UNIVERSITÀ DEGLI STUDI DI PADOVA
DIPARTIMENTO DI INGEGNERIA INDUSTRIALE
CORSO DI LAUREA MAGISTRALE IN INGEGNERIA CHIMICA E DEI PROCESSI INDUSTRIALI

Tesi di Laurea Magistrale in
Ingegneria Chimica e dei Processi Industriali

Environmental optimization of the Northern Italy supply chain for the treatment of residual plastic packaging waste considering waste-to-energy and chemical recycling technologies

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ANNO ACCADEMICO 2021-2022

Abstract

The management of plastic packaging waste is a challenging task due to its massive and high-rate production. Only a small fraction of the plastic packaging waste can be mechanically recycled, while the rest, which is typically denoted as Mixed Plastic Waste (MPW), is incinerated or landfilled.

This Master's thesis proposes an environmental analysis of end-of-life treatment technologies for MPW as an alternative to landfilling: Such technologies comprise: incineration, gasification, and pyrolysis. The analysis is performed over the MPW supply chain, from the collection and sorting out of municipal plastic waste, to the treatment stage according to one of the proposed technologies. Northern Italy is taken as geographic reference. The supply chain is modelled using a Mixed Integer Linear Programming approach.

The supply chain is optimized by minimizing its environmental impact, which is here represented by the net amount of greenhouse gases (GHG) emissions, defined as the difference between direct emissions and potential environmental credits of the supply chain. Two scenarios are analysed: a "base case scenario", where the pyrolysis oil is intended as a crude oil substitution; a "cracking scenario", where pyrolysis oil becomes a fossil naphtha substitution for feeding cracking plants.

Results are compared to economic optima, formulated as maximization of gross profit.

For the base case scenario, the environmental optimum leads to the selection of only pyrolysis plants, whereas the economic optimization selects incineration plants only. The environmental optimum is characterized by a reduction of gross profit of 55%, and of GHG emissions of 51% compared to economic optimum.

On the other hand, in the cracking scenario, the solution of environmental optimization leads to a better environmental and economic performances, which result in a gross profit reduction of only 40% and in GHG emission reduction of 30%, respectively, with respect to this scenario economic optimum.

Riassunto esteso

La produzione mondiale di platica nel 2022 ha superato le 390 milioni di tonnellate, di cui il 44% è costituito da materiali di imballaggio. Gli imballaggi hanno un ciclo di vita molto breve se comparato ad altri materiali plastici, pertanto generano velocemente una quantità di rifiuti molto elevata.
Il riciclo meccanico degli imballaggi è una soluzione che interessa una fetta consistente (il 48%) dei rifiuti da imballaggio, consentendone un'ulteriore vita, a scapito però della qualità del prodotto. Questo tipo di riciclo, tuttavia, non coinvolge tutta la quota di rifiuti, a causa delle impurezze che si trovano al suo interno. La parte rimanente viene definita secondo la terminologia anglosassone *Mixed Plastic Waste* (MPW), ed è composto in maggioranza da varie tipologie di polimeri a cui si uniscono carta, legno e materiali inerti di vario genere, rendendo quindi molto complicato il riciclo meccanico.
In un'ottica di gestione circolare del rifiuto, il conferimento a discarica deve essere scoraggiato, e pertanto strategie alternative devono essere prese in considerazione, che siano in linea con i canoni di sostenibilità economica e ambientale.
In questo senso, tre diverse tecnologie di trattamento per l'MPW sono state analizzate: incenerimento e gassificazione, che appartengono alla categoria *Waste-To-Energy* (recupero energetico a partire dal rifiuto plastico), e pirolisi, che invece è una forma di riciclo chimico.
L'obiettivo di questo studio è in primo luogo un'ottimizzazione ambientale, intesa come minimizzazione di gas serra, dell'intera filiera (*supply chain*) che porta al trattamento dell'MPW. Tale filiera è riferita unicamente al territorio del Nord Italia, pertanto i confini geografici di questo studio sono dati dalle sole regioni dell'Italia settentrionale.
I rifiuti plastici partono dai centri di raccolta, collocati nei capoluoghi di provincia di ciascuna regione. Da qui vengono condotti in centri di smistamento nei quali la frazione riciclabile viene separata dall'MPW. L'MPW deve poi essere trattato secondo una delle possibili tecnologie proposte, generando un recupero energetico in termini di elettricità nel caso di incenerimento e gassificazione, oppure un prodotto chimico quale l'olio di pirolisi, se l'MPW viene pirolizzato. Qualora fosse la pirolisi ad essere scelta come tecnologia di trattamento, per l'olio di pirolisi sono state immaginate due possibili destinazioni. La prima è quella che caratterizza lo scenario standard (*base case scenario*) di questa tesi, ovvero intendere il prodotto della pirolisi come un possibile sostituto del greggio, previo trattamento in una raffineria. La seconda opzione definisce lo scenario alternativo di questo studio (*cracking scenario*), per il quale l'olio di pirolisi non è considerato un possibile sostituto del petrolio, ma come sostituto della nafta alimentata negli impianti di cracking per la produzione di olefine leggere, senza passare per le raffinerie.
Di ciascuno di questi passaggi viene analizzato l'impatto ambientale, espresso come emissioni di CO_2 equivalente, comprendendo anche l'impatto derivato dal trasporto su gomma da un nodo all'altro della filiera delle portate che la che la caratterizzano, ovvero, di volta in volta, rifiuti plastici, MPW, rifiuti solidi da post-trattamento dell'MPW, eventualmente olio di pirolisi.

La scelta di una tecnologia rispetto a un'altra viene svolta secondo criteri di minimizzazione dell'impatto ambientale da gas serra, formulando un problema di ottimizzazione a variabili miste lineari e intere (*Mixed-Integer Linear Programming, MILP*) usando l'algoritmo CPLEX implementato nel software GAMS®.
La funzione obiettivo da minimizzare è composta dalle emissioni nette di gas serra, definita come la differenza tra le emissioni di gas serra dirette e quelle evitate. Ciascuna tecnologia, infatti, presenta un potenziale credito ambientale che viene considerato in questo lavoro. Ad esempio, la generazione di energia elettrica da incenerimento o gassificazione evita l'utilizzo di altre fonti per la sua produzione, evitando un impatto ambientale. Anche la pirolisi ha dei benefici di questa natura, evitando impatti dovuti all'estrazione e al trasporto di greggio nel caso dello scenario standard, oppure evitando gli impatti di raffineria per la produzione di nafta da cracking, nel caso dello scenario alternativo.
L'ottimizzazione ambientale è stata accoppiata all'ottimizzazione economica, già svolta per lo scenario standard da un precedente lavoro di tesi. L'ottimo economico è basato sulla massimizzazione dell'utile lordo, definito come la differenza tra i ricavi complessivi della filiera e i suoi costi. I risultati sono stati confrontati cercando, ove possibile, un compromesso tra le due esigenze.
La tecnologia di trattamento per l'MPW preferita dal punto di vista ambientale è la pirolisi, con emissioni di gas serra stimate in 186909 ktonne di CO_2^{eq}/anno, pur essendo onerosa dal punto di vista economico, portando a un utile lordo di 33.4 M€/anno. Viceversa, l'ottimizzazione economica dello scenario standard vede gli inceneritori come gli impianti preposti al trattamento dell'MPW, in quanto le entrate di una filiera composta da pirolizzatori sarebbero costituite dalla vendita dell'olio di pirolisi raffinato come sostituto del greggio, e queste non sono sufficientemente elevate da far preferire la pirolisi all'incenerimento. L'utile lordo è più del doppio di quanto stimato dall'analisi ambientale, attestandosi in 75.3 M€/anno Questa volta è però l'aspetto ambientale ad essere svantaggiato, perché bruciare MPW porta a consistenti emissioni di gas serra, più del doppio (384221 ktonne di CO_2^{eq}/anno) rispetto all'ottimo ambientale.
Un possibile compromesso è dato dallo sviluppo dello scenario alternativo, in cui l'olio di pirolisi viene trattato come sostituto dell'alimentazione degli impianti di cracking. In questo scenario il prezzo di vendita della nafta è sufficientemente alto da compensare e talvolta superare sia i costi degli impianti di pirolisi che i guadagni derivanti dalla vendita dell'elettricità generata da incenerimento dell'MPW, principale entrata economica rispetto a quelle della pirolisi. Gli utili dell'ottimo ambientale si attestano in 45.3 M€/anno, mentre le emissioni sono stimate in 186348 ktonne di CO_2^{eq}/anno. Se dunque l'ottimizzazione ambientale vede ancora una volta la predilezione di pirolizzatori che però, grazie alla vendita di olio di pirolisi come nafta, consentono un buon profitto, l'ottimo economico propone una filiera mista di pirolizzatori e inceneritori, con consistenti guadagni economici (77.7 M€/anno) ed emissioni ridotte (265149 ktonne di CO_2^{eq}/anno).
In conclusione è stata svolta un'analisi di sensitività, studiando le conseguenze di un calo del prezzo di vendita dell'elettricità prodotta da un impianto di incenerimento. Se da una parte lo scenario standard non è particolarmente influenzato da queste variazioni, lo scenario alternativo risulta

sensibile al calo del prezzo dell’elettricità, preferendo economicamente, man mano che esso diminuisce, trattare le portate di MPW in un pirolizzatore invece che in un inceneritore.

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Acronyms

ACI	=	Automobile club d'Italia
CC	=	Centri comprensoriali
CSS	=	Centri di selezione
CONAI	=	Consorzio Nazionale Imballaggi
COREPLA	=	Consorzio Nazionale per la raccolta, il riciclo e il recupero degli imballaggi in plastica
DOC	=	Diesel oxidation catalyst
EBR	=	End-belt refuse
ECS	=	Eddy current separator
EPA	=	Environmental protection agency
GAMS	=	General algebraic model system
GHG	=	Greenhouse gas
GWP	=	Global warming potential
HDPE	=	High-density polyethylene
HDDT	=	Heavy-duty diesel trucks
HDS	=	Hydrodesulphurization
HDT	=	Heavy-duty trucks
ISPRA	=	Istituto Superiore per la Ricerca e la Protezione Ambientale
IW	=	Industrial waste
LDPE	=	Low-density polyethylene
LHV	=	Low heating value
MILP	=	Mixed Integer Linear Programming
MPW	=	Mixed Plastic Waste
MRF	=	Material Recovery facility
MSW	=	Municipal solid waste
NIR	=	Near infra-red
PET	=	Polyethylene terephthalate
PP	=	Polypropylene
PS	=	Polystyrene
RPL	=	Residual mixed plastic waste
SRA	=	Secondary reducing agent
TEOR	=	Thermal enhanced oil recovery
THC	=	Total hydrocarbons

WCS	=	Western Canadian Select
WtE	=	Waste-to-Energy

Sets

n	$\{n_{1-93}\}$	All the 93 nodes in the model
pr^n	$\{n_{1-47}\}$	Subset of *n* comprising only the 47 Northern Italian provinces
so^n	$\{n_{48-60}\}$	Subset of *n* comprising only the 12 Northern Italian sorting centers
t^n	$\{n_{61-88}\}$	Subset of *n* comprising only the treatment locations *i.e.* the locations of the 25 Northern Italian and of the 3 Northern Italian refineries
$port^n$	$\{n_{89-93}\}$	Subset of *n* comprising only 7 Italian ports
$refi^t$	$\{n_{86-88}\}$	Subset of *t* comprising only the 3 Northern Italian refineries
$notrefi^t$	$\{n_{61-85}\}$	Subset of *t* comprising all the nodes of *t* except the refineries;
$portdep^{port}$	$\{n_{89-91}\}$	Subset of *port* comprising 5 Northern Italian departure ports
$portarr^{port}$	$\{n_{91-93}\}$	Subset of *port* comprising 2 Southern Italian departure ports
k	$\{k_{1-4}\}$	Set of the 4 PL treatment technologies *i.e.* incineration, gasification, Po. pyrolysis and PoPS pyrolysis
ElK^k	$\{k_{1-2}\}$	Subset of *k* comprising only the technologies producing electrical power *i.e.* incineration and gasification
$OilK^k$	$\{k_{3-4}\}$	Subset of *k* comprising only the technologies producing oil *i.e.* Po. pyrolysis and PoPS pyrolysis
$NewK^k$	$\{k_{2-4}\}$	Subset of *k* comprising all the technologies except incineration
$GasK^k$	$\{k_2\}$	Subset of *k* comprising only gasification
InK^k	$\{k_1\}$	Subset of *k* comprising only incineration
s	$\{s_{1-3}\}$	Set of the three plant sizes (small, medium, large) for each technology

Scalars

α	$0\ or\ 1$	α=1 for economic optimization; α=0 for environmental optimization
R	6372.785 [km]	Earth radius
τ	1.4	Average tortuosity factor for Northern Italian territory
η^{W_MPW}	0.521	Average waste-to-MPW conversion factor
$LD_{n,n'}^{Pyr,Inc}$	150 [km]	Fixed linear distance of a pyrolysis plant and an incineration plant
$LD_{n,n'}^{landfill}$	50 [km]	Fixed linear distance of a landfill from a MPW treatment plant
$truckE$	900 [g CO_2^{eq}/km/truck]	Average GHG emission for a HDDT
Cap_{MPW}	12.4 [tonne]	Mass of waste and MPW which a truck can carry
Cap_{Oil}	84 [tonne]	Mass of pyrolysis oil which a truck can carry
Cap_{R}	43 [tonne]	Mass of treatment residues which a truck can carry
ε^{sort}	22.5 [tonne of CO_2^{eq}/ ktonne of waste]	GHG emission factor for sorting centres
ε^{In}	870 [ktonne of CO_2^{eq}/ ktonne of MPW]	GHG emission factor for incineration plants
$\varepsilon^{Gas,pretrt}$	1.6 [Gtonne of CO_2^{eq}/ ktonne of MPW]	GHG emission factor for gasification pretreatments
ε^{Gas}	550 [ktonne of CO_2^{eq}/ ktonne of MPW]	GHG emission factor for gasification
$\varepsilon^{Av,In}$	432.7 [tonne of CO_2^{eq}/ ktonne of MPW]	Avoided GHG emissions from incineration
$\varepsilon^{Av,Gas}$	586.6 [tonne of CO_2^{eq}/ ktonne of MPW]	Avoided GHG emissions from gasification
$\varepsilon^{Av,exctr}$	686.0 [tonne of CO_2^{eq}/ ktonne of MPW]	Avoided oil extraction GHG emissions
$Dist_{n,n',country}^{pipe}$	[km]	Distance covered by a pipeline
$Dist_{n,n',country}^{ship}$	[km]	Sea distances for pyrolysis oil transport
$\varepsilon^{Av,pipe}$	19 [kg of CO_2^{eq}/ ktonne of oil]	Avoided GHG emissions from pipeline oil transport
$\varepsilon^{Av,ship}$	2.4 [kg of CO_2^{eq}/ ktonne of oil]	Avoided GHG emissions from sea transport of oil

$\varepsilon^{Av,Ref}$	4.185 [ktonne of CO_2^{eq}/ ktonne of oil]	Avoided GHG emissions from oil refinement

Parameters

C_{so}	[kilotonne/year]	Capacity of each Northern Italian sorting center
$C^{P}_{InK,s}$	[kilotonne/year]	Scaled-down capacity of each Northern Italian incineration plant
$C^{P}_{NewK,s}$	[kilotonne/year]	Plant capacity of each technology except incineration, and each of their plant sizes s
$LD_{n,n\prime}$	[km]	Matrix of the linear distances among all the supply chain nodes
$ND^{portdep,portarr}_{n,n'}$	[km]	Matrix of the naval distances between oil departure ports and arrival ports
$\varepsilon^{Pyro}_{OilK}$	[tonne of CO_2^{eq}/ ktonne of MPW]	GHG emission factors for PO_PS_Pyrolysis and PO_Pyrolysis plants
η^{R}_{k}	[kilotonne/kilotonne]	MPW-to-solid residues conversion factor
η^{Oil}_{OilK}	[kilotonne/kilotonne]	MPW-to-oil conversion factor
η^{RPL}_{OilK}	[kilotonne/kilotonne]	MPW-to-remaining MPW conversion factor

Continuous variables

$m_{pr,so}^{W}$	[ktonne/year]	Waste flowrate from a province to a sorting centre
$m_{pr}^{W,Av}$	[ktonne/year]	Waste flowrate available in each Northern Italian province
$m_{t,k,s}^{MPW,Plant}$	[ktonne/year]	MPW flowrate going to a treatment plant
$m_{so,t,k,s}^{MPW}$	[ktonne/year]	MPW flowrate going from a sorting centre to a treatment plant
$m_{so}^{MPW,sort}$	[ktonne/year]	Total amount of MPW sent out from a sorting centre
$m_{so}^{MPW,Av}$	[ktonne/year]	Total amount of MPW available in a sorting centre
$m_{t,k,s}^{R}$	[ktonne/year]	Amount of solid residue produced by a MPW treatment plant
$m_{t,OilK,s}^{RPL}$	[ktonne/year]	Remaining MPW sorted out by an MRF of a pyrolysis plant
$m_{so}^{RPL,Tot}$	[ktonne/year]	Total amount of remaining MPW of a pyrolysis plant
$m_{t,OilK,s}^{R,RPL}$	[ktonne/year]	Amount of residue produced incinerating the residual MPW
$m_{so}^{RPL,Tot}$	[ktonne/year]	Total amount of remaining MPW
$m_{t,OilK,s}^{Oil,Av}$	[ktonne/year]	Amount of oil produced by a pyrolysis plant
$m_{t,OilK,s,refi}^{Oil}$	[ktonne/year]	Amount of oil produced by a pyrolysis plant sent to a oil refinery
$m^{R,Tot}$	[ktonne/year]	Total amount of solid residues to be landfilled
GP	[€/year]	Supply chain gross profit
TR	[€/year]	Supply chain total annual revenues
TC	[€/year]	Supply chain total annual costs
$NumbTrucks^{pr}$	[trucks/year]	Number of trucks to transport plastic waste from provinces to sorting centres
$NumbTrucks^{so}$	[trucks/year]	Number of trucks to transport MPW from sorting centres to treatment plants
$NumbTrucks_{oil}^{t,OilK,s}$	[trucks/year]	Number of trucks to transport pyrolysis oil
$NumbTrucks_{RPL}^{t,OilK,s}$	[trucks/year]	Number of trucks to transport remaining MPW to incineration plants

$NumbTrucks_R^{t,k,s}$	[trucks/year]	Number of trucks to transport solid residues from treatment plants to landfills
$E^{W,trans}$	[ktonne of CO_2^{eq}/year]	GHG emissions from plastic waste transportation
$E^{MPW,trans}$	[ktonne of CO_2^{eq}/year]	GHG emissions from MPW transportation
$E^{Oil,trans}$	[ktonne of CO_2^{eq}/year]	GHG emissions from pyrolysis oil road transportation
$E^{RPL,trans}$	[ktonne of CO_2^{eq}/year]	GHG emissions from remaining MPW transportation
$E^{R,trans}$	[ktonne of CO_2^{eq}/year]	GHG emissions from solid residues transportation
E^{trans}	[ktonne of CO_2^{eq}/year]	Total GHG emissions from transportation
E^{sort}	[ktonne of CO_2^{eq}/year]	GHG emissions from sorting centres
$E^{sort,pyro}$	[ktonne of CO_2^{eq}/year]	GHG emissions from sorting centres coupled with pyrolysis plants
$E^{sort,tot}$	[ktonne of CO_2^{eq}/year]	Total amount of sorting centres GHG emissions
$E^{treat,In}$	[ktonne of CO_2^{eq}/year]	GHG emissions from MPW incineration
$E^{treat,Gas}$	[ktonne of CO_2^{eq}/year]	GHG emissions from MPW gasification
$E^{treat,Pyro}$	[ktonne of CO_2^{eq}/year]	GHG emissions from MPE pyrolysis
$E^{RPL,inc}$	[ktonne of CO_2^{eq}/year]	GHG emissions from incinerating remaining MPW of a pyrolysis plant
E^{treat}	[ktonne of CO_2^{eq}/year]	Total amount of GHG emissions from MPW treatment
E^{tot}	[ktonne of CO_2^{eq}/year]	Total amount of supply chain GHG emissions
$E^{Av,In}$	[ktonne of CO_2^{eq}/year]	Total amount of avoided GHG emissions from MPW incineration
$E^{Av,Gas}$	[ktonne of CO_2^{eq}/year]	Total amount of avoided GHG emissions from MPW gasification
$E^{Av,exctr}$	[ktonne of CO_2^{eq}/year]	Avoided GHG emissions related to avoided oil extraction for pyrolysis
$m_{country}^{oil,import}$	[ktonne/year]	Pyrolysis oil which compensates the oil imported from a country
$E^{Av,pipe}$	[ktonne of CO_2^{eq}/year]	Avoided GHG emissions related to avoided pipeline oil transportation
$E^{Av,oil\ trans}$	[ktonne of CO_2^{eq}/year]	Total amount of avoided GHG emissions due to oil transportation
$E^{Av,Pyro}$	[ktonne of CO_2^{eq}/year]	Total amount of avoided GHG emissions from MPW pyrolysis

$E^{Av,tot}$	[ktonne of CO_2^{eq}/year]	Total amount of avoided GHG emissions
E^{Net}	[ktonne of CO_2^{eq}/year]	Net amount of supply chain GHG emissions
$m_{t,OilK,s,portdep}^{OilCrack}$	[ktonne/year]	Pyrolysis oil that is shipped from Northern Italian ports for cracking scenario
$m_{t,OilK,s,portdep,portarr}^{OilShip}$	[ktonne/year]	Pyrolysis oil shipped from a Northern Italian port to a Southern Italian port
$E^{Oil,ship}$	[ktonne of CO_2^{eq}/year]	GHG emissions from pyrolysis oil naval transportation
$E^{Av,Ref}$	[ktonne of CO_2^{eq}/year]	Avoided GHG emissions related to avoided oil refinement
$TC^{Oil,trans}$	[€/year]	Oil road transportation costs
$TC^{Oil,ship}$	[€/year]	Oil naval transportation costs
$TC^{TransTot,Oil}$	[€/year]	Total oil transportation costs
Rev^{Naph}	[€/year]	Revenues from selling pyrolysis oil as fossil naphtha substitute

Binary variables

$\lambda_{t,k,s}^{Plant}$	{0;1}	1 if a plant of technology *k* and size *s* in a treatment node *t* is selected to treat PLASMIX, 0 otherwise

Introduction

Global plastics production exceeded 390 million tons in 2022 and will likely double within the next twenty years. About 44% of the produced plastic is used as packaging material, predominantly consisting of polyolefins (polyethylene (PE), polypropylene (PP)) and polystyrene (PS) (Plastics Europe, 2022).

According to the latest data reported in Plastic Europe (2022), only 35% of the collected plastic waste in Europe is recycled today. The rest is either landfilled (23%) or incinerated for energy recovery (42%) generating an important level of CO_2 emissions. For what concern plastic packaging waste, according to 2020 data for EU27+UK/NO/CH (Plastics Europe, 2022), 46% was recycled, 37% was incinerated for energy recovery, and 17% was landfilled. The last solution, in a circular economy paradigm, should be avoided. Driven by this requirement, during the time period of 2006-2020 plastic packaging waste treatment witnessed an increase in plastic recycling of 110%, energy recovery of 76%, whereas landfilling tendency decreased by 57%. On average, according to 2018 data (Plastics Europe, 2020), 42% of plastic packaging waste is recycled. The new Directive (EU) 2019/904 on Packaging and Packaging Waste sets higher recycling targets per material (50% for plastic packaging by 2025 and 55% by 2030). In Germany and Italy, chemical recycling is applied to a very small percentage of the generic plastic waste (0.2% and 0.1% respectively), however this kind of technology is not applied for packaging waste (Plastics Europe, 2020).

Chemical recycling of solid plastic waste is a paramount opportunity to reduce marine and land pollution and to enable the incorporation of the circular economy principle in today's society. A key challenge is the identification of the leading recycling technologies, minimizing the global warming potential (GWP).

For an optimal handling of packaging plastic waste, two key aspects must be taken into account; namely, an efficient economical management and a thorough minimization of the environmental impact.

This thesis aims to analyse different end-of-life strategies for the fraction of plastic packaging waste (commonly referred to as Mixed Plastic Waste, MPW) that cannot be mechanically recycled. For the reason explained above, that is to create a circular economy for plastics, three alternative strategies to landfilling are explored; i.e. energy recovery through incineration, chemical recycling via pyrolysis and gasification.

Economical optimization of MPW management has already been exploited in a previous Master's thesis (Cieno, 2021). However, a limitation of the mentioned work is the lack of environmental assessment of the proposed alternatives for chemical recycling. This work recognises the need of a thorough investigation of MPW treatment alternatives in terms of both economic and environmental performance. Under these circumstances, this works proposes to investigate the global warming potential (GWP) of the different MPW treatment technologies and to find an optimum solution from

both an environmental and economical point of view. The geographical framework of this work is Northern Italy for mainly two reasons: continuity with the previous study, and availability of data for supply chain facilities. The optimization problem is formulated as a mixed integer linear programming (MILP) model and software GAMS® (General Algebraic Modelling System) is used to solve the optimization through the CPLEX solver.
The thesis is structured as follows.

The first Chapter is an overview of general plastic waste and MPW management for its end-of-life. MPW supply chain is explained and three treatment technologies, i.e. incineration, gasification and pyrolysis, are introduced.
In the second Chapter, the quantification of the supply chain environmental impact is presented, in terms of greenhouse gases emissions. All stages, included transportation, are analysed, taking into account also possible environmental credits.
The third Chapter introduces the mathematical model for the economic and environmental optimization of MPW treatment supply chain. In this Chapter, the "base case" scenario is analysed, according to which if MPW is pyrolyzed, then the pyrolysis oil is sent to oil refineries.
In the fourth Chapter, the cracking scenario is exploited. For this configuration, pyrolysis oil is no more sent to oil refineries, but it is sent to cracking plants as a fossil naphtha substitution. Economic and environmental analysis are performed according to the new MPW supply chain.
Some final remarks and a perspective on future work conclude the thesis.

Chapter 1

An analysis of plastic waste management

Chapter 1 presents an overview of general plastic wastes and of their management, focusing in particular on the Mixed Plastic Waste (MPW) fraction. MPW management is presented both from the current (2022) methodology, both from future perspectives, outlining three different treatment strategies: incineration, gasification and pyrolysis. Finally, scope and objectives of this Master's thesis are explained.

1.1 Plastic wastes and MPW fraction

The plastic waste that goes through the differentiated collection process is mechanically treated for the recovery of the most valuable plastic polymers. However, this process is associated to limited efficiencies also due to the heterogeneity of plastic packaging waste (Kunwar et al., 2015). Increasing the recycling rate is becoming more difficult because waste streams from plastic packaging recovery facilities are very heterogeneous and difficult to separate.

In order to achieve the circular economy of plastics, zero landfilling is needed. Driven by this requirement, 2006-2020 (Plastics Europe, 2020) evolution of plastic packaging waste treatment saw an increase of plastic recycling by 110%, energy recovery by 76%, whereas landfilling tendency decreased by 57%, as shown in Figure 1.1.

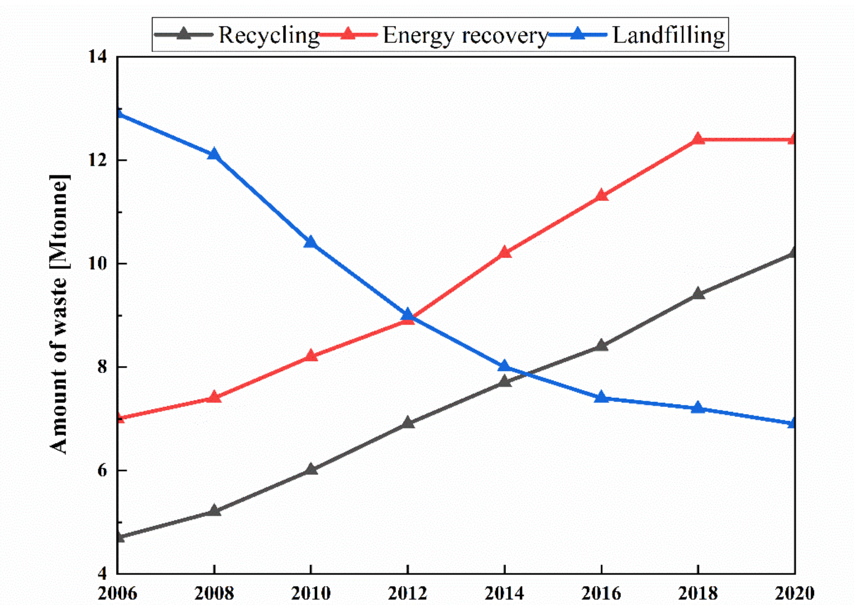


Figure 1.1: *2006-2020 trend of plastic waste treatment [Plastics Europe, 2020]*

The residual fraction resulting from mechanical treatment of plastic waste is called Mixed Plastic Waste (MPW) and is composed by a mixture of polymers, which is, basically, the remaining materials after the sorting of the most easily separable and recyclable plastics. The latter ones being constituted by Polyethylene terephthalate (PET) and of the most valuable polyolefin fractions, mainly high-density polyethylene (HDPE) and polypropylene (PP). The composition of MPW is highly dependent on the type of differentiated waste collection management. Therefore, it varies not only from Country to Country but even from municipality to municipality. Its composition is, consequently, not well defined and it is mainly composed of PP, HDPE and low-density polyethylene (LDPE). Overall, in the Italian context, MPW is composed of a mixture of different materials, including plastic (57%), paper and cardboard (10%), wood (3%), textiles (3%), inert and others (27%) (Gazzotti et al., 2022, Cossu et al., 2017).

