (powder)	600.000 €
Dietary Fiber (powder)	1.000.000 €
Tot.	8.150.000 €

Table 6.16: Preliminary annual revenue estimate

6.8 Capital investment cost estimate

Once the plant design phase was completed, a preliminary Capital Investment Cost Estimation (CAPEX) estimate was calculated. This evaluation take into account the location of the plant in India, as previously mentioned.

The evaluation was made using the Guthrie method, so based on the parameters of the equipment obtained from a first sizing, reported in the equipment list, it was possible to evaluate the single cost through the use of equipment cost graphs (Ulrich-Vasudevan 2004).

The costs obtained were subsequently normalized to the year 2022 using the CEPCI coefficient.

The preliminary CAPEX estimate is equal to 5.800.000 € (+/- 40%).

6.9 Conclusion

At the end of this work, results were obtained that support the use of extraction technology through assisted cavitation; the data were then used for the scale-up and design of an industrial plant, representing an innovation from the point of view of sustainability.

The goal was to be able to identify the optimal operating parameters for the extraction of the antioxidant polyphenolic components, proteins and dietary fibers present in black tea. With the help of qualitative and quantitative analyzes (HPLC) it was also possible to identify the composition of the polyphenolic mix.

The extracts were initially quantified using a rapid analytical test to identify the total polyphenols they contain (*Folin-Ciocalteau*). From the analyzes obtained, it was confirmed that the STL, labeled as waste, had an extremely high content of polyphenols, confirming the feasibility of exploiting this biomass.

The antioxidant power is one of the most important characteristics of black tea, of interest both to the food industry and to the pharmaceutical and cosmetic industries. Through the analyzes carried out, it was found that this is strongly influenced by the operating conditions of the TURBEX system, regardless of the extraction yields. In particular, it is of fundamental importance to identify the optimal rotational speed of TURBEX rotors to optimise biochemical activity as well as radical scavenging power and anti-oxidant power of polyphenol rich extract.

Once the STL of interest was characterized and a set of data concerning the extraction yields of the technology was obtained, it was possible to proceed with the design of the extraction section on an industrial scale. The entire waste valorisation system was therefore designed, replicating the data obtained in the laboratory in terms of yields and operating parameters (L/S, temperature, rotor speed) with a process that was green and economically advantageous. The operating parameters of the plant, designed for the Assam region in India, provide for an inlet flow of dry biomass equal to 1.000 t/y with an inlet moisture content of 70%. A turndown ratio was assumed that ranged from 60 to 110% of the nominal capacity.

The supply of the matrix, arriving from the door-to-door ready to drink tea plant, takes place continuously with biomass characteristics identical to those coming out of the beverage production process (humidity at 70%). It is therefore necessary to dry the biomass not directly processed until it reaches a moisture content not exceeding 10% in order to avoid degradation of the matrix during storage. The heart of the system is the TURBEX extractor which exploits the phenomena of assisted cavitation by weakening the surface of the matrix and favoring the release of the components.

CAE technology increases mass transfer, prevents overheating of the liquid medium and therefore prevents the occurrence of thermal degradation: the mechanical effect induced by the pressure waves of hydrodynamic cavitation promotes the release of bioactive substances from the heart of the matrix, destroying the cell walls and facilitating access of the solvent or extracting medium to the cell content.

A process of this kind is able to convert waste materials into products with high added value, requiring minimal management costs for the plant and the necessary utilities, considering the absence of high temperatures.

The main advantage of the plant considered is certainly the high extraction yield with the same solvent consumption. This involves lower costs both in the purchase of the same and in the recovery phases. Furthermore, the relatively low temperature (30 °C) allows further very substantial energy savings if we consider the high solid-liquid ratio and therefore the large amount of energy that would be required. The concentration section via membranes allows the recovery of the solvent and the concentration of the product stream at reduced costs, avoiding a high energy expenditure in evaporative equipment.

The work concluded by estimating, in analogy to the experimental work, a recovery equal to 61% of the polyphenols initially present in the matrix, estimating an hourly production of 18,8 kg of product, or about 145 ton/y.

As regards proteins and dietary fiber, the extractive yields reach values over 70%, obtaining respectively about 230 ton/y of protein powder and over 240 ton/y of dietary fiber.

Considering the high commercial value of the compounds extracted and the continued growth in demand, a preliminary annual revenue of over 8 million € has been estimated.

This thesis demonstrates how, by making a comparison between conventional and non-conventional methodologies, TURBEX technology inserted within an industrial context represents a valid alternative. The exploitation of this innovation makes possible to convert waste materials into products with high added value, requiring minimum management costs of the plant and of the necessary utilities in line with the principles of Green Chemistry and Green Engineering.

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