The chemical composition analysis was performed by (Cossu et al., 2017) on samples taken from a plastic packaging waste selection plant located in the North of Italy and the results of their work are summarized in Table 1.1 (only elements present in a mass percentage higher than 0.01% were considered). The plant receives the plastic waste fraction of the municipal solid waste collected door to door. These heterogeneous materials cannot find any application other than being used as secondary solid fuel in incinerators or cement plants, in such a case MPW used as a secondary solid fuel it is no longer considered as an energy recovery (nor of course as a chemical recycle), exiting from the circular value chain of recycling. In Italy, MPW is mainly incinerated (57%), used as a substitute for coal burning in cement kilns (27%) or landfilled (16%) (Corepla, 2015).

Table 1.1: *MPW chemical characterization [Cossu et al., 2017]*

Name	Value	Name	Value
Heating value [GJ/tonneTS]	25.3	N [%TS]	1.0
H_2O [%]	23	Cl [%TS]	0.62
TS [%]	77	P [%TS]	0.56
TC [%TS]	70.6	Al [%TS]	0.56
TOC [%TS]	55.4	K [%TS]	0.12
O [%TS]	11.1	Na [%TS]	0.11
H [%TS]	6.4	S [%TS]	0.08
Ca [%TS]	1.1	F [%TS]	0.01

In the last decades (2000-2020), a higher efficiency in the waste sorting process allowed to recover more and more of the recyclable plastic fractions and to better separate them from MPW, avoiding landfilling the whole amount of wastes. A consequence of that has been that landfilled fraction dropped, because more and more polymers have been recovered to be mechanically recycled.

Also recovered MPW fraction witnessed an increase, stepping from 10-15% (1998-2000) to about 50%, referring to 2022 data (Gazzotti et al., 2022). The reason for that is because also for MPW landfilled wants to be avoided, and now a large amount of this not-recyclable fraction is available.

Few literature studies are available for possible large-scale industrial applications for such a big quantity of MPW in the municipal wastes, and this thesis aims to fill this gap by providing an insight into the optimal design of MPW supply chains in terms of both economic and environmental performance, focusing on the Northern Italian region, and complying with the framework of the circular waste economy.

1.2 Plastics recycling and challenges of plastic waste treatment

Four main approaches for plastic waste recycling are defined namely, primary, secondary, tertiary and quaternary recycling (Figure 1.2). Sorted plastics are usually not suitable for direct reprocessing because, for example, they may require cleaning to remove dirt and other contaminants, for instance in the case of food packaging plastic waste. General plastic waste is commonly distinguished in post-industrial waste, usually made of similar polymers, and post-consumer waste, which is the fraction coming from domestic use, and therefore containing all types of polymers and impurities.

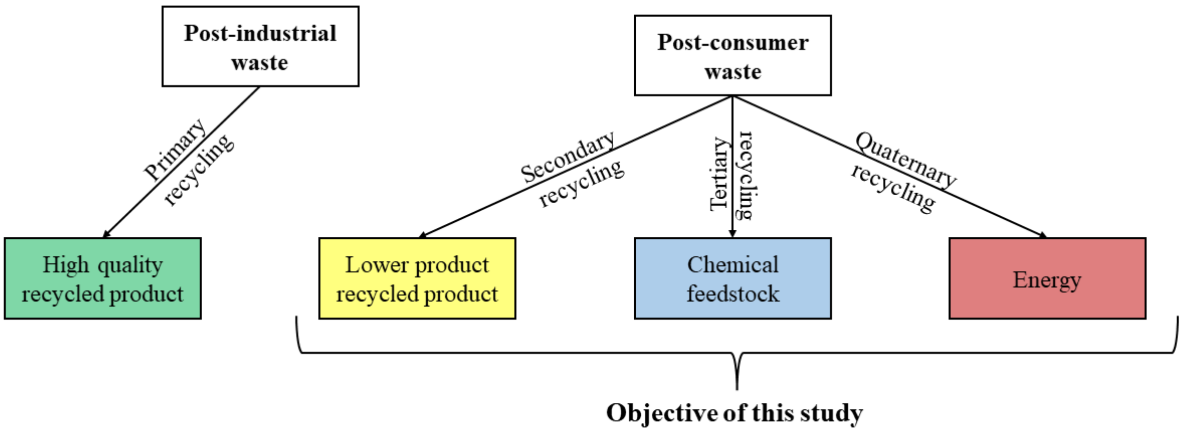


Figure 1.2: *Common classification of plastic recycling strategies*

Primary recycling, also known as re-extrusion, is the recycling of an uncontaminated, single type of polymer, having properties similar to virgin material (Gazzotti et al., 2022; Xia and Zhang, 2017). This process is based on the use of waste plastics that have similar features to the original products. For this reason, materials which undergo primary recycling are not post-consumer waste, as they have to be as clean as possible with the least possible amount of contaminants. Therefore, primary recycling includes only post-industrial waste, and the amount treated is, thus, very limited.

Secondary (mechanical) recycling involves the transformation of the post-consumer plastic waste into usually lower quality materials. Secondary recycling needs preliminary steps such as cleaning, shredding and contaminant separation. Generally, mechanical recycling is associated with downcycling of the material as the material itself undergoes strong chemical-physical stresses that undermine its integrity, resulting in recycled materials with generally lower performances than virgin ones (Gazzotti et al., 2022). However, mechanical recycling can have limited applicability.

Tertiary (chemical) recycling may help to extend the recyclable fraction, and it is also referred only to post-consumer waste. Chemical recycling is based on the idea that some polymers can be depolymerized back to their monomer, and other can only be converted to a general feedstock. The general guidelines to understand if a polymer is suitable for chemical recycling is linked to the relative heat of depolymerization. Polyolefins are suitable for cracking back to general feedstocks, while polyesters and polyamides are perfect to be depolymerized back to their monomers. The main advantage of chemical recycling come from the possibility of turning a material into a valuable feedstock. This approach is particularly significant when dealing with materials that have lost most of their mechanical properties and chemical integrity and, therefore, cannot be employed again for the manufacture of goods. However, tertiary recycling is affected by the purity of the starting material, and it could turn the process into a non-convenient approach from an economical point of view.

Quaternary recycling could be used whenever plastics is mixed with unsorted textile, paper and organic fractions, and thus typical of post-consumer waste. This mixture is turned to hydrocarbon fuels by means of gasification, leading to a mixture of H_2 and CO that can be converted into fuels (or chemicals). Gasification technologies are however quite expensive. Another quaternary recycling choice is thermal degradation of polymers down to CO_2 and H_2O by incinerating the plastics, releasing the energy embedded into the chemical bonds of polymers and allowing a reduction of the accumulation problems related to plastic materials in the environment. Quaternary recycling can be considered the last resort for the recycling of plastic materials and can be applied in all these situations in which the other three approaches would not be applicable. The disadvantages of quaternary recycling involve, first of all, the loss of the chemical energy stored in the polymer bonds. In addition, environmental concerns can arise, given the release of greenhouse gases and other by-products.

1.3 Supply chain definition for MPW treatment and technologies

The Italian supply chain for the management of plastic packaging is regulated by COREPLA (Consorzio Nazionale per la raccolta, il riciclo e il recupero degli imballaggi in plastica), which is a private body entitled to collect, recycle and recover plastic packaging, that is part of CONAI (COnsorzio NAzionale Imballaggi), the Italian Packaging Consortium. The main stages of the traditional plastic packaging supply chain are represented in Figure 1.3 and they are as follows:

- First step of the supply chain is the plastic producer, which turns raw materials into a finite polymer product and distribute it to the consumers;
- After the product's end of life, municipalities collect the packaging plastic waste by differentiated waste collection and send it to district centres (in Italy "Centri Comprensoriali", CC) where all heterogeneous materials such as iron, steel, aluminium, glass are taken away; or, in alternative, the waste by-passes the district centres and it is sent directly to sorting centres (in Italy "Centri di Selezione", CSS);

- sorting centres have the task to sort out similar fractions from the generic plastic waste, for instance, homogeneous fractions, so that they can be recycled mechanically and reprocessed into secondary raw materials and sold to packaging producers;
- from sorting centres, a heterogeneous fraction is sorted out, which is the above-mentioned MPW. This fraction is the residual waste that cannot be mechanically recycled because of its composition. At the end of its life, MPW is generally incinerated, or landfilled, in some cases it can be used in cement plants as secondary solid fuel.

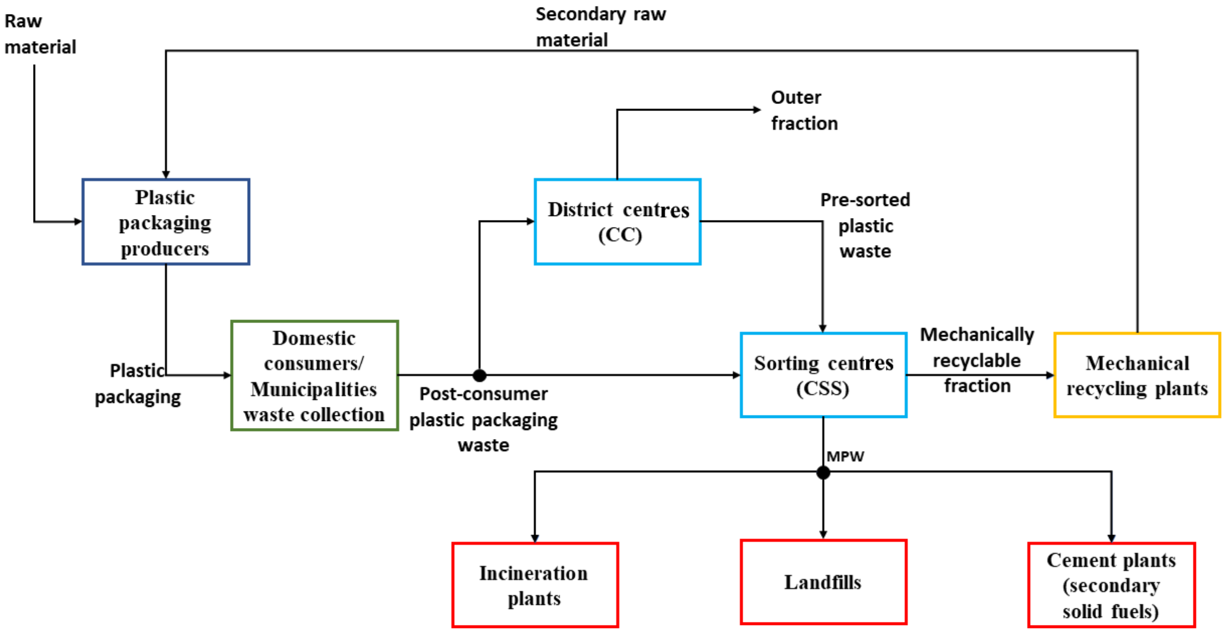


Figure 1.3: *Block Flow Diagram of the Italian traditional packaging waste supply chain*

Once MPW is sorted, however, different pathways may be exploited, as shown in Figure 1.4, and this following supply chain is the one considered in this work.

- Incineration plants will be still considered for the new supply chain;
- Gasification of MPW is one possible new alternative;
- Pyrolysis plants is the other alternative for the new supply chain. If this path is followed, the pyrolysis product (pyrolysis oil) is suited either for being treated in a refinery plant, or to be sent to cracking plants, as an alternative for cracking naphtha.

Landfilling, an industrially employed strategy for MPW end-of-life, is excluded from this work because is far from the idea of waste circular economy. European strategy for waste management imposes that "the following waste hierarchy shall apply as a priority order in waste prevention and management legislation and policy: prevention; preparing for reuse; recycling; other recovery, e.g. energy recovery; and disposal" (Directive 2008/98/EC). Therefore, alternative MPW treatment technologies will be preferred.

Likewise, MPW as a possible fuel for cement plants will not be considered in this work, its heating value and its capability to produce heat is taken into account in another context, i.e. incineration – due to the double purpose of burning the waste and perform energy recovery. From a previous master thesis work (Cieno, 2021), incineration was proven to be the best choice for MPW treatment in the Italian supply chain context, from a purely economic point of view. However, a major drawback of this technology, despite its economic feasibility, is the environmental impact in terms of intensive greenhouse gas (GHG) emissions. Under these circumstances, further assessment is required in order to find a better alternative and try to balance economic and environmental performance over the entire supply chain.

Therefore, the MPW treatment technologies included in the model are, as mentioned before: incineration, pyrolysis and gasification. This works aims at giving an evidence-based decision for the choice of treatment technology, balancing economic and environmental performance.

MPW supply chain illustrated in this thesis is not the complete MPW supply chain shown in Figure 1.3. It starts from plastic collection operated by municipalities and sent to provinces collection centres. Then plastic waste is sent directly to sorting facilities to separate the MPW from the mechanically recyclable fraction. Finally MPW is sent to one of the possible treating stages. The representation of this Master's thesis supply chain is reported in Figure 1.4.

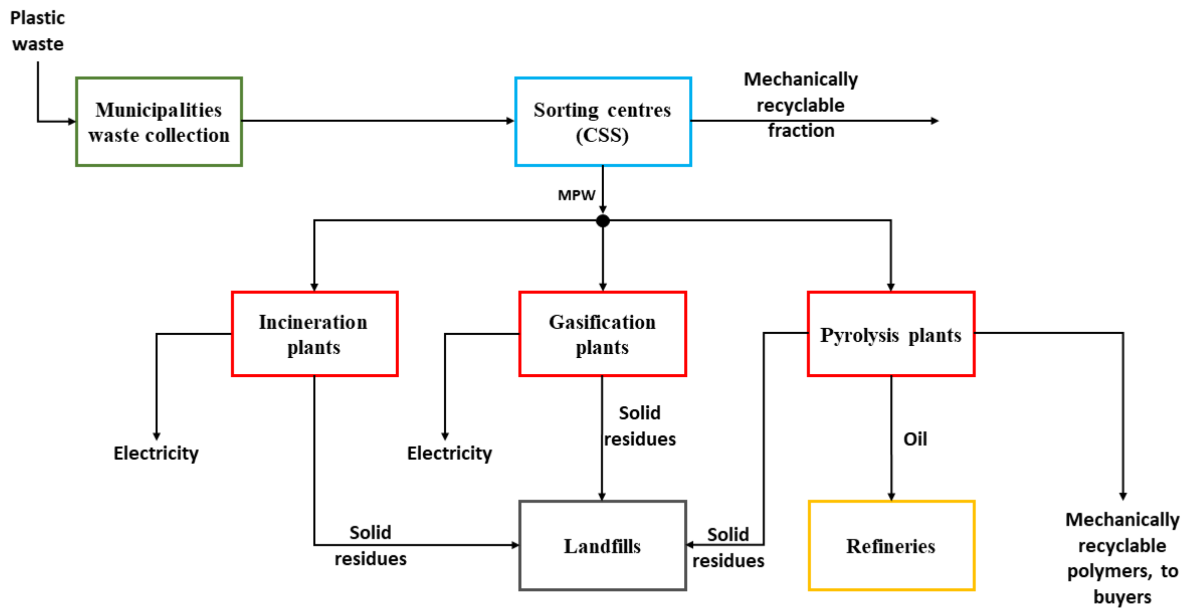


Figure 1.4: *Block Flow Diagram of the Italian alternative packaging waste supply chain*

In the following, the alternative technologies for MPW treatment will be discussed.

1.3.1 Incineration

For the streams of waste for which some form of recycle is not applicable, energy recovery is a valuable path to follow. Combustion of wastes, commonly called incineration, associated to energy recovery (Waste to Energy plants, WtE), is a widespread thermal treatment for different types of waste, both for municipal solid waste (MSW) and for industrial waste (IW). The main interests towards thermal treatments were due to the possibility to reduce mass and volume of wastes that need to be landfilled and to the capability of making a significant energy recovery. Once waste-sorting efficiency has increased, it was possible to limit the presence within MPW of wastes characterized by low heating values. By doing so, it was possible to obtain a waste fraction with higher heating values, from which energy recovery is a very attractive option. Incineration process aims to the complete oxidation of all the chemical species contained in the feedstock material. In the following, MPW is directly incinerated, avoiding any pre-treatment (from an energy recovery point of view the MSW pre-treatment seems not to be advantageous), and used only for the production of electricity, which has been proven to be the best strategy to recover energy from waste (Consonni et al., 2004). The waste can be burnt without the use of any other auxiliary fuels when the LHV exceeds 5-7 GJ/tonne (Komilis et al., 2013), and that is the case for this study, which considers an LHV of approximately 25 GJ/tonne for MPW.

Unlike the case when only thermal energy production is pursued, and only saturated steam is generated, for electricity production superheated steam is needed, which is then supplied to a steam turbine (Figure 1.4) making a Hirn cycle (Rankine cycle with superheated steam).

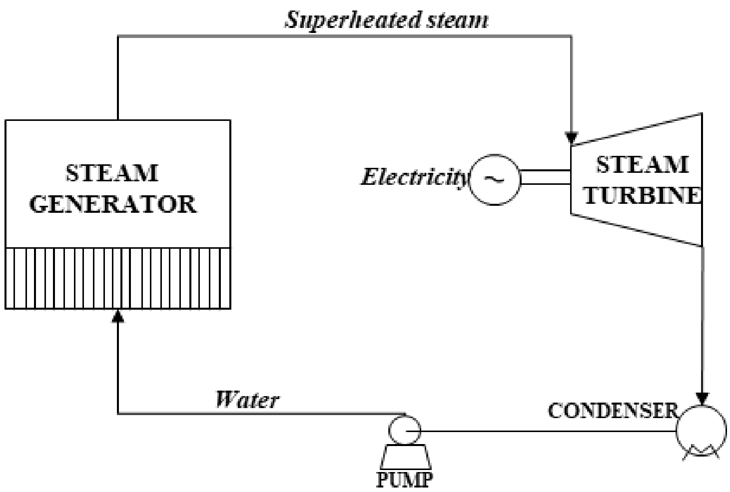


Figure 1.5: *Simplified scheme for electrical production from an incineration plant (Lombardi et al., 2014)*

Incineration plant capacities and scaled-down capacities (i.e. a fraction of the entire plant capacity dedicated only to MPW treatment) are taken from Cieno (2021) and ISPRA ("Istituto Superiore per la Ricerca e la Protezione Ambientale") database, and whenever these data were not found, it was kept the approximation reported in Utilitalia (2019).

If an incineration plant is chosen into the model, its available capacity for MPW treatment is computed based on some assumptions that are comprehensively discussed in Cieno (2021). It is assumed that the incineration plant treats several types of waste, among which MPW represents only a fraction. Therefore, in an incinerator, the maximum dedicated capacity for MPW treatment is reported to be around 21% of the total capacity of the incinerator. The maximum capacities of the incinerators (representing the available capacity for MPW treatment) are presented in Table 1.2.

Table 1.2: *Estimated capacity for Northern Italy incineration plants. An X marks the plant whose capacity has not been found in the ISPRA database and has been estimated with the assumptions found in Utilitalia*

	Region	**City**	**Province**	**Capacity [ktonne/year]**
	Emilia-Romagna	Coriano	RN	149.0
	Emilia-Romagna	Cassana	FE	142.0
	Emilia-Romagna	Forlì	FC	135.0
	Emilia-Romagna	Granarolo dell'Emilia	BO	222.0
	Emilia-Romagna	Modena	MO	237.4
	Emilia-Romagna	Piacenza	PC	118.0
	Emilia-Romagna	Parma	PR	160.0
	Friuli - Venezia Giulia	Trieste	TS	197.0
	Lombardia	Bergamo	BG	75.0
	Lombardia	Dalmine	BG	155.0
	Lombardia	Brescia	BS	981.8
X	Lombardia	Busto Arsizio	VA	133.1
X	Lombardia	Como	CO	106.2
	Lombardia	Corteolona	PV	75.0
	Lombardia	Parona	PV	380.0
	Lombardia	Cremona	CR	140.2
	Lombardia	Desio	MB	91.0
	Lombardia	Milano	MI	635.1
	Lombardia	Trezzo d'Adda	MI	197.6
	Lombardia	Valmadrera	LC	114.0
X	Piemonte	Torino	TO	534.6
	Trentino - Alto Adige	Bolzano	BZ	130.0
	Veneto	Padova	PD	245.0
	Veneto	Schio	VI	98.8

1.3.2 Gasification

Waste gasification is a process aimed to transform a solid fuel to a gaseous fuel (syngas) mainly composed of carbon monoxide and hydrogen, through a partial oxidation of the solid fuel in presence of a sub-stoichiometric oxidant. (Arena et al., 2011) A solid product is generated too, containing char (solid carbonaceous compounds) and ashes (Lombardi et al., 2014). In the case of air gasification, which is the technology considered in this study, part of the fuel is combusted to provide the heat needed to gasify the rest (autothermal gasification). The syngas produced can be either utilized as a fuel gas, as it is considered in this thesis, but it could also be seen as a building block for the production of several chemicals (Malkov, 2004). The solid waste gasification is a complex process which takes place at temperatures generally higher than 600 °C (Arena et al., 2010).

The plastics-to-energy gasification system can, in principle, be fed with one of two mixed plastic wastes. The first one is called EBR (end-belt refuse), and it is MPW which undergoes through mild pre-treatments, in order to reduce moisture and ash content. The alternative feedstock is called SRA (secondary reducing agent), which however is strongly pre-treated and it is unattractive from the economic standpoint (Arena et al., 2011).

In the gasification plant considered, the syngas produced is burnt, and the hot flue gases are used to transfer heat to a steam generator, which produces electrical power through a steam turbine. After that, the steam is condensed and re-fed to the boiler allowing the reiteration of the cycle. A simplified scheme is taken from Arena et al., 2011 and shown in Figure 1.5.

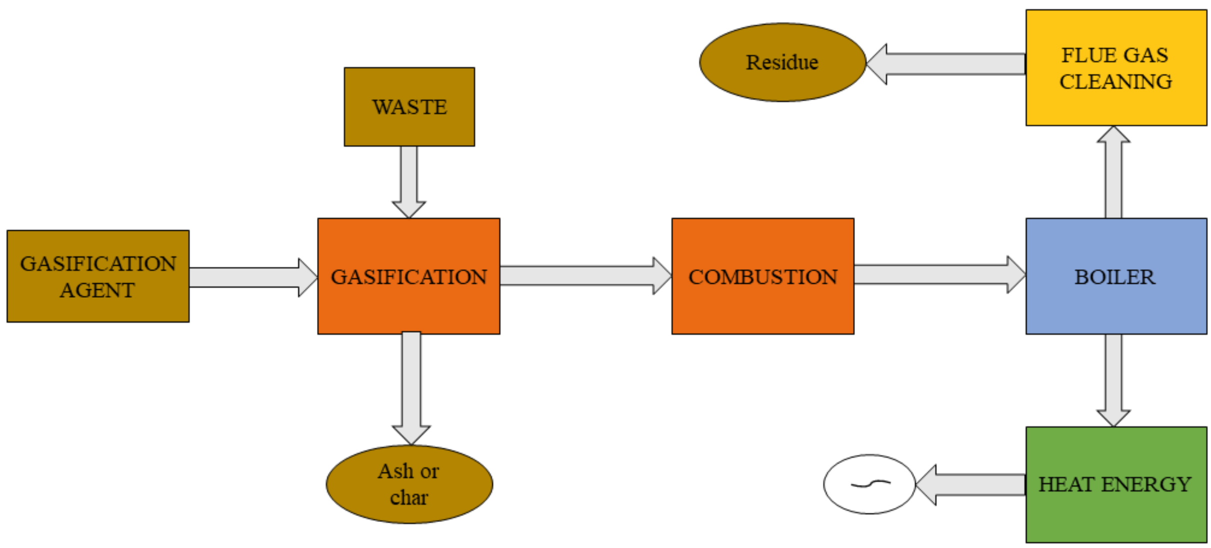


Figure 1.6: *Simplified scheme of a gasification plant for electricity production (Arena et al., 2011)*

1.3.3 Pyrolysis

Pyrolysis is a thermal process which takes place in complete absence of oxygen, heating the entering feed by an external heat source, at temperatures higher than 400°C but generally lower than 800°C (Lomardi et al., 2014). It produces three output streams: gas, liquid (oil) and solid (char), all with combustibile characteristics (the higher the temperature, the larger the gaseous fraction). No oxidation occurs, but the feed undergoes to a thermal degradetion. The most interesting pyrolysis product is pyrolysis oil, both because it is easy to carry and store, but also because it is considered as a heavy fuel oil substitute or as a raw material by the petrochemical industry (Fivga and Dimitriou, 2018). A simplified process scheme of how pyrolysis works is shown in Figure 1.6, taken from Fivga and Dimitriou, 2018 and developed by a recycling company based in UK. The pyrolysis process occurs in a fluidised bed reactor at atmospheric pressure, at a temeprature around 450-600 °C, for the complete plastics degradation (Sørum et al., 2000).

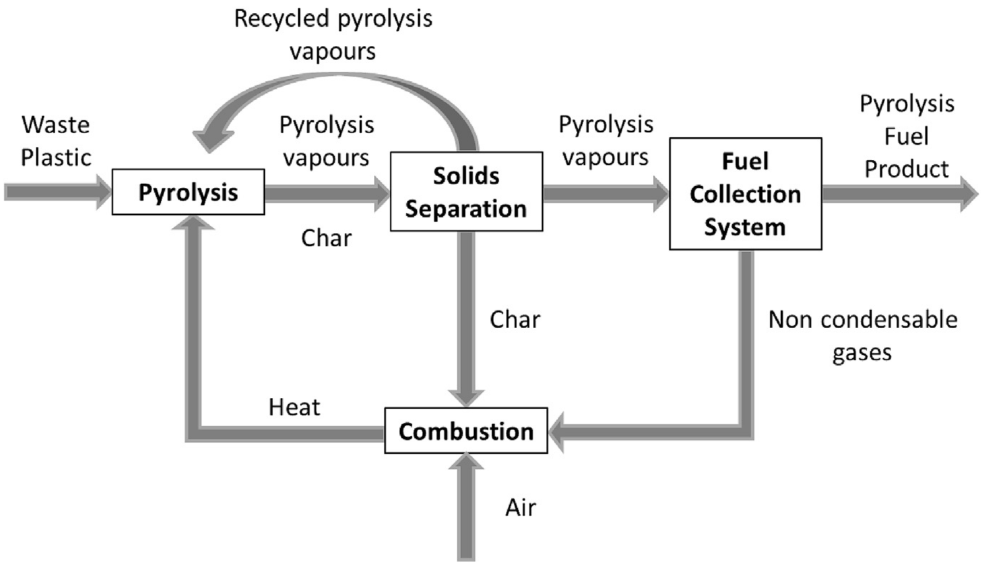


Figure 1.7: *Simplified scheme of a pyrolysis unit (Fivga and Dimitriou, 2018)*

The waste plastics feedstock considered in this study is a mixture of polyethylene (PE), polypropylene (PP), and polystyrene (PS), since this mixture comprises the majority of plastic waste. Typical product yields from pyrolysis are summarized in Table 1.3 and taken from Fivga and Dimitriou, 2018.

Table 1.3: *Product distribution for a pyrolysis reactor [Fivga and Dimitriou, 2018]*

Compound	Weight percentage [$\%_{wt}$]
Ethane	6.49
n-Octane	18.58
n-C14	31.86
n-C18	15.75
n-C25	16.87
n-C30	3.45
Char	7.00

Pyrolysis in an endothermic reaction, which requires a contant source of heat to carry on. One immediate choice can be the one of burning pyrolysis by-products to sustain the reaction (Fivga and Dimitriou, 2018), which means char and non-condensable gases. By doing that the process is made autothermic (except for the start-up period) and no external heating source is required.

1.4 Thesis motivation, scope and objectives

Based on what discussed above, this thesis has one specific objective: optimal design of MPW supply chain, taking into account both the selection of the treatment technologies (i.e. incineration and two chemical recycle alternatives, namely gasification and pyrolysis) and finding the optimal distribution of the material flows among the different entities of the supply chain. In other words, investigate the technology for MPW treatment, once being sorted from general plastic wastes, which best fits in terms of environmental improvement strategy for plastics treatment. Moreover, this study aims to balance economic and environmental performance of the choice of MPW treatment technology.

The model gives the material flows of waste supplied by provinces to sorting centres (constrained by the capacity of each sorting centre), and from the latter one to different processing plants, all located in the Northern Italy. In the case of pyrolysis, the oil generated is sent to refineries, in the base case, or to cracking plants in the alternative scenario, while for the other technologies solid residues are sent to landfills.

The treatment technologies considered in this work are incineration, that is industrially well established, gasification and pyrolysis, some emerging and potentially attractive alternatives.

The environmental impact defined in terms of GHG emissions of the entire supply chain will be considered and is given by the contribution of:

- impact of transportation of plastic waste, MPW and other solid residues;
- impact of sorting centres facilities;
- impact of MPW treatment technologies.

However, not only direct GHG emissions, but also avoided emissions will be accounted for. Each technology, either because it produces electricity directly (incineration and gasification), or for the pyrolysis case, because it allows to avoid emissions derived from extraction or transportation of crude oil, has some environmental "credit". This means that some other GHG emissions, for instance for electricity production or for freight transportation are somewhere else avoided. Thus, the model aims at minimizing the overall net emissions of the entire supply chain, given by the difference between the GHG direct emissions of the overall supply chain and the avoided emissions.

The problem is formulated as a mixed integer linear programming (MILP) model and will be solved using the software GAMS® and CPLEX solver as optimization tool.

Two cases will be studied:

1) First case – base-case scenario – considers that, whether pyrolysis is choses as treatment technology, then pyrolysis oil is sent to Norther Italian refineries to become a substitute for a heavy crude oil;
2) Second case – cracking scenario – it is an alternative scenario for which pyrolysis oil is not sent to refineries, but to cracking plants as a naphtha substitute.

Together with environmental optimization, expressed in terms of GHG emissions, the results will be coupled with economical evaluation of the supply chain, i.e. total cost and revenues, based on the economic analysis conducted in the work of Cieno (2021). An attractive scenario will be the one that not only minimizes the net emissions, but that also maximizes the gross profit from MPW treatment. Therefore, this study aims to balance two conflicting objectives: on one side choosing the best environmental alternative, the ones that allows to minimize the net GHG emissions; on the other side, avoiding that the best environmental approach leads to an economic unfeasibility of the entire supply chain.

Chapter 2

Quantification of supply chain impact

In Chapter 2 the problem of MPW supply chain is investigated, from the point of view of the environmental impact related to its treatment. The supply chain analysed in this Master's thesis work starts with the plastic waste collection; then MPW is separated from the mechanical recyclable wastes; at this point MPW is treated according to one of the proposed technologies (i.e. incineration, gasification or pyrolysis). Each of these stages lead to greenhouse gases emissions, which are quantified with the purpose of minimizing them, taking into account also possible environmental credits.

2.1 Material balances

The aim of this work is the optimal design of MPW treatment supply chain in terms of environmental impact minimization (minimization of CO_2^{eq} emissions of each stage of the supply chain.

The MPW treatment supply chain consists of several consequential steps, which all lead to some GHG emissions: collection of plastic municipal solid wastes (MSW); sorting of the plastic wastes in the sorting centres to separate MPW from mechanical recyclable polymers; MPW treatment with one specific technology, either to perform energy recovery form it, or for a chemical recycling; treatment residues to deliver to landfills; additional possible treatments to be performed over treatment plants products (e.g. oil refinement). All of these steps are necessarily correlated by means of a transportation chain, which allows to move all the flowrates involved from one place to another across all the Northern Italy territory.

A first step is represented by the collection of environmental impact data for each stage of the supply chain. These factors will be expressed in terms of ktonne of CO_2^{eq} per ktonne of flowrate processed in a treatment facility or transported from one place to another. Analysing CO_2^{eq} emissions means that all sources of greenhouse gases (GHG) emissions are considered, from transportation emissions to electricity production emissions, and above all MPW treatment emissions.

The MILP model will give the optimal distribution of the material flows among the different stages of the supply chain aiming at minimizing the overall CO_2^{eq} emissions of the entire supply chain and will return the environmental optimal solution for MPW treatment technology as well. Results will be express in ktonne of CO_2^{eq} per year, but also in ktonne of CO_2^{eq} per ktonne of MPW treated over the entire supply chain.

A first stage in the MPW supply chain is represented by the differentiated waste collection of all plastic wastes by provinces that will end up in sorting centres. In the latter one, the recyclable fraction is separated from the non-recyclable fraction. The precise mass flowrates can be retrieved from 2020 COREPLA Management Report. From this national report it is possible to estimate the amount of recycled fraction and the amount of plastics which is not recycled:

- The total amount of recycled plastics in 2020 is equal to 625.1 ktonnes. From this quantity, the fraction related to the secondary reducing agent (SRA) used in steel plants is subtracted and corresponds to 16.3 ktonnes in 2020. Therefore, the total recyclable flowrate relative to year 2020 is equal to 608.8 ktonnes.
- MPW for COREPLA is summation of different waste amounts: the share of plastics which has been incinerated for energy recovery (467.9 ktonnes in 2020), the share of plastics which has been landfilled (192.5 ktonnes in 2020), and finally a small amount of plastics not directly managed by COREPLA, but entrusted to it from another body, CORIPET (1.3 ktonnes in 2020). Thus, the total amount of MPW is equal to 661.7 ktonnes.

Summing up the two fractions, the total flowrate of plastics processed in Italy in 2020 was 1270.5 ktonnes, of which MPW accounted for about 52% (both incinerated and landfilled). A chart visualization is presented in Figure 2.1, showing the MPW fraction within the whole share of plastic wastes, and its management strategy.
The shares of plastic waste management represented in Figure 2.1 and aforementioned refers to national values, while, when considering each region separately, these values can differ. However, it is decided to consider that these flowrates are valid for the whole Northern Italian territory, making no distinction among regions.

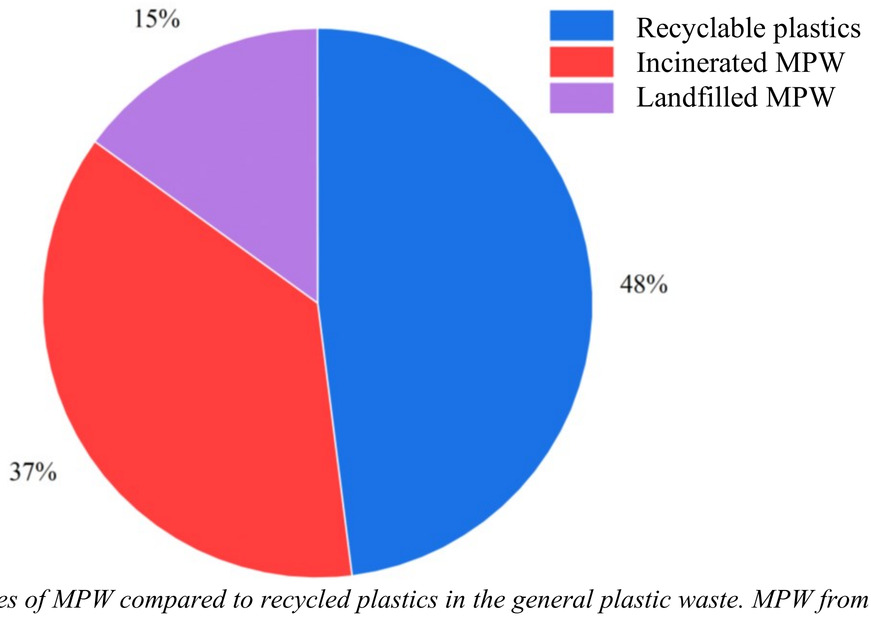


Figure 2.1: *Shares of MPW compared to recycled plastics in the general plastic waste. MPW from CORIPET has been neglected as it is a very small amount (2020 COREPLA management report)*

The second stage in the MPW supply chain is represented by the treatment technology. Once the quantity of MPW sorted out in the sorting centres and separated from the recyclable plastics is quantified, then the entire flowrate is sent to treatment facilities.
Each MPW treatment technology produces some solid residue that must be unavoidably sent to a landfill.

- For what concerns incineration, the solid fraction (ashes) produced after MPW is burnt is 0.076 $tonne_{res}/tonne_{PL}$ (AIDIC, 2014).

- If the MPW is sent to a gasifier, the solid fraction produced is 0.308 $tonne_{res}/tonne_{PL}$ (Arena et al., 2011). However this number is obtained considering that MPW that is actually gasified is not the entire share of MPW that enters in the gasification plant. MPW is first pre-treated, losing 30% of its weight: 15% is ashes and 15% is moisture. At this point, MPW is called End Belt Refuse (EBR) and gasified, and the share of ashes produced is 44% of the treated part. Since only 70% of the initial MPW is treated, the share of ashes produced is not 44% of the amount of MPW that enters the gasification plant, but a smaller fraction, only 30.8%.

- For pyrolysis, the situation is different. Before the pyrolysis unit, there is an additional sorting centre, called Material Recovery Facility (MRF), used to perform a further and more accurate sorting of the MPW (Mastellone, 2020). Pyrolysis plants are not suited to treat all kind of plastics: some pyrolysis plants are designed to treat only polyolefins, and they will be indicated as PO_Pyrolysis, others are designed to treat also Polystyrene, and indicated as PO_PS_Pyrolysis. All the remaining MPW which is sorted out, is sent to an incineration plant and burnt, and this fraction differs whether the plant is a PO_Pyrolysis or a PO_PS_Pyrolysis. Moreover, in the MRF a small amount of the initial MPW is also recovered to be mechanically recycled. Finally, the MRF performs the separation of inerts contained in the entering MPW, which need to be landfilled. An overview of these mentioned fractions is displayed in Figure 2.2 for PO_Pyrolysis and in Figure 2.3 for PO_PS_Pyrolysis.

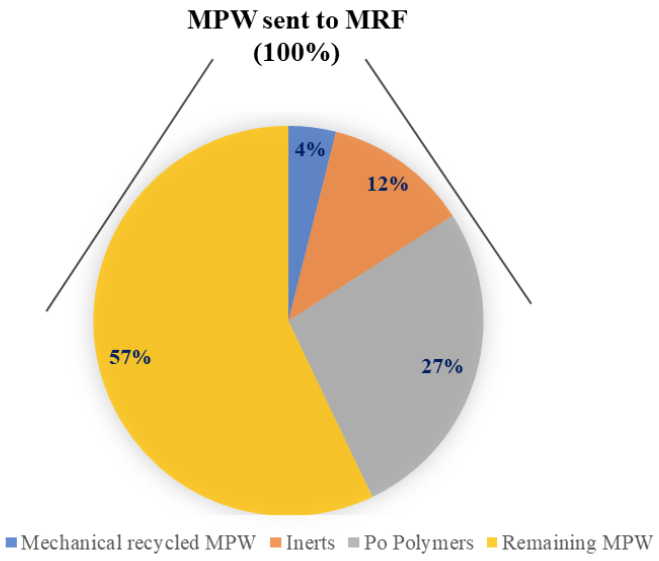


Figure 2.2: *Material balances for a MRF in a PO_Pyrolysis plants*

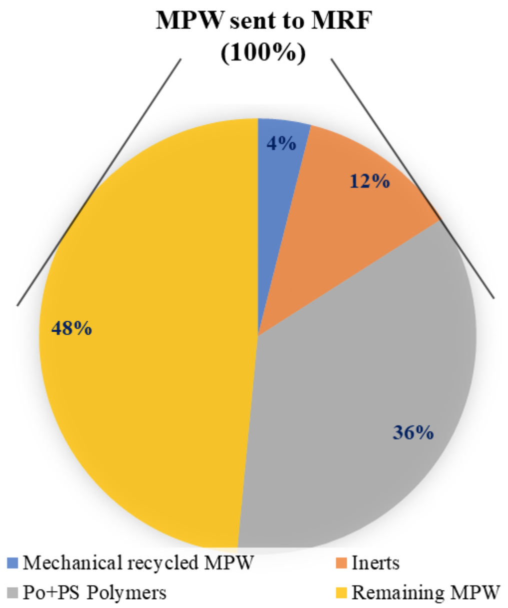


Figure 2.3: *Material balances for a MRF in a PO_PS_Pyrolysis plant*

MPW which is pyrolyzed is thus, only a small fraction of the initial flowrate that enters in the pyrolysis plant (26.97% for a PO_Pyrolysis and 35.58% for a PO_PS_Pyrolysis). Any pyrolysis process is characterized by a pyrolysis efficiency, which in this work is indicated as η_{pyro} and equals to 85.8% (Fivga and Dimitriou, 2018).The residual fraction produced in the pyrolysis is then sent to landfill.

It is now possible to estimate the fraction of pyrolysis oil produced from the MPW that initially entered the pyrolysis plant by multiplying the pyrolysis efficiency by the MPW flowrate that can actually be pyrolyzed, obtaining the "MPW-to-Oil" conversions factors, collected in Table 2.1.

Table 2.1: *MPW-to-Oil conversion factors*

Type of pyrolysis plant	MPW-to-Oil conversion factor
PO_Pyrolysis	0.2314
PO_PS_Pyrolysis	0.3053

The remaining share of MPW that needs to be landfilled is therefore the 14.2% of the treated MPW, i.e., the 3.81% of the initial MPW for a PO_Pyrolysis plant and the 5.02% of the initial MPW for a PO_PS_Pyrolysis plant. Thus, the total amount to be landfilled is the 15.82% for a PO_Pyrolysis plant, and the 17.03% for a PO_PS_Pyrolysis plant.

2.2 Transportation impact assessment

Based on the material balances previously discussed for all the stages of the supply chain, it is possible to evaluate the material flowrates moved from one stage to another, and therefore quantify the transportation emissions and how much they impact on the supply chain.

Transportation stage is a crucial part of the environmental analysis and of the overall supply chain. This study will consider only road transportation to move goods, which is by far the most used transportation system for small distances.

Trucks are commonly employed for merch transportation, and given the large amounts of flowrates considered in this study, it seemed reasonable to consider heavy-duty trucks (HDT). To better estimate the environmental impact of transportation stage in the model, first step was to retrieve data about the number and typology of vehicles in Northern Italy.

From ACI (Automobile Club d'Italia) 2021 database it was possible to determine the energy supply of HDTs, and it came out that less than 1% is gasoline-powered, whereas the major share is based on diesel fuel. Therefore, it makes sense and it is not such a big simplification to consider only diesel engines as source of power and of GHG emissions for transportation in this study.

Besides the power source of a vehicle, another requirement is to assess its environmental emission class, based on the European legislation of emission standards (EURO legislation). The legislation all over the years has become more and more stringent, regulating pollutant emissions. However, countries are not forced to replace old models with more ecologic ones, that is why the vehicle fleet in Northern Italy is still very much variegated, as expressed in Table 2.2.

It is interesting to notice that the largest share actually belongs to pre-Euro legislation, when there were no pollution limitations

Table 2.2: *Composition of heavy-duty diesel trucks (HDDT) in Northern Italy*

Environmental class	Number of vehicles	Share
Euro 0	62150	22.6%
Euro 1	13844	5.0%
Euro 2	35463	12.9%
Euro 3	50988	18.6%
Euro 4	20644	7.5%
Euro 5	40387	14.7%
Euro 6	51165	18.6%

For the purpose of this study, only GHG emissions are worth considering and, for what concerns vehicles emissions, this means CO_2, CH_4 and N_2O emissions, all expressed in terms of CO_2^{eq} and they are presented in Table 2.3.

Legislation does not set limits directly for methane (CH_4), but for all the unburned hydrocarbons (THC, total hydrocarbons). Within THC, CH_4 is a large share, approximately 95% (Quiros et al., 2016).

The same stands also for nitrous oxide (N_2O): it is NO_x family which is regulated, of which N_2O is a very small fraction, only 0.2% (Nitrous Oxide Emissions From Vehicles, Journal of the air & waste management association, J.M. Dasch, 2012).

Table 2.3: *GHG emissions from HDDT based on EURO environmental standards*

<table>
<tr><th>Emission standard</th><th>CO_2 [g/km]</th><th>Reference</th><th>N_2O (NO_x) [g/km]</th><th>Reference</th><th>CH_4 [g/km]</th><th>Reference</th></tr>
<tr><td>Euro 0</td><td>1068.9</td><td rowspan="7">Clairotte et al. (2020)</td><td>0.03 (14.8)</td><td rowspan="5">Hong Huo et al. (2011)</td><td>1.8</td><td rowspan="4">Hong Huo et al. (2011)</td></tr>
<tr><td>Euro 1</td><td>1068.9</td><td>0.02 (9.9)</td><td>1.33</td></tr>
<tr><td>Euro 2</td><td>807.2</td><td>0.02 (10.2)</td><td>0.95</td></tr>
<tr><td>Euro 3</td><td>820.0 [1]</td><td>0.02 (8.1)</td><td>0.29</td></tr>
<tr><td>Euro 4</td><td>833.3</td><td>0.01 (5.3)</td><td>0.09</td><td>Papadopoulos et al. (2020)</td></tr>
<tr><td>Euro 5</td><td>808.2</td><td>0.005 (2.69)</td><td rowspan="2">Ko et al. (2020)</td><td>0 [2]</td><td rowspan="2"></td></tr>
<tr><td>Euro 6</td><td>811.6</td><td>4.2E-4 (0.21</td><td>0 [2]</td></tr>
</table>

[1] Euro 3 CO_2 emissions are not taken from Clairotte et al. (2020) because not reliable (too small value compared to others, small number of tests carried out on that class of vehicles). The value reported is chosen arbitrarily, as an intermediate value.
[2] Methane emissions data for Euro 5 and Euro 6 are set to zero, because the introduction of the DOC (Diesel Oxidation Catalyst) allowed to reduce a lot the emission of unburned hydrocarbons.

Nitrous oxide and methane have a greater global warming potential (GWP) with respect to CO_2, 273 and 28 time greater, respectively (www.epa.gov). Results of GHG emissions expressed in terms of CO_2^{eq} emissions are collected in Table 2.4.

Table 2.4: *GHG emissions of HDDT based on Euro standards*

Emission standard	CO_2^{eq} emissions [g/km]
Euro 0	1127.5
Euro 1	1111.6
Euro 2	839.3
Euro 3	833.6
Euro 4	838.6
Euro 5	809.6
Euro 6	811.7

Performing a weighted average on the share of vehicles belonging to each class, the result is that the actual (2021 data) vehicle fleet emits about 900 g of CO_2^{eq}/km per each truck.

For the MPW and residue transportation, it is chosen a standard capacity of a truck equal to 40 m^3, whereas for the oil transportation from pyrolysis centres, trucks are supposed to have a capacity equal to 43 m^3 (standard on the market).

Supposed that each truck is fully loaded and with no empty spaces, the mass that each truck carries in its path is summarized in Table 2.5.

Table 2.5: *Mass transported by each typology of truck*

Goods transported	Truck capacity [m^3]	Density [tonne/m^3]	Mass transported [tonne]
Waste and MPW	40	0.31	12.4
Residues	40	2.1	84
Oil	43	1.002	43

Chapters 3 and 4 will thoroughly describe the methodology employed in the model to assess the GHG emissions from transport stage.

2.3 Sorting centres impact assessment

Within the supply chain structure, sorting centres are the facilities in charge to separate plastic wastes: partly they are sent to mechanical recycling (48%), the remaining part becoming MPW.

An advanced sorting plant located in Northern Italy is taken as a reference, whose scheme is represented in Figure 2.4. Italian name for indicating MPW is PLASMIX, which is the name reported in Figure 2.4.

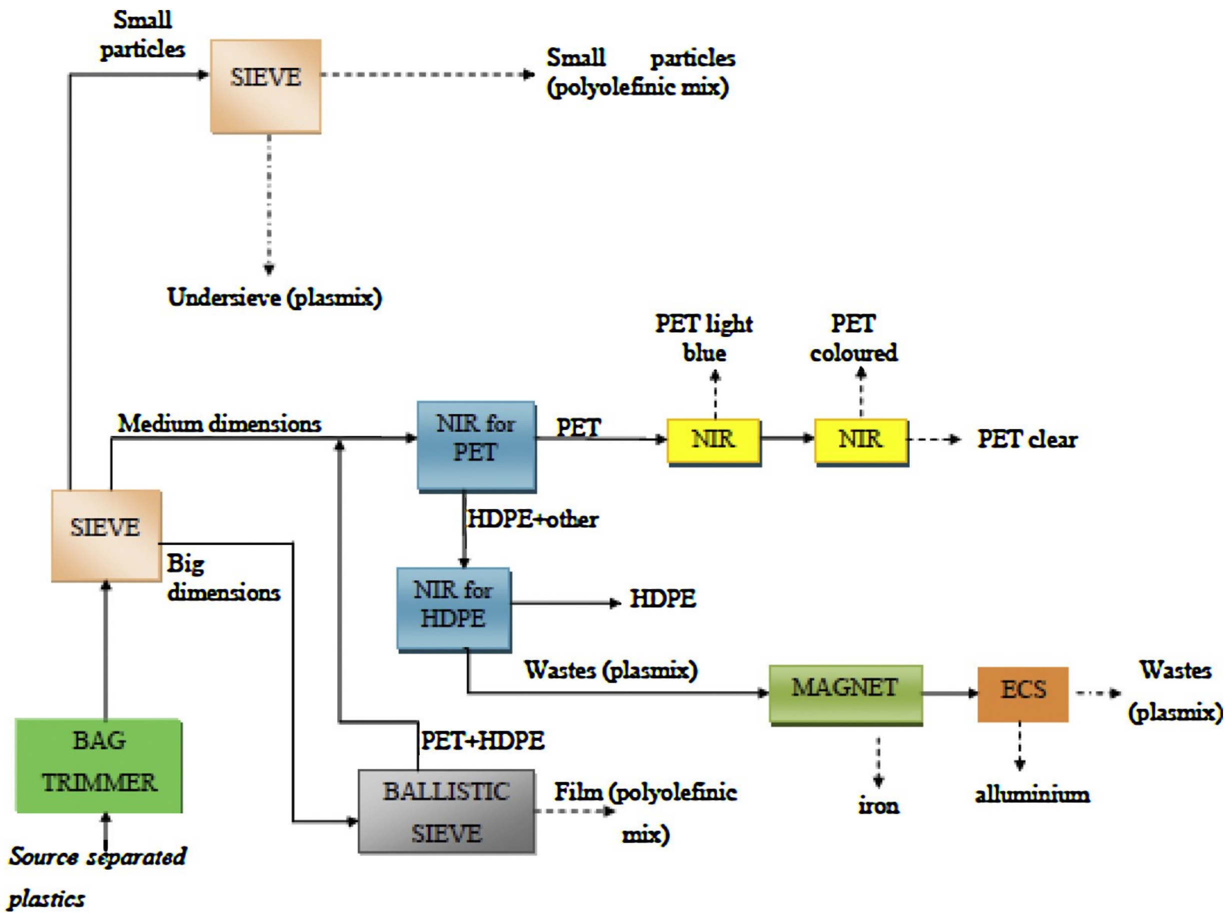


Figure 2.4: *Scheme of a sorting centre functional units (Rigamonti et al., 2013)*

The layout includes a bag trimmer, two sieves and film separation (ballistic sieve), and four NIR (near infra-red) sorting steps. A magnet and an eddy current separator (ECS) allow to recover part of the iron and of the aluminium present in the MPW.

The only source of GHG emissions from a sorting centre comes from the use of these machineries. The electricity consumption for each of the components is retrieved from Rigamonti et al., 2013 and summarized in Table 2.6.

Table 2.6: *Electricity consumption of machineries used in a material recovery facility (MRF)*

Machinery	Quantity	Electricity consumption [kWh/tonne]
Bag Trimmer	1	3
Sieve	3	1
NIR	4	12
Magnet	1	0.75
ECS	1	0.95

Based on these data, the overall electricity consumption is estimated as 55.7 kWh/tonne of plastic waste that enters in the sorting centre.

To compute the GHG emissions derived from the electricity consumption, it is necessary to assess the Italian energy mix.
The standard energetic mix of power for electricity production in Italy is retrieved from 2020 data of TERNA and the data is reported in Table 2.7.

Table 2.7: *Energy sources in Italy (standard mix)*

Energy source	TWh	% on the total
Fossil fuels	161.7	58.06
Pumping	1.9	0.69
Hydroelectric	47.6	17.09
Geothermal	6	2.15
Photovoltaic	24.9	8.94
Wind turbines	18.8	6.75
Biomasses	17.6	6.32
Total	278.5	100

Non-renewable (fossil-based) energy is given by the contribution of natural gas, coal and other solid fuels and oil; their corresponding percentages are shown in Figure 2.5.

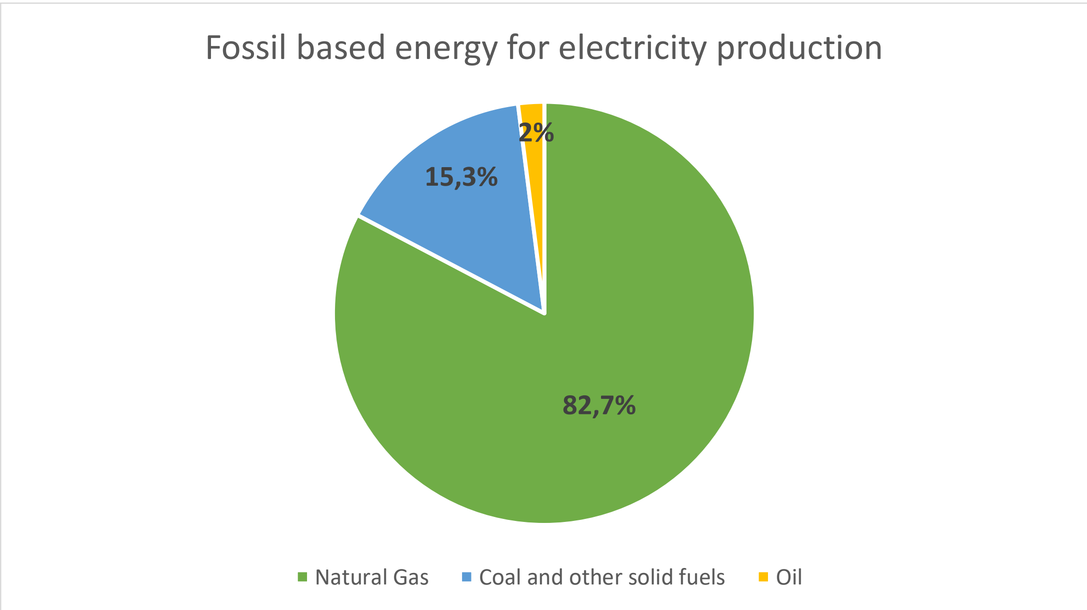


Figure 2.5: Distribution of sources for fossil-based electricity production

Each of these renewable and non-renewable sources of energy have their specific GHG emissions expressed in terms of kg of CO_2^{eq} per kWh of electricity produced and the values are summarized in Table 2.8.

Table 2.8: *GHG emissions associated to the energy sources for production of Italian electricity mix*

Energy Source	GHG emissions [kg CO_2^{eq}/kWh]	Source
Natural gas	0.53	O'Donoughue et al. (2014)
Coal and solid fuels	0.90	N.Wang et al. (2018)
Oil	1.09	De Melo et al. (2019)
Photovoltaic	0.045	Peng et al. (2012)
Hydroelectric and pumping	0.039	L.Wang et al. (2018)
Wind turbines	0.026	L.Wang et al. (2018)
Biomass	0.43	Beagle and Belmont (2019)
Geothermal	0.69	Bravi and Basosi (2013)

Considering the actual mix of energy sources for electricity production in Italy, the GHG emissions are computed and they result equal to 0.4018 kg of CO_2^{eq} per kWh of electricity produced. This calculation is the result of a weighted average of GHG emissions of each source of energy based on the 2020 Italian energy mix.

Due to these considerations, the GHG emissions associated to a generic sorting centre are 2.25E-2 tonne of CO_2^{eq} per one tonne of treated plastic waste.

2.4 Incineration impact assessment

GHG emissions from direct incineration of MPW are modelled according to a real incinerator located in Northern Italy, and the procedure was based on the process data for material and energetic requirements and emissions treatment (Cossu et al., 2017). Also, inert landfilled residues and emissions are accounted for, except for their transportation to landfills.

As discussed in §1.3, in an incineration plant, waste is burnt in a combustion chamber and the heat of combustion is transferred to a steam generator for electricity generation.

An incinerator burns all types of waste and it is reasonable to think that the related emissions change accordingly, and MPW treatment emissions are only a share of the total emissions produced by an incineration plant. However, is the purpose of this study was focused only on MPW supply chain and it will consider only the emissions derived from MPW incineration.

Based on these considerations, the GHG impact is taken equal to 100-persons equivalent per one tonne of treated MPW, which corresponds to 870 tonnes of CO_2^{eq} per one tonne of treated MPW, according to the conversion factor that 1-person equivalent is equal to 8.7 tonne of CO_2^{eq} (Cossu et al., 2017).

In this thesis not only the direct environmental impact will be considered, but also the "environmental credits" will be taken into account. A waste-to-energy technology allows to recover energy from

wastes, generating electricity that, otherwise, should be produced most of the time via fossil fuels, as indicated in §2.3.
One tonne of MPW, according to Economopoulos (2010) is able to produce 0.640 MWh of electric energy. However, this paper considers quite a low heating value for MPW, equal to 11.5 MJ/kg, lower with respect to the one considered by Cossu (2017) and Mastellone (2020), that equals to 25.3 MJ/kg. Therefore, the electricity produced has been rescaled used the latter heating value, and the electricity produced is then estimated equal to 1.077 MWh per one tonne of treated MPW.
Takin into account the Italian energetic standard mix, in order to produce this amount of electricity, the estimated emissions would be equal to 0.4327 tonne of CO_2^{eq}, which is then considered as an avoided impact, so as environmental credit.

2.5 Gasification impact assessment

As discussed in §1.3, for MPW gasification some pre-treatments are needed, and the MPW which is in fact gasified is the end belt refuse (EBR), whose weight is 70% of the initial one.
Firstly, MPW goes through a shredding system, to obtain pieces of smaller dimension; then MPW is sent to an air classifier to eliminate materials of different weights and shape and to reduce ash content (it has been estimated a loss of weight of 15%); and finally drying, to remove a significant share of moisture (another loss of 15% of the initial weight). All of these steps have an environmental impact, but the one of air sieving can be considered negligible (Arena et al., 2011).
Shredding power consumption is found to be 8.75 kWh per one tonne of plastic treated (Cimpan et al., 2016).
As a drying strategy it has been supposed a thermal drying, which is, as Yuan et al. (2017) asserted, neither cost-effective nor environmentally friendly, because a non-renewable energy source is consumed, although thermal drying enables a product with high solid content. Bukhmirov (2015) reported that about 100% of moisture reduction in MSW were achieved at drying temperature of 107-167°C (assumed at an average of 140°C) during 160-260 min, using dry air as hot fluid. Moisture content in generic MPW waste is estimated to be about 23% of the total weight, as shown in Table 1.1. However, after ash removal (15% of the initial solid weight), there is less “dry solid” left, and therefore the relative amount of moisture increases and it is equal to 27%.
The heat required to eliminate moisture is given by an energy balance performed on MPW waste:

$$\dot{Q} = \dot{m}^{dry\,solid} Cp^{dry\,solid}\left(T_i - T_f\right) + \dot{m}^{wat,in} Cp^{wat}\left(T_i - T_{evap}\right) + \dot{m}^{wat,ev} \Delta H^{evap} + \dot{m}^{wat,out} Cp^{wat}\left(T_{evap} - T_f\right) \tag{2.1}$$

where $\dot{Q}$ is the power required to dry the solid wastes, $\dot{m}^{dry\,solid}$ is the mass flowrate of solids entering in the dryer, $Cp^{dry\,solid}$ is the specific heat of the dry solid waste, taken equal to 1.45 kJ/(kg °C) (Fujino and Honda, 2007), T_i is the inlet temperature, assumed to be ambient temperature (25°C), T_f is the final reached temperature (assumed to be 140°C), $\dot{m}^{wat,in}$ is the moisture contained in the

solid waste, assumed to be equal to 27% of the total MPW weight.; Cp^{wat} is the specific heat of water equal to 4.184 kJ/(kg °C), T_{evap} is the evaporation temperature of water (100°C), $\dot{m}^{wat,ev}$ is the moisture eliminated through drying (15% of the MPW weight), ΔH^{evap} is the latent heat of vaporization, equal to 2257 kJ/kg, $\dot{m}^{wat,out}$ is the moisture which is not eliminated and exits along with the MPW, which is then equal to 12% of the total MPW weight (which anyway lost 15% of its weight through ash removal).
Since the mass entering in the facility is a variable, it is more useful to consider a specific energy $\frac{\dot{Q}}{\dot{m_{tot}}}$ instead of an absolute power $\dot{Q}$. Therefore, the equation [2.1] becomes:

$$\frac{\dot{Q}}{\dot{m_{tot}}} = x^{dry\,solid} Cp^{dry\,solid}\left(T_i - T_f\right) + x^{wat,in} Cp^{wat}\left(T_i - T_{evap}\right) + \; x^{wat,ev} \Delta H^{evap} + \; x^{wat,out} Cp^{wat}\left(T_{evap} - T_f\right) \tag{2.2}$$

Where $x^{dry\,solid}$, $x^{wat,in}$, $x^{wat,ev}$ and $x^{wat,out}$ are respectively the mass fraction of dry solid entering in the dryer (73%), the mass fraction of water contained in the MPW entering in the dryer (27%), the mass fraction evaporated due to drying(15%), and the water mass fraction which remains in the MPW after drying (12%).
The result of this calculation is 565 kJ per one kg of waste treated. A 50% power efficiency has been considered (Beigi et al., 2020), therefore the electricity required for drying is equal to 1130 kJ per one kg of waste treated, corresponding roughly to 4100 GWh per one tonne of waste treated.
Overall, the emissions for MPW pre-treatment are estimated to be about 1.6E6 ktonne of CO_2^{eq} per ktonne of treated MPW.

For what concerns the direct impact estimation from EBR gasification, this process is estimated to produce 63 persons equivalent per one tonne of treated EBR (Cossu et al., 2017), roughly equal to 550 tonne of CO_2^{eq} per one tonne of EBR.

Also, gasification is a WTE technology, if the syngas produced is burnt generating heat which can be used to produce electric energy (Figure 1.5).
Once syngas is produced, however, it must be purified: gasification is followed by a wet scrubber, coupled with a water treatment system (Arena et al., 2011). Accounting for the energy expenses due to treatments, the net electrical energy available from gasification is equal to 2.09 MWh (Arena et al., 2011) per one tonne of EBR MPW, which is 30% less than the MPW initially fed to the plant. So, the production of energy is taken equal to 1.46 MWh per one tonne of initially incoming MPW.
To produce this amount of energy, it would be emitted 0.5866 tonnes of CO_2^{eq} starting from the standard Italian energy mix, which is an avoided impact.

2.6 Pyrolysis impact assessment

Pyrolysis does not need any particular pre-treatments, except for, as anticipated in §1.3, an additional sorting step, to allow the pyrolysis plant to work on a purer MPW fraction, constituted of only polyolefins (PO_Pyrolysis) or of polyolefins and polystyrene (PO_PS_Pyrolysis).

The GHG emissions of this additional sorting step are taken equal to the ones considered at the beginning of the supply chain as explained in §2.3, and thus equal to 2.25E-2 tonne of CO_2^{eq} per one tonne of processed MPW.

As indicated in §1.3, to sustain the pyrolysis endothermic reactions, some source of heat is necessary. The most immediate solution is to burn the pyrolysis char and flue gases (Figure 1.6) to provide the heat needed. In the combustion chamber enters char and a gas with the composition reported in Table 2.9. Material balances are performed when feeding 100 kg/h of MPW (after being sorted and further separated to get a plastic residue made of just polyolefins and polystyrene), according to Fivga and Dimitriou (2018).

The thermal duty required, related to this amount of feed, is 41.16 kW, and from burning char and non-condensable gases it is possible to develop 156.7 kW of thermal energy. The remaining amount of energy is too little to be taken into consideration for a thermal recovery.

Table 2.9: *Composition of the gas entering in the combustion chamber of pyrolysis plant*

Gas to combustion	Flowrate [kg/h]
Ethane	6.40
n-Octane	0.60
Water	0.15
Nitrogen	0.37
CO_2	0.27
Hydrogen	0.04
Air for combustion	228

By burning pyrolysis by-products, the process is able to auto-sustain itself, but of course generate some GHG emissions due to combustion of carbonaceous compounds.

It is supposed that the quantity of air fed in the combustion chamber is sufficient to lead to total carbon oxidation, for the following set of reactions:

$$C + O_2 \rightarrow CO_2 \qquad (2.3)$$

$$C_2H_6 + \frac{7}{2} O_2 \rightarrow 2CO_2 + 3H_2O \qquad (2.4)$$

$$C_8H_{18} + \frac{25}{2} O_2 \rightarrow 8CO_2 + 9H_2O \qquad (2.5)$$

According to the amounts reported in Table 2.9, the overall CO_2 emissions are estimated to be 46.54 kg/h, for a feed of 100 kg/h of polyolefin or polyolefins and polystyrene entering in the pyrolysis plant. Therefore, the specific emissions are estimated to be 0.4654 tonne of CO_2^{eq} per one tonne MPW fed to the reactor.

In the case of PO_Pyrolysis, the fraction of MPW which is pyrolyzed is equal to 26.97% of the initial share (Figure 2.2); then the specific emissions are calculated to be 0.1255 tonne of CO_2^{eq} per one tonne of the not yet sorted MPW.

For the PO_PS_Pyrolysis, the fraction of MPW which is pyrolyzed is equal to 35.58% of the initial share (Figure 2.3); then the specific emissions are calculated to be 0.1656 tonne of CO_2^{eq} per one tonne of the not yet sorted MPW.

Pyrolysis is not a waste-to-energy technology like incineration or gasification, but it allows instead to produce oil, that can be sent to refineries for various purposes (not object of this study), following what has been called "base case scenario", or can be directly sent to cracking plants, following the "cracking scenario".

The oil production via pyrolysis avoids all the steps required for the conventional extraction of crude oil from underground reservoirs. This conventional procedure comes together with significant GHG emissions for all its steps, which are now avoided. The avoided emissions come from seven process stages: (i) primary exploration for petroleum; (ii) drilling and development; (iii) production and extraction; (iv) surface processing (emissions from handling of produced crude, water and associated gas); (v) maintenance; (vi) waste disposal. All data are retrieved from El-Houjeiri et al. (2013).

The petroleum chosen is a heavy-density crude oil (Cieno, 2021), both if the oil is produced by a PO_Pyrolysis plant, or whether it is produced from a PO_PS_Pyrolysis. API gravity is considered around 14 and the functional unit is 1MJ of crude petroleum. Since a heavy oil is treated, a thermal enhances oil recovery (TEOR) technology is used, which injects steam to reduce oil viscosity. Because of that, the bulk of the GHG emissions comes from the production stage because of steam generation

The avoided GHG emissions impact is therefore estimated as 16.5 g of CO_2^{eq} per 1MJ of crude oil, that would be emitted for the extraction stage of a heavy crude oil.

The functional unit is 1 MJ of crude oil extracted, but it is more convenient to convert this unit into a mass unit. The LHV for a heavy oil is about 42 MJ/kg. Therefore, the GHG emissions are estimated as 0.672 tonne of CO_2^{eq} per one tonne of extracted oil.

Moreover, a pyrolysis oil does not need any hydrodesulphurization treatment. Crude oil contains a certain amount of sulphur, and when burnt leads to the emission of sulphur dioxide (SO_2), that is corrosive and toxic, and also particulate matter of metal sulphates. Therefore, there has been an increasing concern regarding the sulphur levels in fossil fuels and its derivatives. Sulphur is the third most common element in crude oil composition after carbon and hydrogen, but the total sulphur content of crude oil varies from reservoir to reservoir, with an average content of 0.03 to 7.89% by weight (Soleimani et al., 2007). Hydrodesulphurization (HDS) or hydrotreating is the most commonly used method in the petroleum industry to reduce the sulphur content of crude oil and refined petroleum products. In most cases HDS is performed by co-feeding oil and H2 to a fixed bed reactor packed with an efficient inorganic catalyst (e.g. CoMo/Al2O3 or NiMo/Al2O3). During HDS, the sulphur in the organosulfur compounds is converted to H_2S, at high pressure (1–18 MPa) and high-temperature (200–450 °C).

A typical HDS unit is showed in Figure 2.6, and data for HDS energy consumption are retrieved from Alves et al. (2015) for an oil which contains 0.012 g of sulphur per g of crude oil with 96% removal capability.

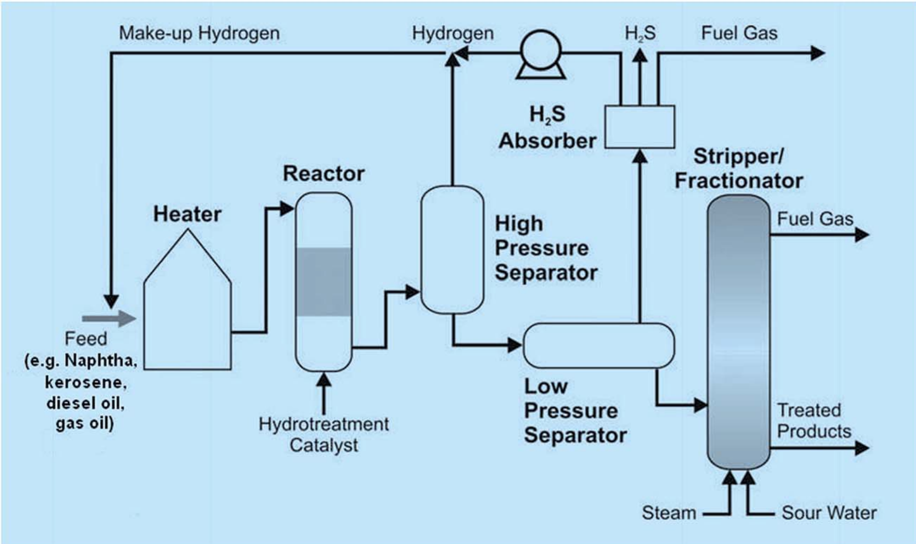


Figure 2.6: *Typical HDS unit in an oil refinery*

The electricity consumption of the process is equal to 1900 Btu per barrel of oil fed, which corresponds to 35.02 kWh per m^3 of oil fed. For the heavy oil considered in this work (density of 1.002 tonne/m^3, typical for a Venezuelan heavy oil), the energy consumption is equal to 34.95 kWh per tonne of oil fed. Starting from the Italian standard energy mix, this would lead to the emissions of 1.404E-2 ktonne of CO_2^{eq} per one ktonne of crude oil, which are summed to the previous avoided emissions from extraction, leading to an overall avoided impact of 0.686 tonne of CO_2^{eq} per one tonne of crude oil.

Italy imports petroleum from around 50 different countries all over the world, and to move oil from one place to another some transportation GHG emissions are unavoidable. The largest amount (MiTE September 2022 data) comes from the countries listed in Table 2.10.

Table 2.10: *Origins of petroleum imported to Italy (2022)*

IMPORT ORIGIN	PERCENTAGE
Russia	29.45
Azerbaijan	13.29
Libya	12.98
Iraq	10.44
Saudi Arabia	8.27
USA	3.55
Kazakhstan	3.25
UK	3.07
Other countries	15.70

Only countries which contribute to more than 3% have been considered.

The petroleum can be moved from one place to another with many transportation strategies. For sake of simplicity, only two means of transport have been considered: oil pipeline and naval transportation. In particular, existing oil pipelines connect the Russian and the Caspian Sea region to Europe. The first exporters (2022 data) are actually countries belonging to this region. From Kazakhstan, oil is transported by ship from the port of Aqtau to Baku, Azerbaijan. From here, the Baku-Supsa pipeline connect the Caspian Sea to the Black Sea. From here, ships transport oil to Europe to the port of Constanța in Romania, and from here the Pan-European Pipeline (PEOP) brings the oil to Trieste, Italy. The path from Russia starts in the city of Al'met'evsk, Tatarstan, and from there the Druzhba pipeline connects Russia to Middle Europe, and one of the branches of this pipeline arrives to Rijeka, going through Hungary, and eventually reaches Trieste.

For all the other origin countries is accounted a naval transportation and the final Italian destination is also in this case Trieste, because it is the largest port for movement of petroleum. The distance is calculated using www.sea-distances.org. All the distances covered both by pipelines and ships are collected in Table 2.11.

Table 2.11: *Distances for oil transportation*

ORIGIN - DESTINATION	DISTANCE
Aqtau - Baku (ship)	380 km
Baku - Supsa (Baku-Supsa pipeline)	833km
Supsa - Costanta (ship)	1072 km
Constanța -Trieste (Pan-European Pipeline, PEOP)	1856 km
Al'met'evsk – Trieste (Druzhba pipeline)	3030 km
As Sidr (Libya) – Trieste (ship)	1822 km
Umm Qasr (Iraq) – Trieste (ship)	8612km
Jeddah (Saudi Arabia) – Trieste (ship)	3735 km
New York (USA) – Trieste (ship)	8990 km
Felixstowe (UK) – Trieste (ship)	5445 km

From Choquette-Levy et al. (2018) the pipeline GHG emissions are estimated as an average of 3g of CO_2^{eq} per 1 barrel of oil transported and for 1 km, equal to 1.88E-5 tonne of CO_2^{eq} per one tonne of oil transported and 1 km.
For naval transportation emissions, instead, accurate data are retrieved from Greene et al. (2020). The average GHG emissions for an oil tanker are estimated as 2.354E-6 tonne of CO_2^{eq} per one tonne of oil transported and 1 km.

Due to the unstable relationships between European Union and the Russian Federation, the commercial trades in terms of energy resources are probably intended to be replaced with imports from other countries. Therefore, the amount of oil imported from Russia can be distributed among the other suppliers, keeping the same proportion (e.g. only the 13.29% of the Russian oil will be now imported from Azerbaijan). If so, the new shares of oil imported to Italy are collected in Table 2.12.

Table 2.12: *Origins of petroleum imported to Italy without Russia (2022)*

IMPORT ORIGIN	PERCENTAGE
Azerbaijan	18.99
Libya	18.55
Iraq	14.87
Saudi Arabia	11.75
USA	5.03
Kazakhstan	4.61
UK	4.35
Other countries	21.85

One alternative scenario to the refining of pyrolysis oil is to send it directly to steam cracking units. Kusenberg et al. (2022) proved that pyrolysis oil leads to higher ethylene yields compared to reference naphtha. It seems a good option to replace it with pyrolysis oil, and this also allows to save refinery GHG emissions. Reference naphtha considered in the work of Kusenberg et al. (2022) has a carbon number range from 5 to 9, which means it is approximately a refined gasoline. From the work of Han et al. (2015), the GHG emissions for refining a gasoline are taken equal to 93 g of CO_2^{eq} per MJ of gasoline. A common value for gasoline heating value is 45 MJ per kg. Based on that, GHG refining emissions are equal to 4185 g of CO_2^{eq} per kg of gasoline, which means 4.185 ktonne of CO_2^{eq} per ktonne of gasoline, which are saved by sending the pyrolysis oil straight to cracking units.
Cracking units, however, are not many in Italy. In fact, only two still working cracking plants remain, and they are located in Southern Italy, precisely in Priolo (Sicily) and Brindisi (Apulia). Therefore, it is needed to model the transportation of pyrolysis oil, first to the Northern Italy ports (Genoa, Trieste, Venice, La Spezia and Ravenna are selected as main ports), and then by ship to Priolo and Brindisi. Sea distances between each possible port of departure to Priolo and Brindisi are calculated using www.sea-distances.org, and they are shown in Table 2.13.

Table 2.13: *Table of distances from one departure port to one arrival port*

	Priolo	**Brindisi**
Genoa	1016 km	1380 km
Trieste	1204 km	690 km
Venice	1233 km	717 km
La Spezia	950 km	1313 km
Ravenna	1145 km	628 km

For the cracking scenario is then needed an additional way of oil transportation from a port of departure, located in Northern Italy, to a port of arrival close to a Southern Italy cracking plant.

Chapter 3

Supply chain model for base case scenario

Chapter 3 focuses on the base case scenario, characterized by the optimal design of MPW supply chain in terms of economic and environmental performance, taking into account both waste-to-energy (i.e. incineration) and chemical recycling (*i.e.* pyrolysis and gasification) technologies, assuming that the pyrolysis oil is sent to refineries. Firstly, the modelling assumptions and inputs are presented, then, the mathematical modelling framework is introduced. Finally, the results of the optimization are presented, comparing the economic optimal solution of the overall supply chain with the environmental optimal one.

3.1 Scenarios overview and preliminary model data

MPW end-of-life does not have only one possible path. Supply chain, as shown in §1.3, allows multiple alternatives for MPW treatment. The objective of the environmental optimization is to find the least impactful in terms of GHG emissions among these possibilities.

In this Chapter, the "base case scenario" is defined and it presents one specific branch of the supply chain that will be analysed. This pathway considers that, if MPW is treated in a pyrolysis plant, then the generated pyrolysis oil is sent to an oil refinery plant. This scenario exploits the possibility of sending the oil in one of the Northern Italian refineries.

The other analysed scenario is called "cracking scenario" and will be discussed in detail in Chapter 4. It considers that, if MPW is pyrolyzed, then the generated pyrolysis oil is shipped to cracking plants in Southern Italy, as it can be a substitute for cracking naphtha, instead of ending in an oil refinery.

The modelling framework for the optimal design of MPW supply chain needs some preliminary data, valid for all scenarios.

The first stage of the supply chain is represented by the plastic waste collection by each province and managed by COREPLA. The exact quantities of plastics collected, together with the geographical location of each provinces (first centres of collection of plastic waste and supply chain starting points) are shown in Table 3.1. Data concerning plastic waste flowrates collected are retrieved from 2021 ISPRA Waste Report ("Rapporto rifiuti urbani", last update January 2022), which refers to wastes collected in 2020.

The exact geographic coordinates of the provinces are retrieved using Google Maps.

Table 3.1: *Latitude and longitude of Northern Italian provinces, and plastic waste flowrates collected in Northern Italian provinces in 2020 [2021 ISPRA Waste Report]*

Region	Province		Latitude	Longitude	Plastic waste flowrate [ktonne/year]
Emilia - Romagna	Bologna	BO	44.496742	11.345222	34.9
Emilia - Romagna	Forlì - Cesena	FC	44.220039	12.045018	15.1
Emilia - Romagna	Ferrara	FE	44.834794	11.621976	14.4
Emilia - Romagna	Modena	MO	44.645848	10.925790	34.2
Emilia - Romagna	Piacenza,	PC	45.053537	9.694090	9.4
Emilia - Romagna	Parma	PR	44.802185	10.327414	17.5
Emilia - Romagna	Ravenna	RA	44.414326	12.200710	12.5
Emilia - Romagna	Reggio Emilia	RE	44.698205	10.631303	26.8
Emilia - Romagna	Rimini	RN	44.058762	12.568068	16.0
Friuli - Venezia Giulia	Gorizia	GO	45.941588	13.621198	3.5
Friuli - Venezia Giulia	Pordenone	PN	45.962561	12.657330	9.6
Friuli - Venezia Giulia	Trieste	TS	45.648506	13.775749	4.7
Friuli - Venezia Giulia	Udine	UD	46.064733	13.233779	16.6
Liguria	Genova	GE	44.410305	8.931285	17.9
Liguria	Imperia	IM	43.886064	8.028091	6.6
Liguria	La Spezia	SP	44.107829	9.828679	7.6
Liguria	Savona	SV	44.309218	8.481112	9.8
Lombardia	Bergamo	BG	45.694429	9.670056	28.4
Lombardia	Brescia	BS	45.540200	10.219685	40.7
Lombardia	Como	CO	45.810023	9.085721	13.7
Lombardia	Cremona	CR	45.133722	10.024653	13.1
Lombardia	Lecco	LC	45.856071	9.393594	4.8
Lombardia	Lodi	LO	45.314438	9.503475	6.3
Lombardia	Monza - Brianza	MB	45.583960	9.273447	21.9
Lombardia	Milano	MI	45.469141	9.190111	93.5
Lombardia	Mantova	MN	45.157362	10.792910	17.3
Lombardia	Pavia	PV	45.184942	9.159794	11.9
Lombardia	Sondrio	SO	46.171046	9.871771	2.8
Lombardia	Varese	VA	45.820290	8.825697	23.6
Piemonte	Alessandria	AL	44.912846	8.615643	16.7
Piemonte	Asti	AT	44.899468	8.205229	7.7
Piemonte	Biella	BI	45.562679	8.059378	5.4
Piemonte	Cuneo	CN	44.393252	7.551655	27.3
Piemonte	Novara	NO	45.446307	8.622484	13.0
Piemonte	Torino	TO	45.071718	7.693879	61.5
Piemonte	Verbania	VB	45.922705	8.551881	6.3
Piemonte	Vercelli	VC	45.324020	8.423643	5.5
Trentino - Alto Adige	Bolzano	BZ	46.499422	11.357046	8.9
Trentino - Alto Adige	Trento	TN	46.069734	11.120847	20.0
Valle d'Aosta	Aosta	AO	45.737453	7.320182	6.8
Veneto	Belluno	BL	46.138039	12.217247	6.0
Veneto	Padova	PD	45.407168	11.877502	25.8
Veneto	Rovigo	RO	45.071190	11.791936	8.3

Veneto	Treviso	TV	45.666220	12.245827	20.2
Veneto	Venezia	VE	45.432392	12.353526	19.9
Veneto	Vicenza	VI	45.547998	11.545843	21.5
Veneto	Verona	VR	45.437972	10.994255	27.4

The next stage of the supply chain consists in sorting MPW out of the general plastic wastes, and this operation is carried out in the sorting centres, as explained in §1.3.

The Northern Italian sorting centres list is retrieved from COREPLA website[1], whereas their geographical location (*i.e.* latitude and longitude) from Google Maps. For what concerns the sorting centres capacity, this work refers to Cieno (2021): it is assumed that the reported capacity is the one assigned to only plastic wastes sorting, which represents only a fraction of the entire sorting centre capacity, that is commonly used for all types of MSW. If no data is found for the plastic waste sorting capacity of a sorting centre, then the overall sorting centre capacity is reported (ISPRA, 2021). In such a case, the reported capacity for processing MPW could be an overestimation, and it could represent one limitation of the model.

The sorting centres geographical locations and capacities are listed in Table 3.2. The sorting centres whose capacity is referred to the overall plant capacity are marked with and X.

Table 3.2: *Geographical location and capacity of Northern Italian sorting centres for processing MPW. Sorting centres whose capacity for treating MPW could be an overestimation are marked with an X [Cieno, 2021]*

	Region	**City**		**Latitude**	**Longitude**	**Capacity [ktonne/year]**
	Emilia -Romagna	Argenta	FE	44.63013	11.82790	100.5
	Emilia -Romagna	Bedonia	PR	44.49210	9.65043	48
	Emilia -Romagna	Cadelbosco di Sopra	RE	44.75608	10.59932	97.4
X	Friuli – Venezia Giulia	San Giorgio di Nogaro	UD	45.80163	13.21678	135
X	Lombardia	Lainate	MI	45.56738	9.05106	100
	Lombardia	Milano	MI	45.46060	9.06734	45
	Lombardia	Montello	BG	45.67725	9.79438	150
X	Lombardia	Verderio Inferiore	LC	45.66424	9.42109	97
	Lombardia	Corsico	MI	45.43533	9.09795	250
	Piemonte	Beinasco	TO	45.02891	7.58979	75
	Piemonte	Cavaglia	BI	45.38293	8.12570	45
	Trentino – Alto Adige	Lavis	TN	46.14455	11.09302	61.2

Once out of the sorting centre facility, MPW can finally be treated according to one of the proposed technologies: incineration, gasification or pyrolysis, representing the following stage of the supply chain.

[1] www.corepla.it

Incineration plants already exist in Northern Italy, and their capacities and locations have been shown in Table 1.2.
For what concerns gasification and pyrolysis plants, there are no already existing industrial scale plants in Italy for MPW treatment. Therefore, some assumptions for their sizes and locations are needed.
Gasification plants sizes are discussed in Cieno (2021) starting from the work of Arena et al. (2011), and the selected plant sizes in terms of thermal load are 4 MW_e, 6 MW_e and 8 MW_e. The thermal load seizes can be converted to MPW feed size according to:

$$C_G = \frac{C_{G,e} \cdot 3600 \cdot 7680}{\eta_e \cdot LHV_{EBR}} \cdot \frac{1}{0.7} \tag{3.1}$$

where C_G is the gasification plant capacity expressed in terms of ktonne of MPW per year; $C_{G,e}$ is the gasification plant capacity expressed in terms of thermal load, *i.e.* in terms of MW_e; 3600 are the seconds in an hour and 7680 are the operating hours of a plant; η_e is the net electrical efficiency, assumed to be equal to 0.237; LHV_{EBR} is the lower heating value of the end-belt refuse (EBR) which is chosen as the gasification plant feed as discussed in §1.3.2, that equals to 31.7 MJ/kg; 0.7 accounts for the 30% material loss (moisture and ashes) after MPW pre-treatments, as discussed in §2.1.
Based on equation (3.1), the gasification plant sizes are shown in Table 3.3.

Table 3.3: *Possible gasification plant sizes*

Technology	Plant size	Capacity [ktonne/year]
	Small	21
Gasification	Medium	31.5
	Large	42.1

For what concerns pyrolysis plant sizes, Cieno (2021) proposes 3 plant sizes, based on the work of Fivga and Dimitriou (2018), of 7.0, 17.5 and 28.0 ktonne of MPW per year.
However, the actual size of a pyrolysis plant needs to accommodate the whole MPW share that enters in the facility, not only the fraction that is actually treated. In fact, as explained in §2.1, MPW goes through an additional sorting stage before being pyrolyzed, in order to recover only the valuable polymers for the oil production, *i.e.* only polyolefins for a PO_Pyrolysis plant or polyolefins and polystyrene for a PO_PS_Pyrolysis plant.
Defining as w the recovered fraction of polymers that can be pyrolyzed, the sizes of the entire pyrolysis plant is calculating as:

$$C_T = \frac{C_P}{w} \tag{3.2}$$

where C_T is the total capacity of the pyrolysis plant, C_P are the capacities calculated based on the work of Fivga and Dimitriou (2018), and w is the polymer recovered fraction which is 26.97% for a PO_Pyrolysis and 35.58% for a PO_PS_Pyrolysis, as discussed in §2.1 and shown in Figure 2.2 and in Figure 2.3.
Based on equation (3.2), the chosen pyrolysis sizes are shown in Table 3.4.

***Table 3.4:** Possible pyrolysis plant sizes*

Technology	Plant size	Capacity [ktonne/year]
PO_Pyrolysis	Small	26.0
	Medium	65.0
	Large	104.0
PO_PS_Pyrolysis	Small	19.7
	Medium	49.3
	Large	78.8

For what concerns the geographical location of the gasification and pyrolysis plants, since no industrial applications are currently existent (November 2022), it was assumed that they can be placed in the same location of an incineration plant. Therefore, the model can decide where to place the gasification and pyrolysis plants, in the case these technologies are selected in the optimal design of the supply chain, and the exact coordinates are presented in Table 1.2, corresponding to the location of the incinerators.
If pyrolysis is chosen by the supply chain model, then one additional step for pyrolysis oil is needed. For the "base case" scenario, pyrolysis oil is sent to an oil refinery. The list of Northern Italian refineries is retrieved from the 2022 Energy, Mobility, Environment Databook (UNEM, 2021). The refinery of Alma Petroli (Ravenna) has been excluded from the list because it is very small compared to the other refineries. Their capacities have been disregarded because they are certainly large enough to accept the oil produced by the MPW supply chain. Their geographical locations are reported in Table 3.5.

***Table 3.5:** Geographical locations of Northern Italian oil refineries*

Region	City		Latitude	Longitude
Lombardia	Sannazzaro	PV	45.10215	8.89747
Liguria	Busalla	GE	44.57225	8.94952
Piemonte	Trecate	NO	45.44020	8.78758

It seems reasonable that in proximity of an oil refinery is located also a pyrolysis plant. Therefore, three additional possible locations can be listed for pyrolysis plants that can co-exist with the refineries, benefiting from economies of scale effects as discussed in Cieno (2021), and therefore, the exact geographic coordinates are identical to the ones of the Northern Italian refineries. For what concerns the sizes and the capacities of pyrolysis plants coupled with oil refineries, they are the same as the stand-alone pyrolysis plants, according to Table 3.4.

Finally, since some treatment residues are always produced by the supply chain, as explained in §2.1, landfilling, even for a small quantity of wastes, is necessary. Due to the large number of Northern Italian landfills (ISPRA database[2]), it was considered a good approximation to impose a fixed distances from treatment plants to landfills equal to 50 km (Cieno, 2021).
The alternative scenario, indicated as "cracking" scenario, as discussed in §2.6 considers that the pyrolysis oil is shipped to cracking plants located in Southern Italy in proximity of the city ports, whose locations are reported in Table 3.6.

Table 3.6: *Geographical locations of Southern Italian cracking plants*

Region	City		Latitude	Longitude
Sicily	Priolo	SR	37.161858	15.200938
Apulia	Brindisi	BR	40.646069	17.987760

In order to ship pyrolysis oil to cracking plants, also some Northern Italian departure ports must be identified. The largest Northern Italian ports are retrieved from www.assoporti.it, and listed in Table 3.7.

Table 3.7: *Geographical locations of Northern Italian main ports*

Region	City		Latitude	Longitude
Liguria	Genoa	GE	44.404148	8.907893
Liguria	La Spezia	SP	44.110574	9.850755
Friuli – Venezia Giulia	Trieste	TS	45.658665	13.763630
Veneto	Venice	VE	45.463087	12.267101
Emilia – Romagna	Ravenna	RA	44.485988	12.244435

3.2 Geographical representation of supply chain nodes

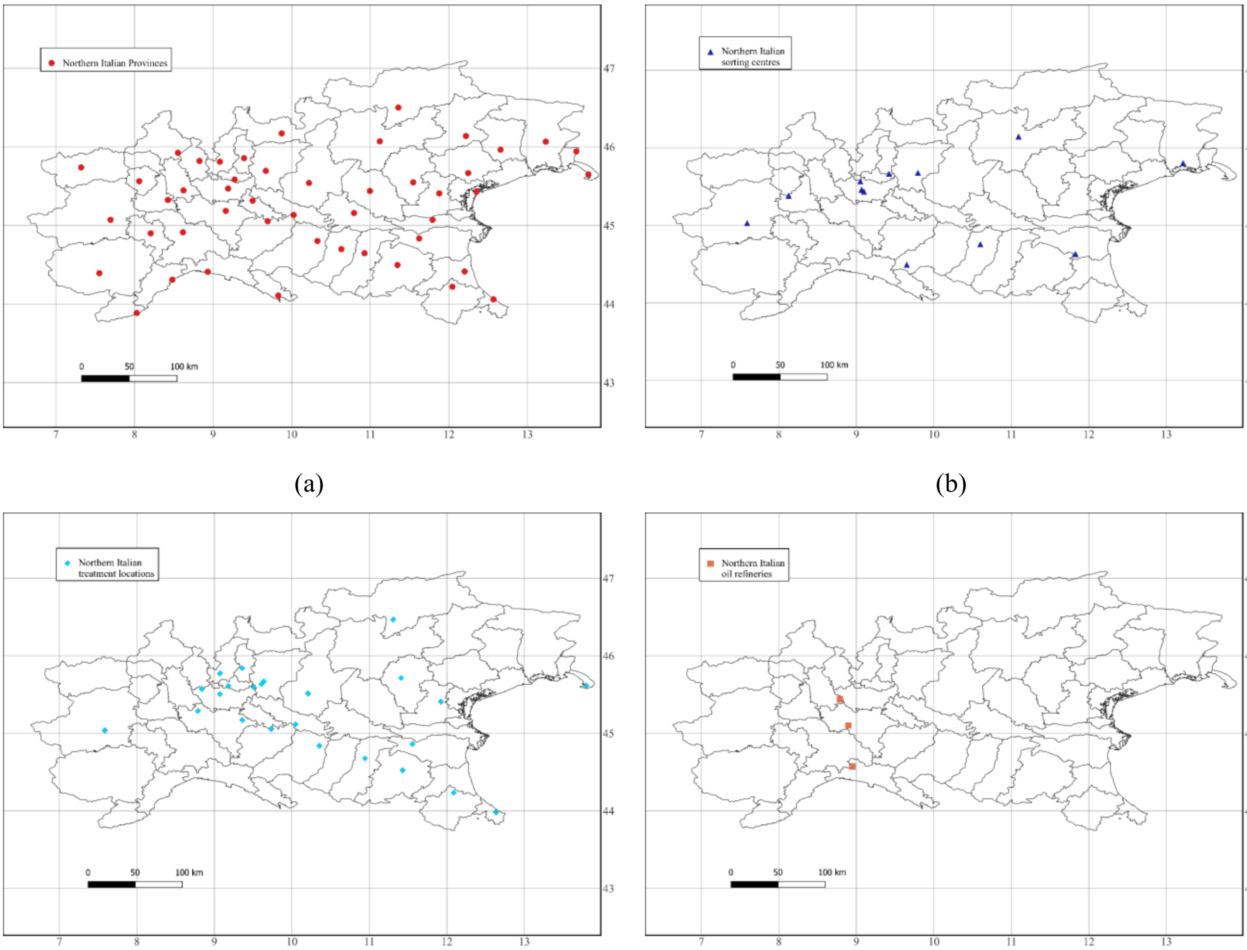
The overall supply chain contains 93 spatially-explicit nodes and they divided into:

- 47 provinces;
- 12 sorting centres;
- 24 treatment locations;
- 3 oil refineries, that can work also as pyrolysis plants;

[2] https://www.catasto-rifiuti.isprambiente.it/index.php?pg=gestnazione&aa=2019&regid=&mappa=8#p

- 5 Norther Italian ports for “cracking scenario”;
- 2 Southern Italian ports and cracking plants for “cracking scenario”.

The exact geographical locations of the nodes contained in the MPW supply chain (MPW SC) are represented in Figures 3.1(a-d) and 3.2.



(a) (b)

(c) (d)

Figure 3.1*: Spatially-explicit nodes in the model: (a) 47 Northern Italian provinces; (b) 12 Northern Italian sorting centres; (c) 24 Northern Italian possible treatment location; (d) 3 Northern Italian oil refineries.*

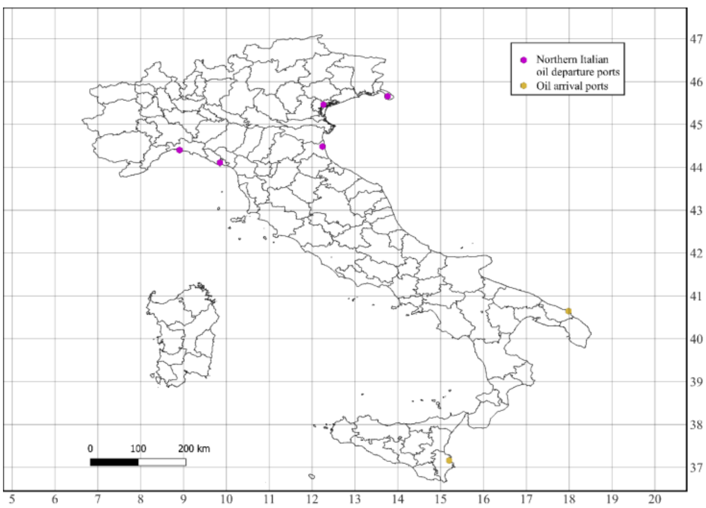


***Figure 3.2**: 7 Italian ports for "cracking" scenario: oil departure ports in Northern Italy and cracking plants ports in Southern Italy*

3.3 Mathematical modelling of MPW supply chain for base case scenario

The modelling framework of the mixed integer linear programming (MILP) aiming at the optimal design of MPW supply chain in terms of both economic and environmental performance is here presented. This chapter will introduce the mathematical model referring to the environmental optimization, while the modelling of the economic optimization is comprehensively described in Cieno (2021).

The spatially-explicit nodes are modelled by the means of a set $n = \{n_{1-93}\}$ containing:

- $pr = \{n_{1-47}\}$ – the subset of the 47 Northern Italian provinces
- $so = \{n_{48-60}\}$ – the subset of the 12 sorting centres
- $t = \{n_{61-88}\}$ – the subset of the 27 treatment locations
- $port = \{n_{89-93}\}$– the subsets of the 5 ports.

The set of technologies, *i.e.* incineration, gasification, PO_Pyrolysis and PO_PS_Pyrolysis is modelled thorough a set *k*, containing:

- *ElK* – the subset of the technologies that can produce electricity, *i.e.* incineration and gasification;
- *OilK* – the subsets of technologies that produce oil, *i.e.* PO_Pyrolysis and PO_PS_Pyrolysis;
- *NewK* – the subset of chemical recycling technologies for MPW treatment proposed in this Master's thesis, *i.e.* gasification, PO_Pyrolysis and PO_PS_Pyrolysis;
- *GasK* – the subset referring to only gasification technology;
- *InK* – the subset referring to only the incineration process.

The different plant sizes are modelled by the means of a set *s*, containing "small", "medium" and "large" sizes.

Other subsets that were defined are:

- *refi*, the subset of the refineries, which is a subset of *t*. Refineries can also be the location for MPW pyrolysis;
- *notrefi*, which is still a subset of *t* and indicates the treatment nodes which are not refineries.
- *portdep*, which is a subset of *port* and indicates the Northern Italian oil departure ports for the "cracking scenario";
- *portarr*, which is still a subset of *port* and collects the pyrolysis oil arrival ports in Southern Italy, in proximity of cracking plants for the "cracking scenario".

3.3.1 Material flowrates

All the flowrates are expressed in ktonne/year.

Regarding the waste flowrates, it has been set that each province *pr* must send out to the sorting centres *so* all its waste, therefore:

$$\sum_{so} m_{pr,so}^{W} = m_{pr}^{W,Av} \quad \forall\, pr \tag{3.3}$$

where $m_{pr,so}^{W}$ is the mass which goes from a province to a sorting centre, and $m_{pr}^{W,Av}$ is the waste available in each Northern Italian province.

The total waste entering a sorting centre *so* cannot exceed the sorting centre capacity, therefore the following constraint is formulated:

$$\sum_{pr} m_{pr,so}^{W} \leq C_{so} \ \forall\, so \tag{3.4}$$

where C_{so} is the capacity of the sorting centre *so*.
The MPW flowrate $m_{t,k,s}^{MPW,Plant}$ to a plant k of size s in a treatment node t is calculated as the sum over all sorting centres *so* of the MPW flowrate sent out by a sorting centre to a treatment plant present in location *t* of technology *k* and size *s*:

$$m_{t,k,s}^{MPW,Plant} = \sum_{so} m_{so,t,k,s}^{MPW} \ \forall\, t,k,s \tag{3.5}$$

For each sorting centre, the sum of all MPW flowrates $m_{so,t,k,s}^{MPW}$ going out of the sorting centre *so* to a treatment plant location *t* of technology *k* of size *s*, equals the overall flowrate of MPW sent out $m_{so}^{MPW,sort}$ of the sorting centre *so* (that is directly correlated to total available MPW $m_{so}^{MPW,Av}$ in the sorting centre), in other words, the entire flowrate of MPW available in a sorting centre *so* has to go to a treatment plant, giving the possibility of splitting the flowrate to multiple location for the treatment plant:

$$m_{so}^{MPW,sort} = \sum_{t,k,s} m_{so,t,k,s}^{MPW} \ \forall\, so \tag{3.6}$$

For each sorting centre *so* the total MPW available $m_{so}^{MPW,Av}$ is calculated as the sum over each province *pr* of the waste flowrates received from the provinces multiplied for the average waste-to-MPW conversion factor η^{W_MPW}:

$$m_{so}^{MPW,Av} = \sum_{pr} m_{pr,so}^{W}\, \eta^{W\_MPW} \quad \forall\, so \tag{3.7}$$

η^{W_MPW} is a scalar equal to 0.521.

Two constraints are set on $m_{so}^{MPW,sort}$ correlating the overall flowrate of MPW that goes out of the sorting centre $m_{so}^{MPW,sort}$, and the total available $m_{so}^{MPW,Av}$ MPW in the sorting centre *so*:

$$0.999 \cdot m_{so}^{MPW,Av} \leq m_{so}^{MPW,sort} \leq m_{so}^{MPW,Av} \quad \forall\, so \tag{3.8}$$

The upper constraint sets that for each sorting centre *so* the total MPW flowrate sent out cannot exceed the total MPW available in the sorting centre. The lower constraint sets that at least 99.9% of the MPW available is sent out to the treatment plants, so that no MPW remains in the sorting centres.
For what concerns the capacity constraints of the treatment plants, there are some considerations to be made. If the plant considered is a gasification or a pyrolysis plant, then the total MPW flowrate coming in cannot exceed the plant capacity but it must cover at least the 70% of the capacity of the plant. If, on the other hand, the plant considered is an incineration plant, the lower boundary is different, because it is sufficient that only a very small MPW flowrate, set at 0.1 ktonne/year, is treated in that plant. This difference is necessary because incineration plants treat various kind of wastes of which MPW is only a fraction, so their capacity is already substantially occupied by all kinds of wastes. This is not true for pyrolysis and gasification plants that are thought to be installed for only MPW treatment. Their lower boundary must be very high, otherwise it would lead to economical unfeasibility of the plant functioning.

$$0.7 \cdot \mathrm{C}_{\mathrm{NewK,s}}^{\mathrm{P}} \cdot \lambda_{\mathrm{t,NewK,s}}^{\mathrm{Plant}} \leq m_{t,NewK,s}^{MPW,Plant} \leq \mathrm{C}_{\mathrm{NewK,s}}^{\mathrm{P}} \cdot \lambda_{\mathrm{t,NewK,s}}^{\mathrm{Plant}} \quad \forall\, t, NewK, s \tag{3.9}$$

$$0.1 \cdot \lambda_{\mathrm{t,InK,s}}^{\mathrm{Plant}} \leq m_{t,InK,s}^{MPW,Plant} \leq \mathrm{C}_{\mathrm{InK,s}}^{\mathrm{P}} \cdot \lambda_{\mathrm{t,InK,s}}^{\mathrm{Plant}} \quad \forall\, t, InK, s \tag{3.10}$$

where $\mathrm{C}_{\mathrm{NewK,s}}^{\mathrm{P}}$ is the capacity of each treatment plant except incineration, and $\mathrm{C}_{\mathrm{InK,s}}^{\mathrm{P}}$ is the capacity of an incineration plant; $\lambda_{\mathrm{t,k,s}}^{\mathrm{Plant}}$ is a binary variable that assumes the value of 1 if there exists a treatment location *t* with a technology *k* of a size *s*, 0 otherwise.
In order to constrain the incineration plants to only one possible size, which is the real, existing one, defined as "large", this corresponding binary variables are set equal to zero:

$$\lambda_{\mathrm{t,InK,s}}^{\mathrm{Plant}} = 0 \quad \forall\, t, InK, s \notin \text{"Large"} \tag{3.11}$$

In the locations corresponding to a refinery, only pyrolysis plant can co-exist:

$$\lambda_{\mathrm{refi,ElK,s}}^{\mathrm{Plant}} = 0 \quad \forall\, refi, ElK, s \tag{3.12}$$

which means that the binary variable $\lambda^{\text{Plant}}_{\text{refi,ElK,s}}$ is fixed to a value of 0 for a refinery location with all the plants producing electricity, *i.e.* incineration and gasification plants, of all sizes *s*.

It is crucial for the model to understand that if a size *s* of a plant of technology *NewK* is chosen in a node *t*, then it must be the only size in that location. Moreover, if a specific plant k is chosen in that node, it must be the only technology possible for that node:

$$\sum_{k,s} \lambda^{\text{Plant}}_{\text{t,k,s}} \leq 1 \qquad \forall\, t \tag{3.13}$$

As explained in §2.1, all the plants produce residues that must be landfilled. The residue fractions from the initial amount of MPW entering the treatment plant are indicated with $\eta^{\text{R}}_{\text{k}}$. They differ from one technology to another and they are collected in Table 3.8.

Table 3.8: *Values of MPW-to-residues conversions for each technology*

Technology	$\eta^{\text{R}}_{\text{k}}$
Gasification	0.3080
Incineration	0.0760
PO_Pyrolysis	0.1201
PO_PS_Pyrolysis	0.1201

The amount of residues is calculated according to:

$$m^{R}_{t,k,s} = m^{MPW,Plant}_{t,k,s} \cdot \eta^{\text{R}}_{\text{k}} \quad \forall\, t, k, s \tag{3.14}$$

where $m^{R}_{t,k,s}$ is the solid residues produced by a plant of technology k of size *s* located in a node *t*, and $\eta^{\text{R}}_{\text{k}}$ stands for the MPW-to-residues conversion parameters previously collected in Table 3.8.
An additional share of solid residues is produced by incinerating the residual mixed plastic waste (RPL) sorted out before the pyrolysis plants, as explained in §2.1. This amount is calculated by multiplying the RPL flowrate produced by each pyrolysis plant for the MPW-to-residues incineration conversion factor $\eta^{\text{R}}_{\text{InK}}$, equal to 0.076:

$$m^{R,RPL}_{t,OilK,s} = m^{RPL}_{t,OilK,s} \cdot \eta^{\text{R}}_{\text{InK}} \quad \forall\, t, OilK, s \tag{3.15}$$

where $m^{R,RPL}_{t,OilK,s}$ is the additional solid residue flowrate produced by incinerating the residual MPW from pyrolysis sorting centres and $m^{RPL}_{t,OilK,s}$ is the residual MPW sorted out, not sent to pyrolysis plant, calculated as:

$$m^{RPL}_{t,OilK,s} = m^{MPW,Plant}_{t,OilK,s} \cdot \eta^{\text{RPL}}_{\text{OilK}} \quad \forall\, t, OilK, s \tag{3.16}$$

where $\eta_{\mathrm{OilK}}^{\mathrm{RPL}}$ is the MPW-to-RPL conversion factor for pyrolysis plants, as shown in Figure 2.2 and Figure 2.3. They differ whether the plant is a PO_Pyrolysis plant or a PO_PS_Pyrolysis plant, as shown in Table 3.9.

Table 3.9: *Values of MPW-to-residues conversions for each technology*

Technology	$\boldsymbol{\eta_{OilK}^{RPL}}$
PO_Pyrolysis	0.5709
PO_PS_Pyrolysis	0.4848

The total residual MPW from pyrolysis sorting is therefore:

$$m_{so}^{RPL,Tot} = \sum_{t,OilK,s} m_{t,OilK,s}^{RPL} \tag{3.17}$$

The oil produced by a plant $m_{t,OilK,s}^{Oil,Av}$ of technology *OilK* (*i.e.* a pyrolysis plant) of size *s* present in a treatment location *t* is calculated by multiplying the MPW flowrate entering the plant and the MPW-to-oil conversion factor $\eta_{\mathrm{OilK}}^{\mathrm{Oil}}$ equal to 0.2314 for PO_Pyrolysis and 0.3053 for PO_PS_Pyrolysis, as previously shown in Table 2.1:

$$m_{t,OilK,s}^{Oil,Av} = m_{t,OilK,s}^{MPW,Plant} \cdot \eta_{\mathrm{OilK}}^{\mathrm{Oil}} \;\forall\, t, OilK, s \tag{3.18}$$

For the “base case scenario”, which is the one developed in this Chapter, all the oil produced in the pyrolysis plants must end up in one refinery:

$$\sum_{refi} m_{t,OilK,s,refi}^{Oil} = m_{t,OilK,s}^{Oil,Av} \cdot \alpha_{\mathrm{Pyr,Refi}}^{\mathrm{LD}} \;\forall\, t, OilK, s \tag{3.19}$$

where $m_{t,refi,OilK,s}^{Oil}$ is the oil flowrate going from a pyrolysis plant to a refinery; $\alpha_{\mathrm{Pyr,Refi}}^{\mathrm{LD}}$ is a correction factor: if it is equal to 1 it means that the oil is produced in a pyrolysis plant which is not coupled with a refinery.

The total amount of residues that must be landfilled is given by:

$$m^{R,Tot} = \sum_{t,k,s} m_{t,k,s}^{R} + \sum_{t,k,s} m_{t,OilK,s}^{R,RPL} \tag{3.20}$$

At this point, the model has all its material balances closed, and therefore it is possible to evaluate all the supply chain costs and revenues, expressed in €/year, and the GHG emissions, expressed as ktonne of CO_2^{eq}/year.

3.3.2 Economic model

The economic optimization modelling framework is presented in Cieno (2021), using the same notations and equations for describing the flowrates present in the supply chain.

The economic objective function aims at maximizing the supply chain annual gross profit (GP), expressed as:

$$ObjFun_{economical} = \min\,(-GP) \quad (3.21)$$

Gross profit *GP* is defined as the difference between the total annual revenues (TR [€/year]) and total annual costs (TC [€/year]):

$$GP = TR - TC \quad (3.22)$$

Cieno (2021) contains all economic details concerning the calculation of supply chain costs and revenues.

3.3.3 Environmental model

GHG emissions can be assigned to multiple sources, such as:

- transport stage – GHG emissions related to transporting via trucks the flowrates from one node to another;
- GHG emissions related to sorting centres facilities, as explained in §2.3;
- GHG emissions due to MPW treatment according to one of the selected technologies, as explained in §2.4, §2.5 and §2.6.

3.3.3.1 Transport GHG emissions

Firstly, the transport related GHG emissions will be discussed.

In order to evaluate the transportation GHG emissions, it is necessary to determine the linear distance from one node to another, and that is done adopting the spherical law of cosines presented in d'Amore and Bezzo (2017):

$$LD_{n,n'} = \cos^{-1}[\sin(lat_n) \cdot \sin(\mathrm{lat}_{n'}) + \cos\,(\mathrm{lat_n}) \cdot \cos\,(lat_{n'}) \cdot \cos\,(\mathrm{long_n} - long_{n'}) \cdot \mathrm{R} \quad (3.23)$$

where lat_n and $lat_{n'}$ are the latitude of node n and n' respectively, $\mathrm{long_n}$ and $\mathrm{long}_{n'}$ are the longitudes of node n and n' respectively, and R is the earth radius, equal to 6372.785 km.

Then, the number of trucks needed to transport the waste flowrate from provinces to sorting centres is calculated:

$$NumbTrucks^{pr} = \frac{m_{pr,so}^{W}}{Cap_{MPW}} \ \forall \, pr \tag{3.24}$$

where $NumbTrucks^{pr}$ is the number of trucks needed to transport the province waste $m_{pr,so}^{W}$ from provinces to sorting centres, and Cap_{MPW} is the mass of waste or MPW that each truck can carry, equal to 12.4 tonne/truck, as expressed in Table 2.5.

The number of trucks needed to move MPW from sorting centres to treatment plants is calculated as:

$$NumbTrucks^{so} = \frac{m_{so}^{MPW,Av}}{Cap_{MPW}} \ \forall \, so \tag{3.25}$$

where $NumbTrucks^{so}$ is the number of trucks needed to transport MPW available $m_{so}^{MPW,Av}$ from sorting centres to treatment plants.

To calculate the number of trucks needed to move oil produced by pyrolysis plants to refineries:

$$NumbTrucks_{oil}^{t,OilK,s} = \frac{m_{t,OilK,s,refi}^{Oil}}{Cap_{Oil}} \ \forall \, t, OilK, s, refi \tag{3.26}$$

where $NumbTrucks_{oil}^{t,OilK,s}$ is the number of trucks needed to transport the oil produced $m_{t,OilK,s,refi}^{Oil}$ by pyrolysis plants to refineries, and Cap_{Oil} is the mass of oil that each truck can carry, equal to 43 tonne/truck, as expressed in Table 2.5.

The number of trucks needed to move the remaining MPW from pyrolysis sorting centres to incineration plants is calculated as:

$$NumbTrucks_{RPL}^{t,OilK,s} = \frac{m_{t,OilK,s}^{RPL}}{Cap_{MPW}} \ \forall \, t, OilK, s \tag{3.27}$$

where $NumbTrucks_{RPL}^{t,OilK,s}$ is the number of trucks needed to move the remaining MPW $m_{t,OilK,s}^{RPL}$ from pyrolysis sorting centres to incineration plants.

The number of trucks needed to move the solid residues from plants to landfills is calculated as:

$$NumbTrucks_{R}^{t,k,s} = \frac{m_{t,k,s}^{R,Tot}}{Cap_{R}} \ \forall \, t, k, s \tag{3.28}$$

where $NumbTrucks_R^{t,k,s}$ is the number of trucks needed to move the solid residues $m_{t,k,s}^{R,Tot}$ from plants to landfills, and Cap_R is the mass of residues that each truck can carry, taken equal to 84 tonne/truck, as shown in Table 2.5.

Transport GHG emissions are present in different stages of the supply chain. First, the waste flowrate collected by the provinces must end up in a sorting centre:

$$E^{W,trans} = \left[\sum_{pr,so} (NumbTrucks^{pr} \cdot LD_{n,n'}^{pr,so} \cdot truckE) \right] \cdot \tau \tag{3.29}$$

where $E^{W,trans}$ are the GHG emissions related to the transportation of the waste flowrate from the provinces to the sorting centres, expressed as ktonne of CO_2^{eq} per one ktonne of transported mass; $LD_{n,n'}^{pr,so}$ is the linear distance from a province collection point to a sorting centre, expressed in km according to (3.21); $truckE$ is the emission factor of each truck, equal for each kind of mass transported and taken approximately equal to 900 g of CO_2^{eq} per km and per truck, as explained in §2.2; τ is the tortuosity factor, equal to 1.4 (Zamboni et al., 2009).
Then, the MPW sorted out must be transported to the treatment facilities:

$$E^{MPW,trans} = \left[\sum_{so,t,k,s} NumbTrucks^{so} \cdot LD_{n,n'}^{so,t} \cdot truckE) \right] \cdot \tau \tag{3.30}$$

where $E^{MPW,trans}$ are the GHG emissions related to the transportation of the MPW from the sorting centre to a treatment location and $LD_{n,n'}^{so,t}$ is the linear distance of a treatment plant from sorting centre.
If a pyrolysis plant is chosen, then the oil produced must be transported to the refineries:

$$E^{Oil,trans} = \left[\sum_{t,refi,OilK,s} NumbTrucks_{Oil}^{t,OilK,s} \cdot LD_{n,n'}^{t,refi} \cdot truckE) \right] \cdot \tau \tag{3.31}$$

where $E^{Oil,trans}$ are the emissions for the transportation of the oil from a pyrolysis plant to a refinery, and $LD_{n,n'}^{t,refi}$ is the linear distance of a pyrolysis treatment plant from a refinery.

If pyrolysis is chosen as treatment technology for MPW, then also the remaining MPW must be transported to an incineration plant:

$$E^{RPL,trans} = \left[\sum_{t,OilK,s} (NumbTrucks_{RPL}^{t,OilK,s} \cdot \alpha_{\mathrm{Pyr,Inc}}^{\mathrm{LD}} \cdot LD_{n,n'}^{Pyr,Inc} \cdot truckE) \right] \cdot \tau \tag{3.32}$$

where $E^{RPL,trans}$ are the GHG emissions related to the transportation of the residual MPW sorted out in the pyrolysis plant and sent to an incineration plant, where it will be burnt, as discussed in §2.1; $\alpha_{\mathrm{Pyr,Inc}}^{\mathrm{LD}}$ is a correction factor for the LD if the pyrolysis plant is located next to a refinery: if it is the case, every refinery has an incinerator with itself, so $\alpha_{\mathrm{Pyr,Inc}}^{\mathrm{LD}}$ is equal to 0 (no transport emissions); otherwise, $LD_{n,n'}^{Pyr,Inc}$ expresses a fixed linear distance from a pyrolysis plant and an incineration structure equal to 150 km (Cieno, 2021).

All the residues from each treatment location are sent to a landfill:

$$E^{R,trans} = \left(NumbTrucks_{R}^{t,k,s} \cdot LD_{n,n'}^{landfill} \cdot truckE\right) \cdot \tau \qquad (3.33)$$

where $E^{R,trans}$ are the GHG emissions related to the transportation of the residue to the landfills, with a fixed linear distance $LD_{n,n'}^{landfill}$ of 50 km (Cieno, 2021).

At this point, it is possible to calculate all the transport related GHG emissions:

$$E^{trans} = E^{W,trans} + E^{MPW,trans} + E^{Oil,trans} + E^{RPL,trans} + E^{R,trans} \qquad (3.34)$$

3.3.3.2 Sorting centres GHG emissions

The evaluation of the sorting centre emissions is here reported:

$$E^{sort} = \sum_{pr} m_{pr,so}^{W} \cdot \varepsilon^{sort} \quad \forall\, pr \qquad (3.35)$$

where E^{sort} are the GHG emissions of the sorting centre; ε^{sort} is the emission factor for a sorting centre facility, equal to $2.25 \cdot 10^{-2}$ ktonne of CO_2^{eq} per ktonne of waste.

Pyrolysis plants have sorting centres coupled with them, with their corresponding GHG emissions:

$$E^{sort,pyro} = \sum_{so,t,OilK,s} m_{so,t,OilK,s}^{MPW,out} \cdot \varepsilon^{sort} \qquad (3.36)$$

Therefore, the overall emissions related to sorting centres are:

$$E^{sort,tot} = E^{sort} + E^{sort,pyro} \qquad (3.37)$$

3.3.3.3 MPW treating technologies GHG emissions

The emissions related to the MPW treatment depend on the typology of the selected technology.

If MPW is incinerated, then the treatment GHG emissions are evaluated as:

$$E^{treat,In} = \sum_{t,InK,s} m_{t,InK,s}^{MPW,Plant} \cdot \varepsilon^{In} \tag{3.38}$$

where ε^{In} is the incineration emission factor, equal to 870 ktonne of CO_2^{eq} per one tonne of treated MPW, as explained in §2.4.
If gasification is chosen for MPW treatment, then its emissions are related both to MPW pre-treatment and for MPW gasification:

$$E^{treat,Gas} = \sum_{t,GasK,s} m_{t,GasK,s}^{MPW,Plant} \cdot \varepsilon^{Gas,pretrt} + 0.7 \cdot m_{t,GasK,s}^{MPW,Plant} \cdot \varepsilon^{Gas} \tag{3.39}$$

where $\varepsilon^{Gas,pretrt}$ is the emission factor related to pre-treatment, that equals to $1.6 \cdot 10^6$ ktonne of CO_2^{eq} per ktonne of treated MPW. Gasification is performed only over a fraction of initial MPW share which enters the gasification plant. This share is called EBR and it is the 70% of the whole amount of MPW, as explained in detail in §2.5. The gasification emission factor ε^{Gas} is considered equal to 550 ktonne of CO_2^{eq} per one ktonne of EBR, as shown in §2.5.
If MPW is chosen to be pyrolyzed, then the related emissions are expressed as:

$$E^{treat,Pyro} = \sum_{t,OilK,s} m_{t,OilK,s}^{MPW,Plant} \cdot \varepsilon_{OilK}^{Pyro} + E^{RPL,inc} \tag{3.40}$$

where $\varepsilon_{OilK}^{Pyro}$ is the pyrolysis emission factor, equal to 0.1255 ktonne of CO_2^{eq} per one ktonne of the MPW entering the pyrolysis plant, in the case of PO_Pyrolysis; ε^{Pyro} is equal to 0.1656 ktonne of CO_2^{eq} per one ktonne of the MPW in the case of PO_PS_Pyrolysis. This emissions are related to MPW sorted out in the pyrolysis MRF, as explained in §2.6. $E^{RPL,inc}$ is the share of GHG emissions due to incinerating the remaining MPW which cannot be pyrolyzed. It is equal to:

$$E^{RPL,inc} = m_{so}^{RPL,Tot} \cdot \varepsilon^{In} \tag{3.41}$$

Total treatment GHG emissions due to MPW treatment are the sum of these contributions:

$$E^{treat} = E^{treat,In} + E^{treat,Gas} + E^{treat,Pyro} \tag{3.42}$$

Thus, total direct GHG emissions due to MPW supply chain are defined as:

$$E^{tot} = E^{trans} + E^{sort} + E^{treat} \tag{3.43}$$

3.3.3.4 Avoided GHG emissions

As explained in Chapter 2, all technologies have some environmental credits, called avoided emissions, expressed as ktonne of avoided CO_2^{eq} emissions per one ktonne of treated MPW.
Incineration allows to generate electricity, avoiding emitting CO_2^{eq} for its production:

$$E^{Av,In} = \sum_{t,InK,s} m_{t,InK,s}^{PL,Plant} \cdot \varepsilon^{Av,In} + \sum_{t,OilK,s} m_{t,OilK,s}^{RPL} \cdot \varepsilon^{Av,In} \tag{3.44}$$

where $E^{Av,Gas}$ is the avoided GHG emissions due to the production of electricity from incineration; $\varepsilon^{Av,In}$ is the avoided emission factor for incineration, which is equal to 0.4327 ktonne CO_2^{eq} per ktonne of MPW treated, as explained in §2.4.
If electricity is generated by gasifying MPW, then the avoided emissions are calculated as:

$$E^{Av,Gas} = \sum_{t,GasK,s} m_{t,GasK,s}^{MPW,Plant} \cdot \varepsilon^{Av,Gas} \tag{3.45}$$

where $\varepsilon^{Av,Gas}$ is the avoided emission factor for gasification, which is equal to 0.5866 ktonne CO_2^{eq} per ktonne of MPW treated, as shown in §2.5.
For what concerns pyrolysis, the avoided emissions are related to avoided extraction and avoided transportation for crude oil.

$$E^{Av,exctr} = \sum_{t,OilK,s} m_{t,OilK,s}^{Oil,Av} \cdot \varepsilon^{Av,exctr} \tag{3.46}$$

where $E^{Av,exctr}$ are the avoided extraction emissions and $\varepsilon^{Av,exctr}$ is the avoided emission factor for extraction, which is equal to 0.672 ktonne of CO_2^{eq} per ktonne of oil, as explained in §2.6.
Oil is imported to Italy according to a certain percentage from a certain country. It is simulated that the oil produced via pyrolysis is able to compensate the oil imported according to the import percentage:

$$m_{country}^{oil,import} = \sum_{t,OilK,s} m_{t,OilK,s}^{Oil,Av} \cdot Perc_{country} \tag{3.47}$$

where $m_{country}^{oil,import}$ is the oil produced via pyrolysis which compensates according to the percentage $Perc_{country}$ the oil imported from a certain country. $Perc_{country}$ is the import share from each country from which Italy imports oil, and these percentage are found in Table 2.10.
Moreover, a distinction is done for the oil transported by ship and the oil transported by pipeline, because the GHG emission factors are different, and often it is needed a percentage of means of transport, because the transportation can be both by ship and by pipeline, as discussed in §2.6:

$$E^{Av,pipe} = \sum_{country} m_{country}^{oil,import} \cdot Perc_{pipe\_transp,country} \cdot Dist_{n,n',country}^{pipe} \cdot \varepsilon^{Av,pipe} \tag{3.48}$$

where $E^{Av,pipe}$ is the avoided impact due to transportation of oil via pipeline: a percentage $Perc_{pipe\_transp,country}$ is needed because the oil from a country may have mixed means of transportation (partly by pipeline, partly by ship), and it represents the percentage of oil which is transported in this case by pipeline from the considered country; $Dist_{n,n',country}^{pipe}$ is the distance covered by the pipeline, assumed linear; $\varepsilon^{Av,pipe}$ is the avoided emission factor related to the pipeline transportation, and it is equal to $1.9 \cdot 10^{-5}$ ktonne of CO_2^{eq} per ktonne of oil and km. Details of percentage of pipeline transportation, distance covered by the pipeline and transportation emission factor are found in §2.6.

Likewise, for the naval transportation:

$$E^{Av,ship} = \sum_{country} m_{country}^{oil,import} \cdot Perc_{ship\_transp,country} \cdot Dist_{n,n',country}^{ship} \cdot \varepsilon^{Av,ship} \tag{3.49}$$

In this case $Perc_{ship\_transp,country}$ is the percentage of oil which is transported by ship from the country taken into consideration; $Dist_{n,n',country}^{ship}$ is not considered linear, as explained in §2.6 and shown in Table 2.11, but retrieved in www.seadistance.org ; $\varepsilon^{Av,ship}$ is the avoided emission factor related to the naval transportation, and it is equal to $2.4 \cdot 10^{-6}$ ktonne of CO_2^{eq} per ktonne of oil and km, as shown in §2.6.

The total avoided impact due to the oil transportation is evaluated as:

$$E^{Av,oil\ trans} = E^{Av,pipe} + E^{Av,ship} \tag{3.50}$$

The avoided emissions when pyrolysis is chosen are therefore:

$$E^{Av,Pyro} = E^{Av,exctr} + E^{Av,oil\ trans} \tag{3.51}$$

Now, it is possible to evaluate all the avoided emissions as:

$$E^{Av,tot} = E^{Av,Gas} + E^{Av,In} + E^{Av,Pyro} \tag{3.52}$$

At this point, it is possible to evaluate the net emissions due to the MPW supply chain:

$$E^{Net} = E^{tot} - E^{Av,Tot} \tag{3.53}$$

which is actually the environmental objective function to be minimized through MILP (mixed integer linear programming) approach in GASM®:

$$ObjFun_{envirnonmental} = \min\,(E^{Net}) \tag{3.54}$$

As explained in §1.4, minimizing the net GHG emissions is not the only purpose of this Master's thesis. Also economical optimization is included, and the mathematical formulation is comprehensively explained in Cieno (2021). The only difference with respect to the cited previous work is the amount of plastic waste collected by provinces, that was updated to the latest 2021 data, according to Table 3.1. Therefore, the multi-objective optimization considers the following objective function:

$$ObjFun = \min\{\alpha \cdot (-GP) + (1-\alpha) \cdot E^{net}\} \tag{3.55}$$

where *GP*[€/year] is the annual gross profit of the MPW supply chain, representing the economic objective function, E^{net} is the net GHG emissions of the supply chain, representing the environmental objective function, and α represent a weight that can take the value of 0 or 1, allowing to perform either economic optimization (for α = 1 – referring to as the economic optimum) or environmental optimization (for α = 0 – referring to as the environmental optimum).

3.4 Optimization results for base case scenario

This work differs from Cieno (2021) economical optimization since some parameter has been updated, such as the plastic waste flowrates shown in Table 3.1 that have been updated to the latest (2021) data, which return an overall bigger amount of plastic wastes to treat.

Secondly, an important economic parameter has been changed, that is the oil selling price. According to Cieno (2021), pyrolysis oil can be compared to a heavy crude oil. If pyrolysis oil comes from a PO_Pyrolysis oil, then it has been compared to Brent Oil; if pyrolysis oil results from a PO_PS_Pyrolysis plant, it is associated to WCS oil.

Selling prices are obtained averaging the oil prices in the past two years (January 2021 – October 2022). For what concerns Brent Oil, the data was retrieved from www.marketwatch.com , whereas for WCS price trends was obtained from www.economicdashboard.alberta.ca/oilprice. Also the currency change from USD to Euro is averaged in this temporal frame, and considered equal to 0.8941 €/USD. Oil selling prices and are shown in Table 3.10.

Table 3.10: *Oil selling prices for pyrolysis oil*

Type of crude oil	Pyrolysis technolgy	Selling price [€/ktonne]
Brent Oil	PO_Pyrolysis	551274
WCS	PO_PS_Pyrolysis	402743

Finally, the last parameter that have been updated is the electricity selling price. Electricity can be produced by PLASMIX incineration or gasification, as explained in §1.3. Updating to the latest available data (ARERA, 2022) which refers to 2021 electricity prices, the average electricity cost is found to be 124989 €/GWh, consistently higher than the one reported by Cieno (2021).

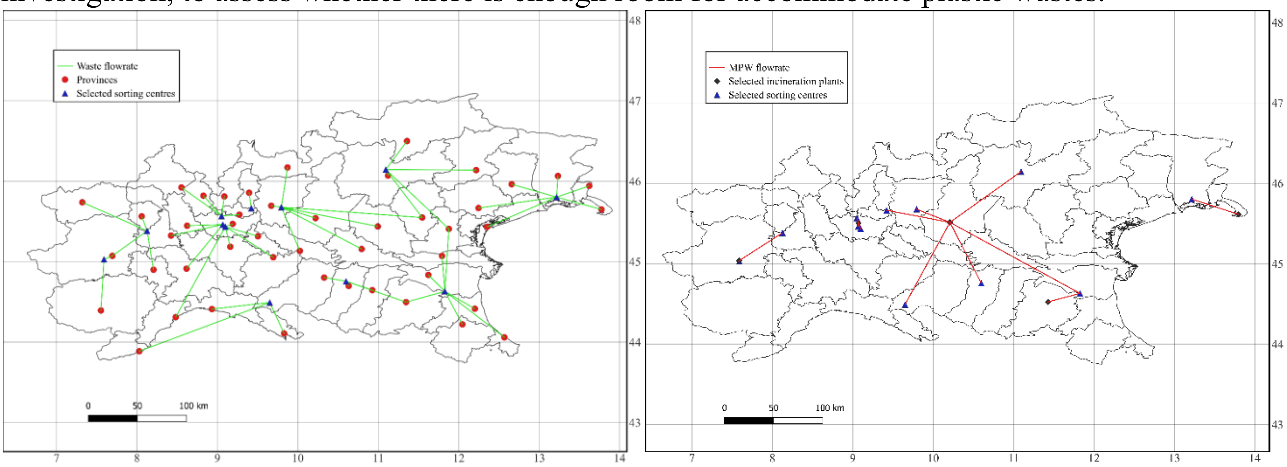
3.4.1 Economic optimization results

The economic optimization entails an annual gross profit of 75.3 M€/year, a higher value with respect to the one reported in Cieno (2021), due to the increase of electricity selling price.
In terms of environmental performances, the overall GHG emissions of the economically optimized base case scenario are quantified as 384221 ktonne of CO_2^{eq}/year.
The economic breakdown is shown in Table 3.14, whereas the environmental performances of the economic optimum are presented in detail in Table 3.15.
The results of the economic optimization are presented in the following: Firstly, in Table 3.11 there are listed the selected sorting centres for economically optimized base case scenario, whereas the supply chain configuration is presented in Figure 3.3: Figure 3.3(a) shows the plastic waste flowrates, collected by the provinces and sent to sorting centres for MPW recovery, while Figure 3.3(b) presents the selected treatment technologies, once MPW is separated, it must be treated according to one of the possible technologies.

__Table 3.11:__ Selected sorting centres for economically optimized base case scenario and amount of waste received

Selected sorting centre		Amount of waste received [ktonne/year]
Argenta	FE	100.5
Bedonia	PR	32.1
Cadelbosco di Sopra	RE	97.4
San Giorgio di Nogaro	UD	74.5
Lainate	MI	65.5
Milano	MI	35.2
Montello	BG	132.4
Verderio Inferiore	LC	4.8
Corsico	MI	130.8
Beinasco	TO	75.0
Cavaglia	BI	33.6
Lavis	TN	61.2

Waste flowrate is distributed quite equally among the Northern Italian sorting centres, as shown in Figure 3.3 (a). Sorting centres whose capacity could be an overestimation, *i.e.* San Giorgio di Nogaro, Lainate and Verderio Inferiore, are occupied respectively at 55%, 65.5% 4.8% of their capacity. Especially for San Giorgio di Nogaro and Lainate, this might be a situation which needs further investigation, to assess whether there is enough room for accommodate plastic wastes.



(a) (b)

***Figure 3.3:** Supply chain configuration of base case scenario – economic optimum: (a) Plastic waste flowrate from provinces to selected sorting centres, (b) MPW flowrate from sorting centres to incineration plants*

The MPW treatment supply chain is not much different from the one illustrated in the work of Cieno (2021), even if some changes in the model input data have occurred. There are more treatment locations, as the amount of plastic wastes and consequentially of MPW increased. However the selection of treatment technology did not move from incineration. It is true that oil prices increased, making pyrolysis a potentially attractive option, but electricity cost has increased more than double. The consequence is that, from a purely economic point of view, it is still preferable to burn MPW and sell electric energy than to pyrolyze it to obtain pyrolysis oil. In Table 3.12 are listed the treatment plants for economical optimized base case scenario. It is always preferred the closest plant, to reduce transport costs.

Table 3.12: *Selected MPW treatment facilities for the economically optimized base case scenario*

Treatment location		**Technology**	**Amount of MPW treated [ktonne/year]**
Trieste	TS	Incineration	38.8
Brescia	BS	Incineration	209.6
Torino	TO	Incineration	56.6
Milano	MI	Incineration	120.6
Granarolo	BO	Incineration	13.5

Both absolute economic results for costs and revenues, and relative results per mass of treated MPW are considered. It has been estimated that the total amount of MPW in the Northern Italy supply chain is equal to 439 ktonne/year.

The economic profit and costs can come from different sources of MPW treatment supply chain, as shown in Table 3.13.

Treatment tariff incomes and revenues from selling recycled polymers obtained from the additional sorting step before pyrolysis are retrieved from Cieno (2021) based on COREPLA data.

Table 3.13: *Possible economical revenues for MPW supply chain model*

Revenue	**Price [€/ktonne]**
PO_Pyrolyis Oil	551274
PO_PS_Pyrolysis Oil	402743
Treatment tariff	210000
Recycled polymers	378500
Electricity	124989 [1]

[1] For electricity, the price of selling is expressed in [€/GWh].

On the other hand, expenses of the base case scenario are of three different types:

- Transport costs for the entire supply chain;
- Landfill costs, for MPW treatment residues;
- MPW treatment costs.

In Table 3.14 is presented a breakdown of costs and revenues for the economical optimization of the base case scenario.

Table 3.14: *Costs and revenues breakdown for economically optimized base case scenario*

Revenues			Expenses		
Source of profit	**Revenues [€/year]**	**Revenues [€/ktonne$_{PL}$]**	**Expenses**	**Costs [€/year]**	**Costs [€/ktonne$_{PL}$]**
Electricity	59.1 million	134613	**Transport costs**	19.2 million	43591
Treatment revenues	92.2 million	210000	**Landfill costs**	7.0 million	15960
			Treatment costs	49.9 million	112934
Tot revenues	151.3 million	344515	**Tot costs**	76.1 million	172485
Gross profit [€/year]			75.3 million		
Gross profit [€/ktonne$_{PL}$]			171461		

Revenues are almost double than total costs for MPW supply chain. The largest share of revenues comes from the gate tariff, cashed in by the plants when it accepts MPW. However, also electricity selling price is a considerable share of supply chain revenues.
For what concerns supply chain costs, MPW treatment costs take two-third of all costs, suggesting that this is the supply chain economical largest influence.

After developing an environmental model for MPW supply chain, it is possible also to evaluate the environmental impact of the economically optimized base case scenario, in terms of GHG emissions. Emissions are related to three contributions:

- Transportation GHG emissions of the supply chain;
- Sorting centres GHG emissions;
- MPW treatment GHG emissions.

Also in this case, direct GHG emissions and GHG avoided impacts are expressed both in absolute values, *i.e.* in ktonne$_{CO2eq}$/year, and for relative amount of treated MPW, *i.e.* in ktonne$_{CO2eq}$/ktonne$_{PL}$. Environmental breakdown of economically optimized base case scenario is shown in Table 3.15.

Table 3.15: *Emissions and avoided impacts breakdown for the economically optimized base case scenario*

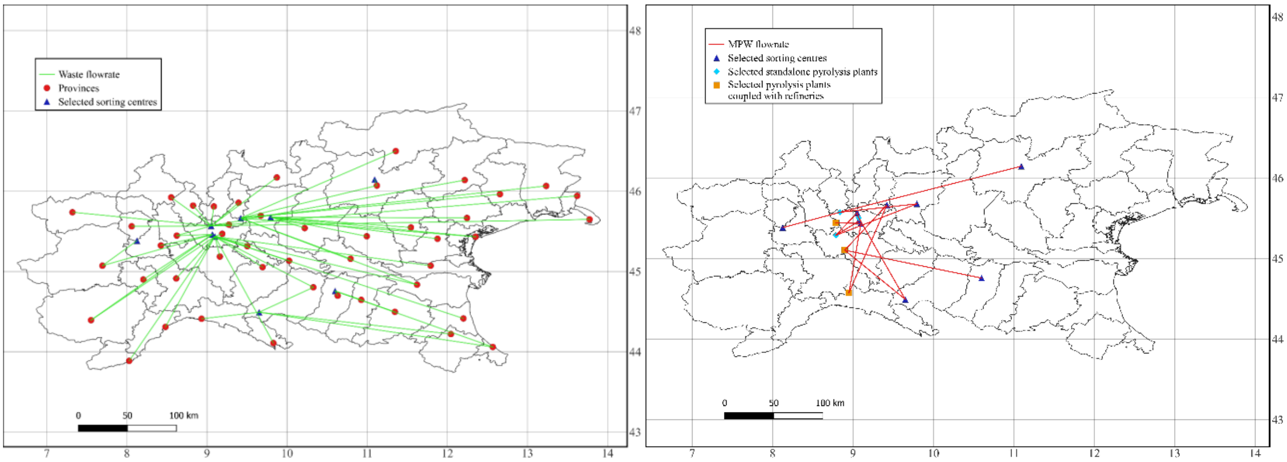
Emissions			**Avoided impacts**		
Source of emissions	**Emissions [ktonne$_{CO2eqe}$/year]**	**Emissions [kton$_{CO2eq}$/ ktonne$_{PL}$]**	**Source of avoided impacts**	**Avoided impact [ktonne$_{CO2eq}$/year]**	**Avoided impact [ktonne$_{CO2eq}$/ ktonne$_{PL}$]**
MPW treatment	382076	870.0			
Transportation	2316	5.3	**Incineration**	190	0.4
Sorting centres	19	0.02			
Tot emissions	384411	875.4	**Tot avoided impacts**	190	0.4
Net emissions [ktonne$_{CO2eq}$/year]			384221		
Net emissions [ktonnen$_{CO2eq}$/ktonne$_{PL}$]			875.0		

It appears immediately clear that almost the total share of GHG emissions comes from MPW incineration. All other contributions, direct or avoided, are very small.
In the case of economic optimization of base case scenario, the only possible avoided impact comes from the electricity produced by incineration plants, the latter one being the only MPW treatment technology selected in the supply chain.

3.4.2 Environmental optimization results

The purpose of this Master's thesis is the optimal design of MPW supply chain in terms of GHG emissions minimization. In order to do so, a mathematical model which optimizes environmentally the MPW management was developed and integrated to the already existing economic mathematical model, allowing to assess also the economic performance of the environmental optimal solution.
The environmentally optimized base case scenario is characterized by the presence of only pyrolysis plants for MPW treatment, as they have proven to be the least impactful technologies in terms of GHG emissions. In terms of environmental performances, the overall GHG emissions of the environmentally optimized base case scenario are equal to 186909 ktonne of CO_2^{eq}/year, more than two times lower with respect to the GHG emissions relative to the economic optimum.
On the other hand, the environmental optimum yields a Gross Profit of 33.4 M€/year, which is less than the half of what the economic optimization provides.

The economic breakdown is shown in Table 3.18, whereas the environmental performances of the environmental optimum are presented in detail in Table 3.19.
The MPW supply chain configuration of the environmental optimum is shown in Figure 3.4 and Figure 3.5.
In Table 3.16 there are listed the selected sorting centres for environmentally optimized base case scenario, and the supply chain configuration is presented in Figure 3.4: Figure 3.4(a) shows the plastic waste flowrates, collected by the provinces and sent to sorting centres for MPW recovery, while Figure 3.4(b) presents the selected treatment technologies, once MPW is separated, it must be treated according to one of the possible technologies. Finally Figure 3.5 concludes MPW supply chain, showing the pyrolysis oil flowrates that need to end up in one of the refineries.



(a) (b)

Figure 3.4: *Supply chain configuration of base case scenario – environmental optimum: (a) Plastic waste flowrate from provinces to selected sorting centres, (b) MPW flowrate from selected sorting centres to treatment locations*

The supply chain tends to send the plastic wastes to the Northwest sorting centre. That is because the final stage of supply chain, *i.e.* oil refinement, is concentrated in that geographic area, therefore the model selects the location of the pyrolysis plants closer to the refineries, minimizing as much as possible the transport GHG emissions.

Table 3.16: *Selected sorting centres for environmentally optimized base case scenario and amount of waste received*

Selected sorting centre		**Amount of waste received [ktonne/year]**
Bedonia	PR	48.0
Cadelbosco di Sopra	RE	97.4
Lainate	MI	100.0
Milano	MI	45.0
Montello	BG	150.0
Verderio Inferiore	LC	97.0

Corsico	MI	250.0
Cavaglia	BI	45.0
Lavis	TN	10.6

From Table 3.16, it is observed that Lainate and Verderio Inferiore sorting centres are fully occupied in their capacity. This could be a limitation of the input data, because the capacity of the mentioned sorting centres was assumed to be equal to their entire capacity, and not only to the capacity of the sorting centres to treat MPW. Additional investigation is required in order to reflect the real capacity of those sorting centres to manage the MPW fraction.
It is anyway evident the tendency from the supply chain to occupy at full capacity the sorting centres, when Table 3.16 is compared to Table 3.2, instead of choosing multiple facilities.
From Figure 3.4(b) it can be observed that only pyrolysis plants are chosen, as previously mentioned, both in stand-alone pyrolysis plants, and in pyrolysis facilities located in proximity of oil refineries. This difference is highlighted in the map. The plants and their typology are listed in Table 3.17.

Table 3.17: *Selected MPW treatment facilities for the environmentally optimized base case scenario*

Treatment location		Refinery	Typology	Size	Amount of MPW treated [ktonne/year]
Busto Arsizio	VA	No	PO_PS_Pyrolysis	Large	78.8
Parona	PV	No	PO_PS_Pyrolysis	Large	78.8
Milano	MI	No	PO_PS_Pyrolysis	Medium	44.7
Sannazzaro	PV	Yes	PO_PS_Pyrolysis	Large	78.8
Busalla	GE	Yes	PO_PS_Pyrolysis	Large	78.8
Trecate	NO	Yes	PO_PS_Pyrolysis	Large	78.8

Three of the six selected treatment locations are pyrolysis plants located in proximity of oil refineries. This choice is easily explained in order to avoid unnecessary oil transportation from pyrolysis plants to refineries, since they are the last stage of the supply chain. It is also always preferred the largest size for pyrolysis plants, because it is less impactful to send the MPW flowrate in one plant instead of splitting it in different treatment locations. The pyrolysis plant of Milano is of medium size, but this is for numerical reason, *i.e.* there is no reason to choose a large plant if the flowrate which is left to be treated can be accepted in a medium size plant.
For what concerns the pyrolysis plant typology, the choice is always a PO_PS_Pyrolysis plant. As explained in §2.6, PO_PS_Pyrolysis returns a greater amount of GHG emissions compared to PO_Pyrolysis, respectively 0.1656 ktonne of CO_2^{eq} per one ktonne of treated MPW and 0.1255 ktonne of CO_2^{eq} per one ktonne of treated MPW. Nevertheless, the PO_PS_Pyrolysis is still more convenient if looking at the amount of remaining MPW of both technologies, as shown in Figure 2.2 and 2.3. The share of remaining MPW for PO_Pyrolysis amounts to 57%, compared to 48% of

PO_PS_Pyrolysis. Remaining MPW end-of-life is incineration, the technology which by far emits the largest amount of greenhouse gases. Therefore, it is preferable to choose a PO_PS_Pyrolysis, which is capable to treat a larger amount of MPW.

If MPW is treated in a stand-alone pyrolysis plant, then pyrolysis oil needs to be sent to a refinery, which is typical the closest refinery to the pyrolysis plants, as shown in Figure 3.5.

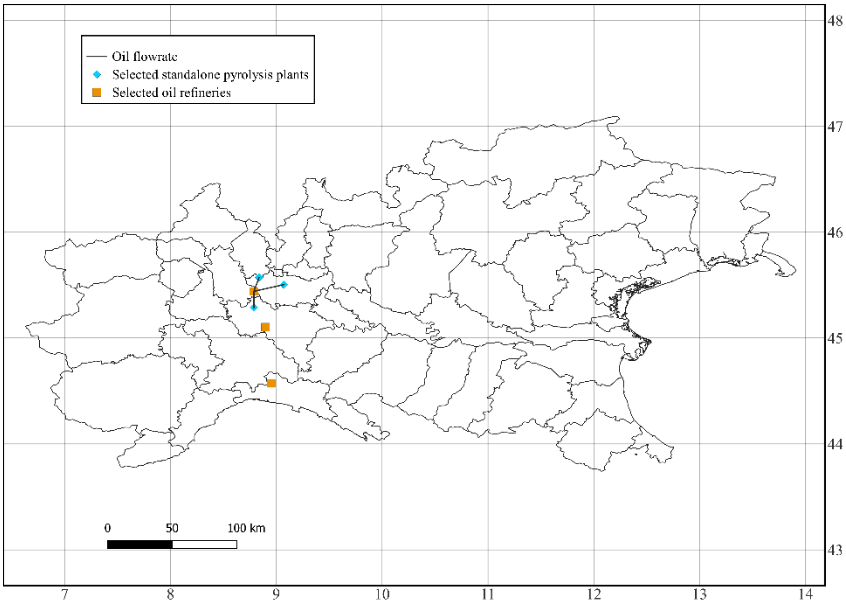


Figure 3.5: *Pyrolysis oil flowrate from pyrolysis plant to oil refineries for the environmentally optimized base case scenario*

Oil flowrate tends to be sent to the closest refinery, whenever it is not produced in a pyrolysis plant coupled itself with a refinery.

In Table 3.18 is presented the breakdown of costs and revenues for the environmental optimization of the base case scenario.

__Table 3.18:__ Costs and revenues breakdown for environmentally optimized base case scenario

Revenues			Expenses		
Source of profit	**Revenues [€/year]**	**Revenues [€/ktonne$_{PL}$]**	**Expenses**	**Costs [€/year]**	**Costs [€/ktonne$_{PL}$]**
Electricity	28.6 million	65148	**Transport costs**	41.1 million	93586
Oil	53.9 million	122779			
Recycled polymers	6.5 million	14800	**Landfill costs**	19.1 million	43491
Treatment revenues	92.2 million	210000			
			Treatment costs	87.6 million	199468
Tot revenues	181.2 million	412598	**Tot costs**	147.8 million	336565
Gross profit [€/year]			33.4 million		
Gross profit [€/ktonne$_{PL}$]			76053		

Costs and revenues breakdown shows that revenues are actually higher for the environmentally optimized scenario compared to economic optimum, due to the oil selling which is added to a still consistent income from electricity selling. However both transport costs and treatment costs are consistently higher. The raise in transport costs is explained by the larger distances covered by plastic waste flowrate from provinces to sorting centres, as shown in Figure 3.4(a) if compared to Figure 3.3(a). The treatment costs, on the other hand, reflects the higher costs of a pyrolysis plants with respect to an incineration plant. This is due to the fact that the overall pyrolysis plant has an additional sorting step, whose costs and efficiencies are included in the cost and efficiency of the pyrolysis plant. This sorting step is needed to ensure the quality of the feed to the pyrolysis reactor. Also, the landfill costs are significantly higher with respect to those entailed by the economic optimal supply chain (almost 3 times higher), due to increasing flowrate of total solid residue generated by the pyrolysis in the supply chain.

The GHG emissions breakdown are summarized in Table 3.19.

Table 3.19: *Emissions and avoided impacts breakdown for the environmentally optimized base case scenario*

Emissions			Avoided impacts		
Source of emissions	**Emissions [ktonne$_{CO2eq}$/year]**	**Emissions [ktonne$_{CO2eq}$/ ktonne$_{PL}$]**	**Source of avoided impacts**	**Avoided impact [ktonne$_{CO2eq}$ /year]**	**Avoided impact [ktonne$_{CO2eq}$/ ktonne$_{PL}$]**
MPW treatment	185118	421.5	**Pyrolysis**	95.9	0.2
Transport	1950	4.4	**Incineration**	92.0	0.2
Sorting centres	29	0.07			
Tot emissions	187097	426.0	**Tot avoided impacts**	187.9	0.4
Net emissions [ktonne$_{CO2eq}$/year]			186909		
Net emissions [ktonnen$_{CO2eq}$/ktonne$_{PL}$]			425.6		

Net GHG emissions of the environmental optimum are less than the half of GHG emissions of economic optimum. However, within the MPW treatment emissions, the largest share is due to remaining MPW incineration after the pyrolysis process, as shown in Table 3.20.

Table 3.20: *MPW treatment GHG emissions breakdown for the environmentally optimized base case scenario*

Source of MPW treatment emissions	Emissions [ktonne$_{CO2eq}$/year]	Emissions [kton$_{CO2eq}$/kton$_{PL}$]
Pyrolysis	73	0.2
Incineration	185045	421.3

On the other hand, avoided impacts are very similar to the ones presented in the economic optimum, however, in the environmental optimal solution, they are almost equally distributed among avoided impacts from incineration of the remaining MPW and avoided impacts from pyrolysis process.

3.5 Chapter conclusions

The base case scenario considers that, whenever the MPW treatment supply chain includes pyrolysis plants, the oil produced by this technology is sent to oil refineries.
This scenario has been optimized both economically and environmentally. For the economic optimization, also environmental results have been shown, and vice versa environmental analysis is coupled with economic considerations.
Environmental optimization differs completely from the economical optimization of the supply chain in terms of selected technologies for MPW treatment.
Economically optimized base case scenario, which has been comprehensively explained in Cieno (2021), selects only incineration plants for MPW supply chain, entailing a Gross Profit of about 75.3 M€/year, however the incineration process is the most impactful technology in terms of GHG emissions, and the overall net GHG emissions are quantified and equal to 384221 ktonne of CO_2^{eq}/year (more than double with respect to the environmental optimum).
On the other hand, environmental optimization, which is the purpose of this study, leads only to the selection of pyrolysis plants for MWP treatment, belonging to the PO_PS_Pyrolysis typology. This allows to cut the GHG emissions by half with respect to the economical optimization, entailing a level of GHG emissions of about 186909 ktonne of CO_2^{eq}/year. However, the environmental optimum solution leads to a poor economic performance, if compared to the economic optimal solution, yielding an annual gross profit of about 33.4 M€/year, half with respect to the gross profit of the economic optimum.

Chapter 4 would investigate another option, proposing an alternative scenario, which tries to match economic and environmental demands.

Chapter 4

Supply chain model for cracking scenario

Chapter 4 presents the MPW supply chain alternative scenario, called "cracking scenario". The technologies which are available for treating MPW remain the same (*i.e.* incineration, gasification or pyrolysis). However, if pyrolysis is chosen, the pyrolysis oil is not sent to oil refineries, like in the base case scenario explained in Chapter 3, but it is sent to cracking plants as a substitution for cracking naphtha.

This Chapter shows model assumptions and equations, then presents the economic and environmental results for the alternative scenario.

4.1 Cracking scenario overview and preliminary model data

MPW management might lead to different pathways, as explained in previous chapters. The one proposed in this Chapter refers to the work of Kusenberg et al. (2022), which proposes that pyrolysis oil is blended with fossil naphtha in a 1:3 (weight-based) mixing ratio and fed to a steam cracking unit to produce ethylene. Pyrolysis oil blended with fossil naphtha leads to higher ethylene yields when compared to fossil naphtha feedstock.

Based on these assumptions, whenever MPW supply chain considers pyrolysis, the oil produced is then sent to Italian cracking plants.

Only two cracking plants are still working in Italy, and they are both located in the Southern Italy, far from the MPW treatment locations, as shown in Table 3.6.

Therefore, when pyrolysis oil is produced in the plants listed in Table 1.2 and in Table 3.5, it needs to be sent to a one of the Northern Italian ports, whose locations are shown in Table 3.7. Pyrolysis oil is then shipped to cracking plants to become a fossil naphtha substitute.

This scenario has two important possible advantages. The first is of environmental nature. Pyrolysis has proven to be the least environmentally impactful treatment strategy for MPW, as shown in Chapter 3. Additionally, if pyrolysis oil is chosen as a substitution for fossil naphtha, some GHG emissions from crude oil refinement are also avoided, as explained in §2.6.

The other potential benefit from the alternative scenario is in terms of economic performance. Naphtha has generally higher selling prices with respect to crude oil prices, shown in Table 3.10, which makes the alternative scenario more economically attractive than base case scenario when pyrolysis is chosen.

Naphtha selling price is averaged from January 2021 to October 2022, and these trends were retrieved from https://tradingeconomics.com/commodity/naphtha, and the final selling price was assumed to be 706.9 \$/tonne, which, considering currency change from USD to Euro equal to 0.8941 €/USD, leads to a final price of 632052 €/ktonne.

Naval transportation GHG emissions have been estimated in §2.6. On the other hand, naval transportation cost has not been considered in this Master's thesis so far. In the following, the approach for computing the naval transportation cost is presented.

From Giarola et al. (2011) it is possible to estimate naval transportation costs starting from ethanol transportation costs. Ethanol naval transportation costs are estimated to be 0.064 €/ktonne/km. Pyrolysis oil naval transportation costs are thus calculated as:

$$UTC_{oil} = UTC_{EtOH} \cdot \frac{\rho_{EtOH}}{\rho_{oil}} \quad (4.1)$$

Where UTC_{oil} is the unitary naval transportation cost for pyrolysis oil; UTC_{EtOH} is the unitary naval transportation cost for ethanol; ρ_{EtOH} is the ethanol density, equal to 0.7891 tonne/m^3; ρ_{oil} is the pyrolysis oil density, estimated to be 1.002 tonne/m^3, as shown in Table 2.5.

Thus, the naval transportation costs for pyrolysis oil from Northern Italian ports to cracking plants is estimated to be 50 €/ktonne/km.

4.2 Mathematical modelling of MPW supply chain for cracking scenario

The mathematical structure of MPW supply chain model stays the same of the base case scenario, for material flowrates, for the economic part, and also for environmental equations, with some differences due to the final destination of pyrolysis oil, which are here presented.

4.2.1 Environmental model for cracking scenario

Some new equations need to be defined for cracking scenario model related to environmental model. The number of tucks which carry the pyrolysis oil to Northern Italian ports are calculated as:

$$NumbTrucks_{oil}^{t,OilK,s,portdep} = \frac{m_{t,OilK,s,portdep}^{OilCrack}}{Cap_{Oil}} \quad \forall\, t, OilK, s, portdep \quad (4.2)$$

where $NumbTrucks_{oil}^{t,OilK,s}$ is the number of trucks needed to transport the oil $m_{t,OilK,s,portdep}^{OilCrack}$ that has to be shipped from Northern Italian ports, and Cap_{Oil} is the mass of oil that each truck can carry, equal to 43 tonne/truck, as expressed in Table 2.5.

Thus, the related oil transport GHG emissions towards Northern Italian ports are quantified as:

$$E^{Oil,trans} = \left[\sum_{t,portdep,OilK,s} NumbTrucks_{Oil}^{t,OilK,s,portdep} \cdot LD_{n,n'}^{t,portdep} \cdot truckE) \right] \cdot \tau \tag{4.3}$$

where $E^{Oil,trans}$ are the emissions for the transportation of the oil from a pyrolysis plant to an oil departure port, $LD_{n,n'}^{t,portdep}$ is the linear distance of a pyrolysis treatment plant from an oil departure port, $truckE$ is the emission factor of each truck, equal for each kind of mass transported and taken approximately equal to 900 g of CO_2^{eq} per km and per truck, as explained in §2.2; τ is the tortuosity factor, equal to 1.4 (Zamboni et al., 2009).
The total quantity of oil which is produced by pyrolysis plants needs to be sent to Northern Italian departure ports:

$$\sum_{portdep} m_{t,OilK,s,portdep}^{OilCrack} = m_{t,OilK,s}^{Oil,Av} \;\; \forall\, t, OilK, s \tag{4.4}$$

where $m_{t,OilK,s}^{Oil,Av}$ is the flowrate of oil produced by a pyrolysis plant.
The overall amount of oil $m_{t,OilK,s,portdep}^{OilCrack}$ that needs to be shipped from a Northern Italian port must be sent to a Southern Italian port, by ship:

$$\sum_{portarr} m_{t,OilK,s,portdep,portarr}^{OilShip} = m_{t,OilK,s,portdep}^{OilCrack} \;\forall\, t, OilK, s, portdep \tag{4.5}$$

where $m_{t,OilK,s,portdep,portarr}^{OilShip}$ is the flowrate that is moved by ship from a departure port to an arrival port in proximity of a cracking plant.
Therefore, the amount of GHG emissions produced by transporting the pyrolysis oil by ship from one port to another are computed as:

$$E^{Oil,ship} = \sum_{t,OilK,s,portdep,portarr} m_{t,OilK,s,portdep,portarr}^{OilShip} \cdot ND_{n,n'}^{portdep,portarr} \cdot \varepsilon^{ship} \tag{4.6}$$

where $ND_{n,n'}^{portdep,portarr}$ are the naval distances from one departure port to an arrival port, listed in Table 2.13, and ε^{ship} is the naval environmental impact, taken equal to as $2.354 \cdot 10^{-6}$ tonne of CO_2^{eq} per one tonne of oil transported per 1 km, as explained in §2.6.
The total GHG emissions, due to oil transportation, are thus calculated as:

$$E^{TransTot,Oil} = E^{Oil,trans} + E^{Oil,ship} \tag{4.7}$$

The total GHG emissions for cracking scenario MPW supply chain are calculated:

$$E^{trans} = E^{W,trans} + E^{MPW,trans} + E^{TransTot,Oil} + E^{RPL,trans} + E^{R,trans} \tag{4.8}$$

Pyrolysis oil sent to cracking plants is a substitution for fossil naphtha, which is obtained after crude oil refinement. In such way, crude oil refining emissions are avoided, providing a feed for cracking plants ready to be used.

The avoided GHG emissions of crude oil refinement are quantified to be:

$$E^{Av,Ref} = \sum_{t,OilK,s} m^{Oil,Av}_{t,OilK,s} \cdot \varepsilon^{Av,Ref} \tag{4.9}$$

where $\varepsilon^{Av,Ref}$ is the avoided emission factor for crude oil refinement, taken equal as 4.185 ktonne of CO_2^{eq} per ktonne of oil, which are saved by sending the pyrolysis oil straight to cracking units, as explained in §2.6.

The total GHG avoided emissions by treating MPW according to the cracking scenario hypotheses are therefore:

$$E^{Av,tot} = E^{Av,Gas} + E^{Av,In} + E^{Av,Pyro} + E^{Av,Ref} \tag{4.10}$$

where $E^{Av,Gas}$, $E^{Av,In}$ and $E^{Av,Pyro}$ are avoided GHG emission for gasification, incineration and pyrolysis, as commented in §3.3.3.4.

4.2.2 Economic model for cracking scenario

Also the economic model is affected in some equations by the new assumptions of the cracking scenario.

The transport costs due to the movement of pyrolysis oil $TC^{Oil,trans}$ from pyrolysis plants to departure ports are defined as:

$$TC^{Oil,trans} = \left[\sum_{t,portdep,OilK,s} m^{OilCrack}_{t,OilK,s,portdep} \cdot LD^{t,portdep}_{n,n'} \cdot \mathrm{UTC}^{oil}) \right] \cdot \tau \tag{4.11}$$

where UTC^{oil} is the unitary transport cost factor when moving oil on-wheel, equal to 127 €/ktonne/km (Cieno, 2021).

The pyrolysis oil ship transport costs from one Northern Italian departure port to a Southern Italian arrival port are estimated as:

$$TC^{Oil,ship} = \sum_{t,OilK,s,portdep,portarr} m^{OilShip}_{t,OilK,s,portdep,portarr} \cdot ND^{portdep,portarr}_{n,n'} \cdot \mathrm{UTC}^{ship} \quad (4.12)$$

where UTC^{ship} is the unitary transport cost for oil naval transport, estimated in €/ktonne of oil/km, as explained in §4.1.
Thus, the total pyrolysis oil transport costs are:

$$TC^{TransTot,Oil} = TC^{Oil,trans} + TC^{Oil,ship} \quad (4.13)$$

Therefore, the total transport costs UTC^{trans} when MPW is treated according to the cracking scenario hypotheses are estimated as:

$$TC^{trans} = TC^{W,trans} + TC^{MPW,trans} + TC^{TransTot,Oil} + TC^{RPL,trans} + TC^{R,trans} \quad (4.14)$$

where $TC^{W,trans}$, $TC^{MPW,trans}$, $TC^{RPL,trans}$ and $TC^{RPL,trans}$ are the total transport costs for plastic waste, MPW, residual MPW and residues, respectively, calculated according to Cieno (2021) economic model.
Substituting fossil naphtha with pyrolysis oil generates revenues Rev^{Naph} for MPW supply chain. It is assumed that pyrolysis oil is purchased by cracking plants at the same naphtha selling price:

$$Rev^{Naph} = \sum_{t,OilK,s} m^{Oil,Av}_{t,OilK,s} \cdot MP^{Naph} \quad (4.15)$$

where MP^{Naph} is the market price of naphtha, estimated in 632052 €/ktonne, as discussed in §4.1.
Total revenues Rev^{tot} are quantified in:

$$Rev^{tot} = Rev^{El} + Rev^{Mech} + Rev^{T,Tot} + Rev^{Naph} \quad (4.16)$$

where Rev^{El}, Rev^{Mech}, $Rev^{T,Tot}$ are respectively the revenues from selling electricity, from selling mechanically recyclable polymers and from "gate tariff", according to Cieno (2021) economic model.

The objective functions are identical to the ones reported in Chapter 3.

4.3 Optimization results for cracking scenario

Cracking scenario opens a new possible pathway for MPW management. Within the supply chain, the Northern Italian oil refineries are substituted by cracking plants located in the Southern Italy.
In this paragraph, results of economic and environmental optimum for this scenario will be shown and commented.

4.3.1 Economic optimization results

The cracking scenario economic optimum differs from the base case economic optimum. The MPW supply chain considers selling pyrolysis oil as a naphtha substitution, no more as a crude oil substitution. This generates a different income due to the difference in market price between crude oil (Brent or WCS, which are the ones considered in this Master's thesis) and fossil naphtha, as shown in Table 4.1, suggesting that selling pyrolysis oil as cracking naphtha is more economically advantageous than selling it as a crude oil substitute.

Table 4.1: *Difference in pyrolysis product revenues*

Type of product	Selling price [€/ktonne]
Brent Oil	551274
WCS	402743
Naphtha	632052

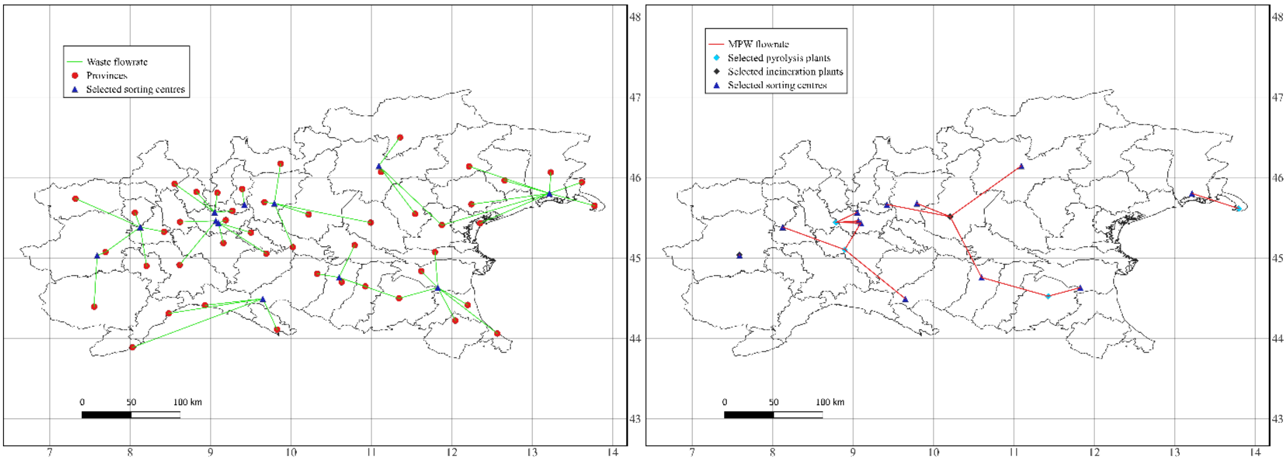
The economic optimization of cracking scenario yields a Gross Profit of 77.7 M€/year, which is a slightly higher value with respect to the economically optimized base case (which entailed a Gross Profit of 75.3 M€/year).
Economic optimum leads to GHG net emissions equal to 265149 ktonne of CO_2^{eq}/year, 30% less than what economically optimized base case supply chain emits (384221 ktonne of CO_2^{eq}/year). The reason for that is the selection of pyrolysis technology in the supply chain that co-exist with incinerators, the first one being less environmentally impactful for MPW treatment compared to the incineration plants, which were the only selected technology for base case economic optimum.
The economic breakdown is shown in Table 4.4, whereas the environmental performances of the economic optimum are presented in detail in Table 4.5.
The results of the economic optimization are presented in the following: Firstly, in Table 4.2 there are listed the selected sorting centres for economically optimized cracking scenario, whereas the supply chain configuration is presented in Figure 4.1: Figure 4.1(a) shows the plastic waste flowrates, collected by the provinces and sent to sorting centres for MPW recovery, while Figure 4.1(b) presents

the selected treatment technologies, once MPW is separated, it must be treated according to one of the possible technologies. Then, Figure 4.2 illustrates the path of produced oil from pyrolysis plants to Northern Italian departure ports. Figure 4.3 concludes MPW supply chain shown the sea path towards Southern Italian cracking plants.

Table 4.2: *Selected sorting centres for economically optimized cracking scenario and amount of waste received*

Selected sorting centre		**Amount of waste received [ktonne/year]**
Argenta	FE	100.5
Bedonia	PR	41.9
Cadelbosco di Sopra	RE	94.4
San Giorgio di Nogaro	UD	105.9
Lainate	MI	65.5
Milano	MI	29.7
Montello	BG	112.5
Verderio Inferiore	LC	4.8
Corsico	MI	121.0
Beinasco	TO	75.0
Cavaglia	BI	39.1
Lavis	TN	50.7

Waste flowrate is distributed quite equally among the Northern Italian sorting centres, as shown in Figure 4.1 (a). Sorting centres whose capacity could be an overestimation, *i.e.* San Giorgio di Nogaro, Lainate and Verderio Inferiore, are occupied respectively at 78%, 66% and 5% of their capacity. Especially for San Giorgio di Nogaro and Lainate sorting centre, the capacity is close to the maximum acceptable value of waste entering the facility. Also in this case, further investigations are suggested.



(a) (b)

Figure 4.1: *Supply chain configuration of cracking scenario – economic optimum: (a) Plastic waste flowrate from provinces to selected sorting centres, (b) MPW flowrate from sorting centres to treatment plants*

Supply chain selects 6 MPW treatment plants: 4 PO_PS_Pyrolysis plants and 2 incineration plants, as listed in Table 4.3.

Table 4.3: *Selected MPW treatment facilities for the economically optimized cracking scenario*

Treatment location		Technology	Amount of MPW treated [ktonne/year]	Size
Torino	TO	Incineration	39.1	
Brescia	BS	Incineration	134.9	
Sannazzaro	PV	PO_PS_Pyrolysis	76.1	Large
Trecate	NO	PO_PS_Pyrolysis	78.8	Large
Granarolo	BO	PO_PS_Pyrolysis	55.2	Large
Trieste	TS	PO_PS_Pyrolysis	55.2	Large

Thus, two kinds of technologies, *i.e.* incineration and pyrolysis, are in competition in the economic optimum. The chosen size is always the largest possible, because of advantageous large-scale effects (Cieno, 2021) from the economic standpoint. Selected pyrolysis plants belong to PO_PS_Pyrolysis technology, differently to what happened in base case economic optimization. The reason for that, even though PO_PS_Pyrolysis plants are more expensive, is that the oil yield is greater than PO_Pyrolysis technology, and this leads to greater revenues from selling pyrolysis oil as naphtha substitution.

The competition between technologies is explained by the comparable revenues obtainable from electricity, *i.e.* from incineration, and from naphtha selling, *i.e.* from pyrolysis. Once again supply chain is very sensitive to prices fluctuations. In order to highlight this aspect, a sensitivity analysis performed of electricity price will be shown in the Appendix.

Based on the latest (November 2022) available data, MPW is preferentially treated in a pyrolysis plant that is located in the surroundings of a departure port for shipping the oil, reducing as much as possible the costs related to truck transport , as illustrated in Figure 4.2.

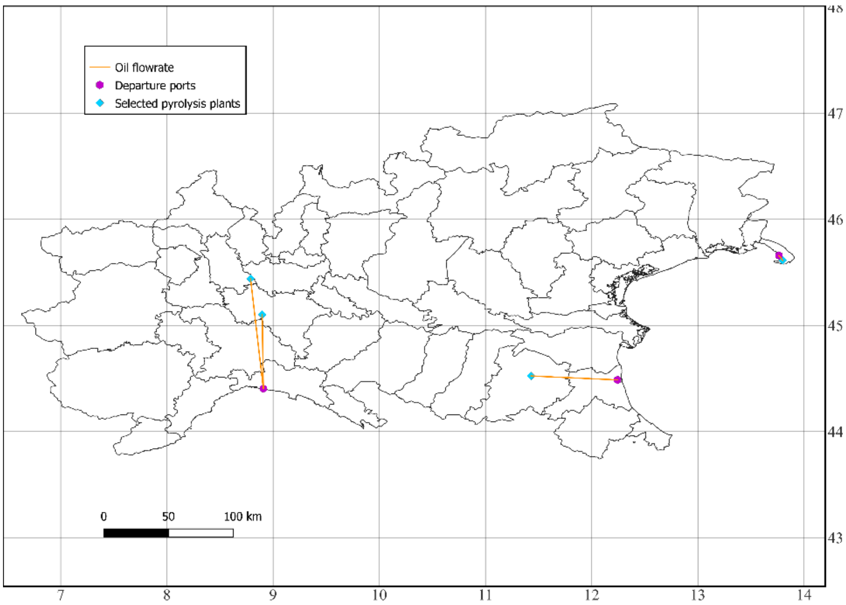


Figure 4.2: *Pyrolysis oil flowrate from pyrolysis plants to Northern Italian departure ports for economically optimized cracking scenario*

From Figures 4.1 and 4.2 it can be observed that the MPW treatment locations that are further away from the shores (consequently further away from the departure ports for oil shipping) commonly adopt incineration as a treatment technology (as in the case of Brescia location). Even though a pyrolysis plant can be selected in that treatment location, the solver opts for an incineration plant to avoid additional transport costs from the treatment plant to Northern Italian ports.

Finally, the pyrolysis oil is shipped to the Southern Italian ports located close to cracking plants, as shown in Figure 4.3.

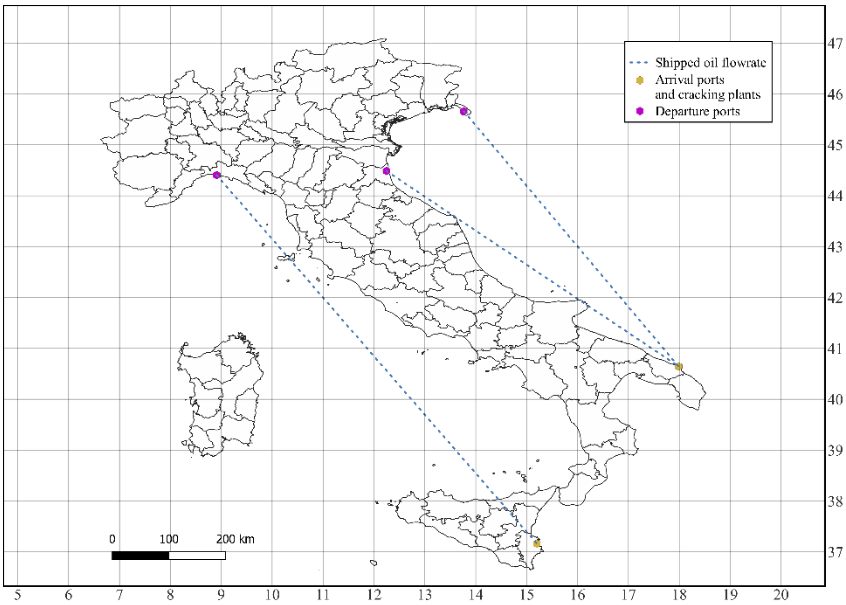


Figure 4.3: *Pyrolysis oil flowrate shipped from Northern Italian ports to Southern Italian ports located close to cracking plants for economically optimized cracking scenario*

Table 4.4 presents the cost and revenues breakdown for economic optimization of cracking scenario.

Table 4.4: *Costs and revenues breakdown for economically optimized cracking scenario*

Revenues			**Expenses**		
Source of profit	**Revenues [€/year]**	**Revenues [€/ktonne$_{PL}$]**	**Expenses**	**Costs [€/year]**	**Costs [€/ktonne$_{PL}$]**
Electricity	40.7 million	92675	**Transport costs**	25.6 million	58292
Naphtha	51.2 million	116584			
Recycled polymers	3.9 million	8880			
Treatment revenues	92.2 million	210000	**Landfill costs**	14.3 million	31878
			Treatment costs	70.5 million	160530
Tot revenues	188.1 million	428308	**Tot costs**	110.4 million	251383
Gross profit [€/year]			77.7 million		
Gross profit [€/ktonne$_{PL}$]			176925		

When cracking scenario is economically optimized, revenues are 25% higher than the economically optimized base case scenario, as summarized in Table 3.14. The observed increase in the total revenues of the supply chain is mainly due to selling both naphtha from pyrolysis and electricity from incineration. Even if the revenues from selling electricity drop about by 31% in the cracking scenario with respect to the base case scenario, the contribution of selling naphtha from pyrolysis plants has a considerable contribution. In addition, a small contribution to the total revenues is also due to selling the recyclable polymers from the overall pyrolysis plants.

However, also the total cost of the supply chain (i.e. 110.4 M€/year) is with about 45% higher with respect to the base case economic optimum (which entailed a total cost of about 76 M€/year), due to the presence of pyrolysis plants, a more expensive technology than incinerators (Cieno, 2021). The choice of pyrolysis as the treatment technology affects also the transport costs, that show an increase of about 33% with respect to the base case scenario, but also the landfill costs that doubles in the cracking scenario, compared to the base case scenario

Overall, the economic optimum for cracking scenario entails a Gross profit of 77.7 M€/year, slightly higher than the Gross profit of the economic optimum of base case scenario (i.e. 75.3 M€/year).

The GHG emissions breakdown is summarized in Table 4.5.

Table 4.5: *Emissions and avoided impacts breakdown for the economically optimized cracking scenario*

Emissions			**Avoided impacts**		
Source of emissions	**Emissions [ktonne$_{CO2eq}$/year]**	**Emissions [ktonne$_{CO2eq}$/ ktonne$_{PL}$]**	**Source of avoided impacts**	**Avoided impact [ktonne$_{CO2eq}$ /year]**	**Avoided impact [ktonne$_{CO2eq}$/ ktonne$_{PL}$]**
MPW treatment	263256	599.4	**Pyrolysis**	57.9	0.1
			Refineries	338.7	0.8
Transport	2396	5.5	**Incineration**	130.9	0.3
Sorting centres	25	0.06			
Tot emissions	265677	605.0	**Tot avoided impacts**	527.6	1.2
Net emissions [ktonne$_{CO2eq}$/year]				265149	
Net emissions [ktonnen$_{CO2eq}$/ktonne$_{PL}$]				603.8	

The environmental performance expressed in terms of the level of GHG emissions of the entire supply chain of the economic optimum of cracking scenario shows intermediate result between the economic and environmental optimum of the base case scenario, as already discussed in Chapter 3. Specifically, total direct GHG emissions of the MPW supply chain of the economic optimum in the case of cracking scenario is equal to 265677 ktonne$_{CO2eq}$/year:+40% with respect to the environmentally optimized base case scenario and -30% with respect to the economically optimized base case scenario. The main source of GHG emissions is MPW treatment. Emissions are unevenly distributed between incineration and pyrolysis, mainly being assigned to the first one, as shown in Table 4.6.

Table 4.6: *MPW treatment GHG emissions breakdown for the economically optimized cracking scenario*

Source of MPW treatment emissions	**Emissions [ktonne$_{CO2eq}$/year]**	**Emissions [kton$_{CO2eq}$/kton$_{PL}$]**
Pyrolysis	44	0.1
Incineration	263212	599.3

Avoided impacts, presented in Table 4.5, result to be quite large (528 ktonne of CO_2^{eq}/year) if compared to base case scenario economic optimum (190 ktonne of CO_2^{eq}/year). This is due to higher environmental credits from avoided refinery emissions, which are not necessary if the fossil naphtha that has to be refined in the cracking plants, is replaced with pyrolysis oil.

4.3.2 Environmental optimization results

Environmental optimization of cracking scenario differs from base case environmental optimum. Supply chain still prefers pyrolysis over other technologies, but final destination of pyrolysis oil is no more a refinery, like in the base case scenario, but a cracking plant.

Environmental performances are quantified in 186348 ktonne of CO_2^{eq}/year, which is a slightly lower value than base case environmental optimization (which is 186909 ktonne of CO_2^{eq}/year), entailing a Gross Profit of 45.8M€/year (+37% higher with respect to the already mentioned scenario).

The economic breakdown is shown in Table 4.9, whereas the environmental performances of the environmental optimum are presented in detail in Table 4.10.

The MPW supply chain configuration of the environmental optimum is shown in Figure 4.4 and Figure 4.5.

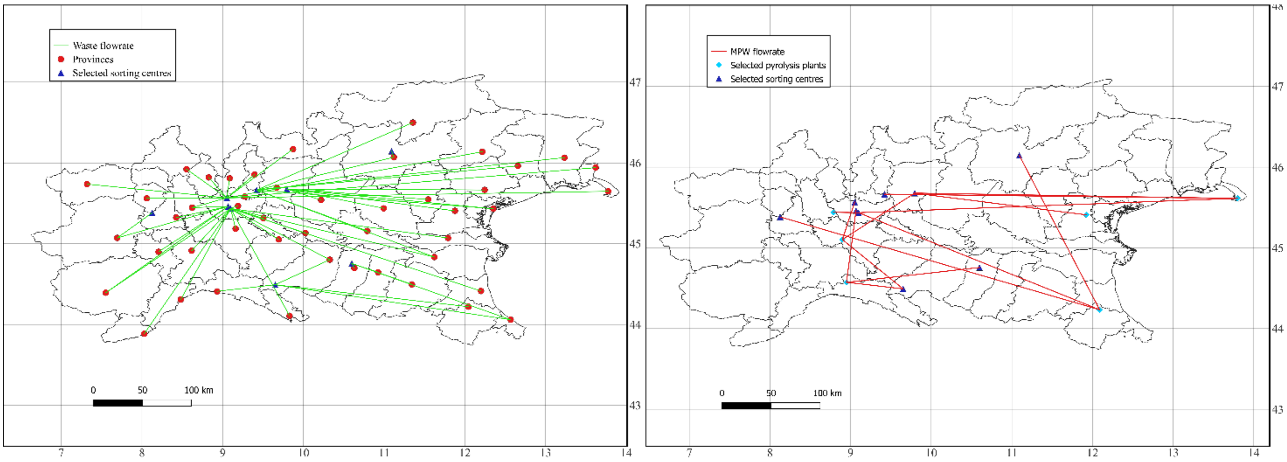
In Table 4.7 there are listed the selected sorting centres for environmentally optimized cracking scenario, and the supply chain configuration is presented in Figure 4.4: Figure 4.4(a) shows the plastic waste flowrates, collected by the provinces and sent to sorting centres for MPW recovery, while Figure 4.4(b) presents the selected treatment technologies, once MPW is separated, it must be treated according to one of the possible technologies. Finally Figure 4.5 and Figure 4.6 conclude MPW supply chain, showing the pyrolysis oil flowrates which is transported by truck to one Northern Italian port to be shipped to Southern Italy cracking plants.

Table 4.7: *Selected sorting centres for environmentally optimized cracking scenario and amount of waste received*

Selected sorting centre		Amount of waste received [ktonne/year]
Bedonia	PR	48.0
Cadelbosco di Sopra	RE	97.4
Lainate	MI	100.0
Milano	MI	45.0
Montello	BG	150.0
Verderio Inferiore	LC	97.0
Corsico	MI	250.0
Cavaglia	BI	45.0
Lavis	TN	10.6

Both Lainate and Verderio Inferiore sorting centres are occupied at full of their reported capacity. Therefore, like in the base case environmental optimization, this is a critical situation to monitor. Environmental optimized supply chain sees its sorting facilities preferentially fully occupied instead of dividing the plastic waste flowrate in more sorting centres.

Waste flowrate to sorting centres and successive distribution of MPW among treatment locations are shown in Figure 4.4.



(a) (b)

Figure 4.4: *Supply chain configuration of cracking scenario – environmental optimum: (a) Plastic waste flowrate from provinces to selected sorting centres, (b) MPW flowrate from selected sorting centres to treatment locations*

MPW flowrate is sent only to PO_PS_Pyrolysis plants, preferentially of large size, as shown in Table 4.8.

Table 4.8: *Selected MPW treatment facilities for the environmentally optimized cracking scenario*

Treatment location		**Typology**	**Size**	**Amount of MPW treated [ktonne/year]**
Forlì	FC	PO_PS_Pyrolysis	Large	78.8
Trieste	TS	PO_PS_Pyrolysis	Large	78.8
Padova	PD	PO_PS_Pyrolysis	Medium	44.7
Sannazzaro	PV	PO_PS_Pyrolysis	Large	78.8
Busalla	GE	PO_PS_Pyrolysis	Large	78.8
Trecate	NO	PO_PS_Pyrolysis	Large	78.8

Environmental results of cracking scenario do not differ much in terms of selected technologies from environmentally optimized base case scenario, whose treatment facilities are listed in Table 3.17. Once again, all pyrolysis plants belong to PO_PS_Pyrolysis technology, which is the least impactful, as explained in §3.4.2. The selected size is always the largest possible, except for one plant (Padova in this case), to allow to treat the remaining share of waste which was not possible to accommodate in other plants.

Transport GHG emissions, as shown in Table 4.10, represent a very small fraction of the overall GHG emissions, so large MPW movement towards plants located close to the Italian coast are tolerated.

Final stage of the MPW supply chain is the naval transportation from Northern Italian ports (Figure 4.5) to Southern Italian cracking ports (Figure 4.6).

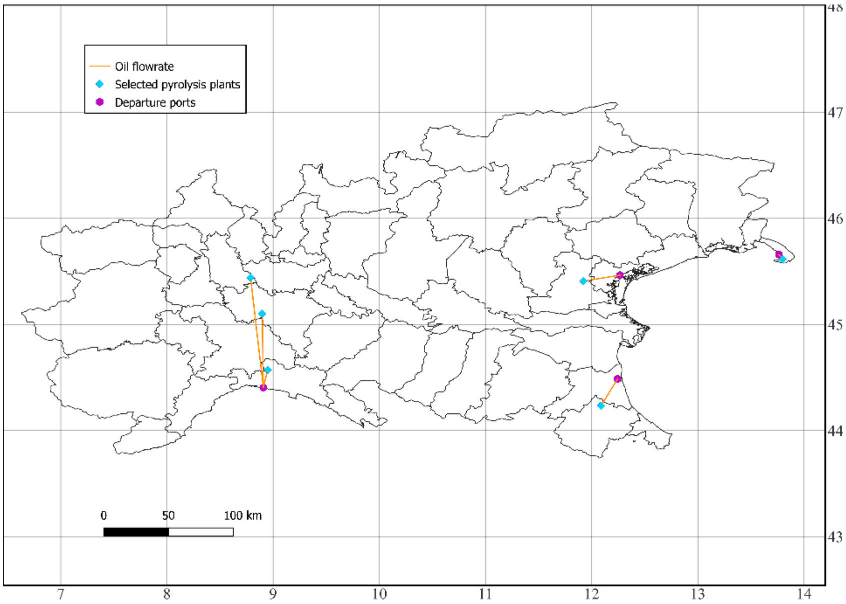


Figure 4.5: *Pyrolysis oil flowrate from pyrolysis plants to Northern Italian departure ports for environmentally optimized cracking scenario*

Supply chains selects treatment plants as close as possible to Northern Italian ports. At this point pyrolysis oil can be sent to cracking plants.

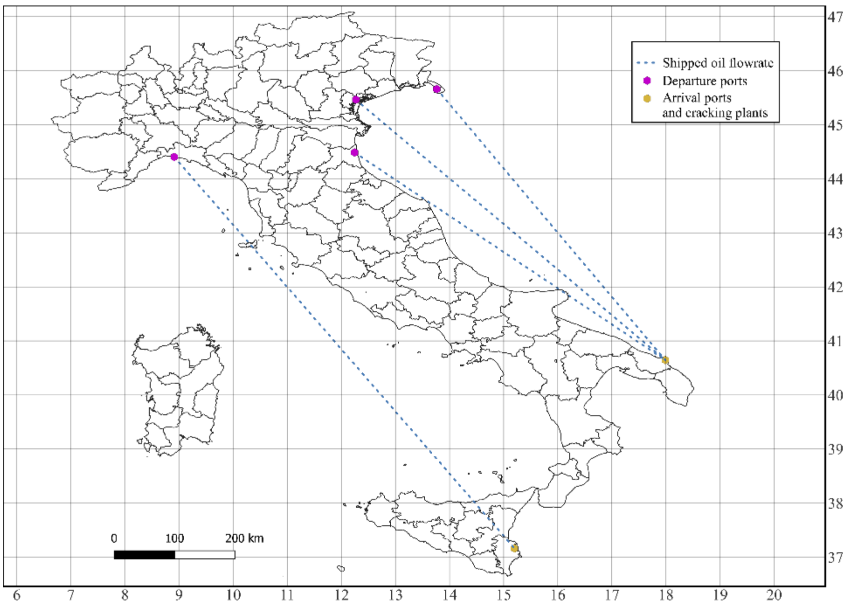


Figure 4.6: *Pyrolysis oil flowrate shipped from Northern Italian ports to Southern Italian ports located close to cracking plants for environmentally optimized cracking scenario*

In Table 4.9 is presented the economic breakdown of the cracking scenario environmental optimum.

Table 4.9: Costs and revenues breakdown for environmentally optimized cracking scenario

Revenues			**Expenses**		
Source of profit	**Revenues [€/year]**	**Revenues [€/ktonne$_{PL}$]**	**Expenses**	**Costs [€/year]**	**Costs [€/ktonne$_{PL}$]**
Electricity	28.6 million	65123	**Transport costs**	59.4 million	135255
Naphtha	84.6 million	192636			
Recycled polymers	6.5 million	14801	**Landfill costs**	19.1 million	43491
Treatment revenues	92.1 million	210000			
			Treatment costs	87.6 million	199467
Tot revenues	211.9 million	482501	**Tot costs**	166.1 million	378213
Gross profit [€/year]			45.8 million		
Gross profit [€/ktonne$_{PL}$]			104288		

Comparing economical results of the two optimum – economic and environmental – it is evident that both revenues and expenses are higher for the environmental optimization. Naphtha revenues are comparable to treatment revenues, which confirms the potential economic benefit of this scenario, adding an important diversification factor for incomes. On the other hand, all costs witness an increase from economic optimum of this scenario. Transportation costs are not irrelevant on the supply chain economy, proving that transportation has a different impact when it is seen from an environmental or an economic perspective. In fact, economic optimization preferentially minimizes transportation distances, whereas environmentally optimized supply chain allows for wider movement of the goods. When comparing the economic results of the two environmental optima, *i.e.* of the base case and of the cracking scenario, it is immediately evident the larger profit from selling pyrolysis oil as naphtha rather than as crude oil substitute, leading to almost a 20% increase in incomes. However, also transportation costs are subjected to an increase of 45% due to the additional naval costs.
Overall Gross Profit is estimated in 45.8 M€/year, which is an intermediate value between economical optima of both scenarios, about 40% less, and Gross Profit of environmentally optimized base case scenario, compared to which is almost 40% more.

Table 4.10 presents the GHG emissions breakdown for cracking scenario environmental optimum.

Table 4.10: *Emissions and avoided impacts breakdown for the environmentally optimized cracking scenario*

Emissions			**Avoided impacts**		
Source of emissions	**Emissions [ktonne$_{CO2eq}$/year]**	**Emissions [ktonne$_{CO2eq}$/ ktonne$_{PL}$]**	**Source of avoided impacts**	**Avoided impact [ktonne$_{CO2eq}$ /year]**	**Avoided impact [ktonne$_{CO2eq}$/ ktonne$_{PL}$]**
MPW treatment	185118	421.5	**Pyrolysis**	95.9	0.2
			Refineries	560.4	1.3
Transport	1950	4.4	**Incineration**	92.0	0.2
Sorting centres	29	0.07			
Tot emissions	187097	426.0	**Tot avoided impacts**	748.3	1.7
Net emissions [ktonne$_{CO2eq}$/year]			186348		
Net emissions [ktonnen$_{CO2eq}$/ktonne$_{PL}$]			424.3		

Environmentally optimized cracking scenario shows the smallest amount of net GHG emissions of all scenarios. The direct GHG emissions of cracking scenario economic optimum, estimated in 187097 ktonne of CO_2^{eq}/year, are exactly the same of the environmentally optimized base case scenario (even though supply chain differs in some selections), but avoided impacts are higher, for the environmental credit for not refining crude oil (748 ktonne of CO_2^{eq}/year compared to 188 ktonne of CO_2^{eq}/year).

4.4 Chapter conclusions

The cracking scenario considers a modification for MPW supply chain with respect to the base case scenario. Whenever MPW is sent to pyrolysis treatment facilities, then the pyrolysis oil is not sent to oil refineries as a crude oil substitute, but it is sold to cracking plants as a fossil naphtha replacement. The reason for considering an alternative scenario is given, from the economic standpoint, by the attractive naphtha selling price, which is higher compared to crude oil selling prices. Moreover, this is a fortunate alternative also from the environmental point of view because it avoids some oil refinement GHG emissions.

Both economic and environmental optimizations show better results when compared to base case scenario: Gross Profit of economic optimum is higher for the cracking scenario (77.7 M€/year compared to 75.3 M€/year), and also GHG net emissions are lower for the cracking scenario environmental optimum (186348 ktonne of CO_2^{eq}/year compared to 186909 ktonne of CO_2^{eq}/year of base case scenario).

However, the most significant result of cracking scenario is trying to match economic and environmental demands. Economic optimization leads to the best Gross Profit of the two scenarios, and in addition to that, net GHG emissions are 30% lower than base case economic optimum (265149 ktonne of CO_2^{eq}/year compared to 384221 ktonne of CO_2^{eq}/year).

Likewise, cracking scenario environmental optimization, apart from granting the lowest net GHG emissions of both scenarios, is more economically attractive than base case environmental optimization. Gross Profit is almost 40% higher (45.8 M€/year compared to 33.4 M€/year of the base case environmental optimum).

In conclusion, two possible trade-offs are possible developing the cracking scenario. If economic optimum is chosen, then the highest Gross Profit is achieved, emitting however 40% more of GHG compared to the best economic alternative. If, instead, the environmental optimum is chosen, then the GHG emissions are the lowest possible, but Gross Profit is estimated to be 40% less compared to the most attractive economic solution.

Conclusions

This Master's thesis focused on possible solutions for the Mixed Plastic Waste (MPW) end-of-life. Alternative options to landfilling were considered: MPW incineration, gasification and pyrolysis. All these alternatives were analysed from the environmental perspective, quantifying the net GHG emissions (expressed as the difference between direct GHG emissions and avoided GHG emissions) of the entire supply chain, which includes also sorting centres facilities and transportation. Gasification of MPW was never an option, because both environmentally and economically unsustainable.

Two scenarios were proposed: the first one is the base case scenario, which considers that, whenever MPW is treated in a pyrolysis plant, then the pyrolysis oil is sent to an oil refinery to become a crude oil substitution. The alternative scenario was defined as cracking scenario, because pyrolysis oil is meant to be a fossil naphtha substitution for cracking plants located in Southern Italy, where it is transported by ship.

The objective was to find the environmental optimum for MPW supply chain in Northern Italy, namely the configuration of typology and locations of treatment plants allowing for the lowest net GHG emissions. The supply chain optimization was formulated as a mixed integer linear programming (MILP) model. The environmental optimum was then compared to the economically optimized configuration of the supply chain.

The economic and environmental optima for the base case scenario resulted to be represented by very different configurations. If the supply chain was economically optimized, then Gross Profit, defined as the difference between the supply chain revenues and costs, was quite high (75.3 M€/year), but all the selected MPW treatment plants were incinerators, which is the most environmentally impactful technology, leading to 384221 ktonne of CO_2^{eq}/year. When the base case was optimized environmentally, the situation was the reverse: net GHG emissions were low, estimated in 186909 ktonne of CO_2^{eq}/year, due to the selection of only pyrolysis plants (the least environmentally impactful technology), but also Gross Profit was substantially lower than economic optimum, quantified in 33.4 M€/year.

The cracking scenario led to a different situation. The economic and environmental optimizations were closer to each other in terms of Gross Profit and net GHG emissions. Economic optimum led to a Gross Profit estimated in 77.7 M€/year, the highest of both scenarios, and to net GHG emissions quantified in 265149 ktonne of CO_2^{eq}/year, 30% less than the GHG emissions relative to the economically optimized base case scenario. The economic optimum selected a mixed solutions for

MPW treatments, composed of 4 pyrolysis plants and 2 incineration plants. On the other hand, when the cracking scenario was optimized environmentally, the supply chain is once again based on pyrolysis plants only. The Gross Profit results to be 45.8 M€/year, an intermediate value between the environmentally optimized base case scenario and the economic optima of both scenarios. For what concerns net GHG emissions, the cracking scenario environmental optimum leads to the smallest emissions, quantified in 186348 ktonne of CO_2^{eq}/year.
The base case optimization results show that economic and environmental interests are difficult to reconcile. Environmental optimum is obtained against environmental objectives, and vice versa.
On the other hand, the development of an alternative scenario which considers pyrolysis oil as fossil naphtha substitution for cracking plants, leads to possible trade-offs. It is possible to decide whether to give more importance to economic or environmental perspective, but it is always convenient to exploit pyrolysis technology in some extent, which becomes a crucial stage in the MPW supply chain.
It is important to underline that the largest part of the GHG emissions even when pyrolysis plants are chosen, derives from the incineration of the remaining share of MPW which cannot be pyrolyzed. It could be a good environmental strategy to investigate other possible uses for this plastic fraction, which has a variable polymers composition.
In the Appendix a sensitivity analysis can be found, where the electricity selling price was varied. It was observed that if the electricity market price gets low enough, than pyrolysis might become an attractive option, even when gross profit is maximised.
One limitation of this Master's thesis is related to the fact that the investigation only focuses on the Northern Italian MPW supply chain. Enlarging the geographical boundaries of this study would allow to create a more complete and efficient supply chain, to which all Italian regions can contribute. An evidence is given by the selection of Southern Italian cracking plants.
Furthermore, it should be noted the optimisation results depend on several parameters, such as MPW composition (which is various for its own nature), or sorting efficiency, which represent the specific features of the supply chain being analysed and the available data. The effect of changes in such data should be assessed for a more comprehensive representation of optimal configurations. Price fluctuations, too, could determine substantial differences in the supply chain configuration, and this should be accounted for, e.g. via tailored sensitivity analyses.
Finally, the cracking scenario is based on data and assumptions concerning a non-mature technology; this means that some uncertainty will affect the reliability of results.

Appendix

Sensitivity analysis – change in electricity selling price

Chapters 3 and 4 analysed MPW supply chain for base case and cracking scenario respectively, leading to different results that were previously discussed.
However, both scenarios are strongly influenced by some parameters whose values are extremely volatile. It is the case of the selling prices of hydrocarbons (oil, naphtha) and electricity, which determine the preference of a technology over another.
In this Appendix a sensitivity analysis is performed on the electricity selling price. The aim is to identify how the electricity selling price influences the optimal design of MPW supply chains in terms of maximising the economic performance (i.e. the gross profit).

A.1 Statement of the problem

As discussed in §3.4, one important input data for MPW supply chain economic optimization is the electricity selling price. This parameter is crucial to estimate the supply chain economic performances.
Incineration and gasification technologies for MPW treatment allow to generate electric energy, exploiting the heat released by burning MPW or from MPW gasification. The electricity produced can consequentially be sold to the National electricity network, acting as a supply chain income.
Gasification plants are never considered in this Master's thesis, because nor economically nor environmentally competitive, due to too high costs and high GHG emissions. However, incineration plants are the most economically attractive solution for MPW treatment, because of relatively low fixed and operational costs (Cieno, 2021). On the other hand, burning MPW generates a massive amount of GHG emissions, when compared to pyrolysis plants, which are, on the other hand, the most environmentally sustainable choice. With low costs and high revenues from selling electricity, economic optimum always indicates incineration as the selected MPW treatment technology. However, electricity selling prices are susceptible to fluctuations. For instance, from ARERA (2022) data, 2021 electricity selling prices for Italian market witnessed an almost four-times increase from

January (60 €/MWh) to December (280 €/MWh), and from these 2021 values have been retrieved an average selling price of 124989 €/GWh.
If electricity prices drop again, and at the same time revenues from pyrolysis technology remain high enough, *i.e.* pyrolysis oil sold as crude oil for base case scenario and as fossil naphtha replacement for cracking plants in the cracking scenario, then pyrolysis becomes an economically interesting option, in addition to the fact that it is the environmentally preferred MPW treatment technology.
Based on these considerations, a sensitivity analysis is performed varying the electricity selling price, from the actual value (124989 €/GWh) down to its 40% (49995.6 €/GWh), which is a quite close value to the one reported by Cieno (2021), according to 2020 electricity selling prices, estimated in 52346 €/GWh.
All other economic data inputs are kept constant, in particular oil selling prices (551274 €/ktonne for PO_Pyrolysis plants and 402743 €/ktonne for PO_PS_Pyrolysis plants), representing the main revenues that distinguishes the pyrolysis from other technologies in the base case scenario, and naphtha selling price (632052 €/ktonne) which is the most relevant revenue in the cracking scenario from pyrolysis.
Sensitivity analysis impacts only economic optimum, since no environmental data are changed.
The reason for that is to investigate under what circumstances economic and environmental objectives match.

A.2 Sensitivity analysis for electricity selling price - base case economic optimum

Base case scenario economic optimization, as discussed in §3.4.1, leads to the selection of incineration plants for MPW treatment, while pyrolysis plants are not present into the MPW SC configuration.
The sensitivity analysis performed on this scenario considers fixed all the economic parameters except for the electricity selling prices, which is lowered from 2021 average value (124989 €/GWh) down to its 40% (49995.6 €/GWh).
The decision variables that are tracked are: MPW treatment plants selected – technology and their number (Figure A.2, Tables A.1-A.3), gross profit of the supply chain (Figure A.1) The changes in the net GHG emissions is also discussed (Figure A.3).

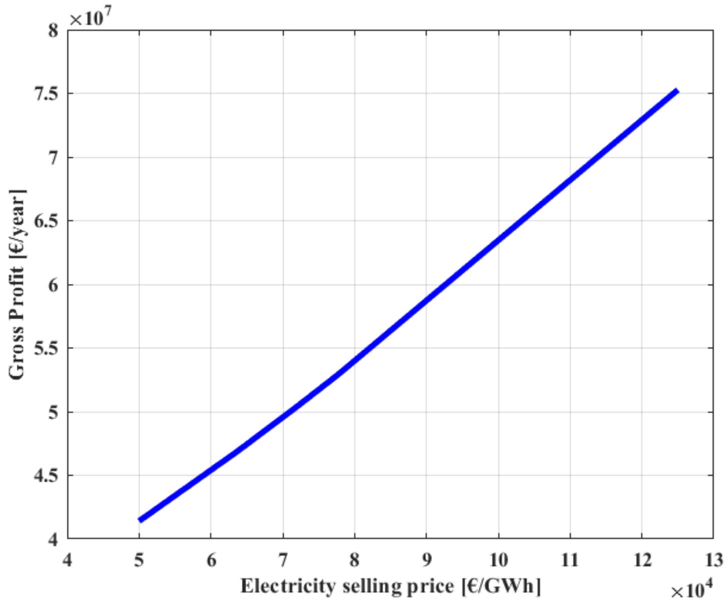


Figure A.1: *Change in Gross Profit for the economically optimized base case scenario when changing electricity selling price*

Gross Profit decreases almost linearly when electricity selling price is lowered, stepping from 75.3 M€/year to 41.4 M€/year, a decrease of about 45 %, suggesting that the drop in electricity cost is not compensated by any another supply chain revenue.

In Figure A.2(a) it is shown the thresholds of the electricity price which allows to step from one number of pyrolysis plants (zero at the beginning, for base case scenario) to another, while Figure A.2(b) shows the whole number of MPW treatment plants in the entire supply chain.

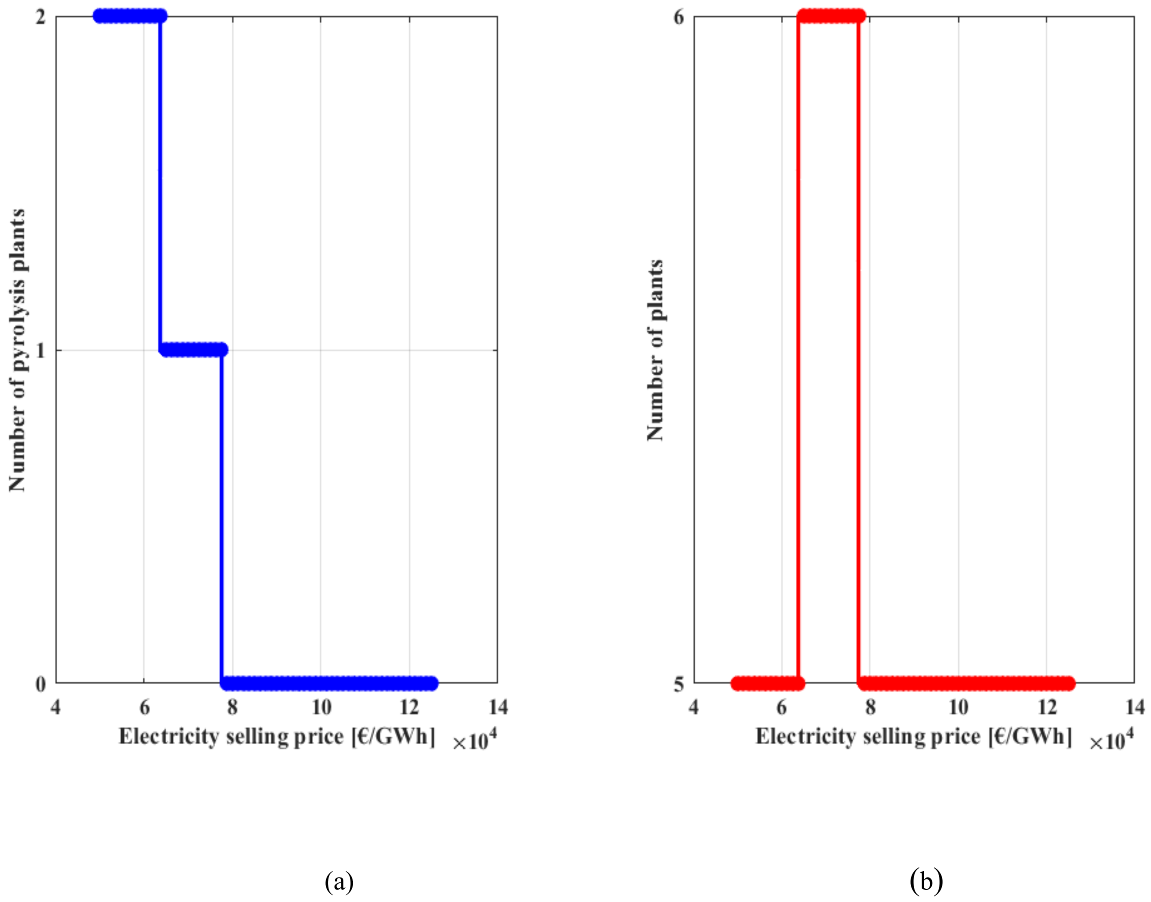


Figure A.2: *Economically optimized base case scenario change in MPW treatment plants: number of pyrolysis plants (a) chosen by supply chain and total number of treatment plants (b) in the supply chain*

Only when electricity selling price decreases by 38% with respect to its initial value, reaching the market price of 77500€/GWh, then supply chain finds economically advantageous to insert the first pyrolysis plant. This first plant, as it is shown in Figure A.3(b), does not initially substitute an incineration plant, but is added to the previous ones.

An actual substitution is operated as the electricity selling price is lowered to 49% of its initial value, down to 63750 €/GWh. At this point another pyrolysis plant is added and one incineration plant is eliminated from the supply chain.

By further lowering the electricity selling price until it reaches the lowest value considered in this analysis, no other changes are observed in the supply chain configuration.

Tables A.1-A.3 list the changes in the number and typology of MPW treatment plants when sensitivity analysis is carried out, then reference scenario is the situation reported in Table 3.12.

Table A.1: *Change in typology and number of MPW treatment plants when electricity selling price is lowered of 38% of its initial value*

Treatment location		**Technology**	**Amount of MPW treated [ktonne/year]**
Trieste	TS	Incineration	38.8
Brescia	BS	Incineration	209.6
Torino	TO	Incineration	39.1
Milano	MI	Incineration	68.4
Granarolo	BO	Incineration	13.5
Trecate	NO	PO_Pyrolysis	72.8

Comparing Table 3.12 and Table A.1, the only difference is an additional PO_Pyrolysis plant of large size in Trecate (NO), which is a pyrolysis plant coupled with and oil refinery. Some MPW flowrate is subtracted from Milano and Torino incineration plants and sent to Trecate, where MPW is turned into pyrolysis oil and refined in the same location to become a crude oil substitution. Pyrolysis plant belongs to PO_Pyrolysis technology, which is more economically sustainable solution than PO_PS_Pyrolysis technology, but it is also more environmentally impactful, as explained in §2.6.

There is also an intermediate step, shown in Table A.2, which does not lead to any modification in number or typology of MPW treatment plants, but only changes in the flowrates are observed, such as a lower flowrate sent to Milano incineration plant (from 68.4 ktonne of MPW/year to 37.2 ktonne of MPW/year). This flowrate is instead directed to Trecate pyrolysis plant (from 72.8 tonne of MPW/year to 104.0 ktonne of MPW/year). This modification occurs when electricity selling price was decreased by 42% with respect to its initial value, and equals 72000 €/GWh.

Table A.2: *Change in typology and number of MPW treatment plants when electricity selling price is lowered of 42% of its initial value*

Treatment location		**Technology**	**Amount of MPW treated [ktonne/year]**
Trieste	TS	Incineration	38.8
Brescia	BS	Incineration	209.6
Torino	TO	Incineration	39.1
Milano	MI	Incineration	37.2
Granarolo	BO	Incineration	13.5
Trecate	NO	PO_Pyrolysis	104.0

__Table A.3:__ Change in typology and number of MPW treatment plants when electricity selling price is lowered of 49% of its initial value

Treatment location		Technology	Amount of MPW treated [ktonne/year]
Trieste	TS	Incineration	38.8
Brescia	BS	Incineration	206.4
Torino	TO	Incineration	39.1
Trecate	NO	PO_Pyrolysis	82.1
Sannazzaro	PV	PO_Pyrolysis	72.8

By further lowering the electricity selling price by 49% of its initial value, some important modification in the MPW treatment supply chain is observed. The number of pyrolysis plants selected become two replacing two incineration plants (Torino and Granarolo). Also in this case, the additional pyrolysis plant (Sannazzaro) is a large PO_Pyrolysis plant located in proximity of an oil refinery.

Therefore, after changing electricity selling price, some modifications in the MPW treatment supply chain are possible. Less incineration plants and more pyrolysis plants appear, and this leads to a drop in GHG emissions, shown in Figure A.3.

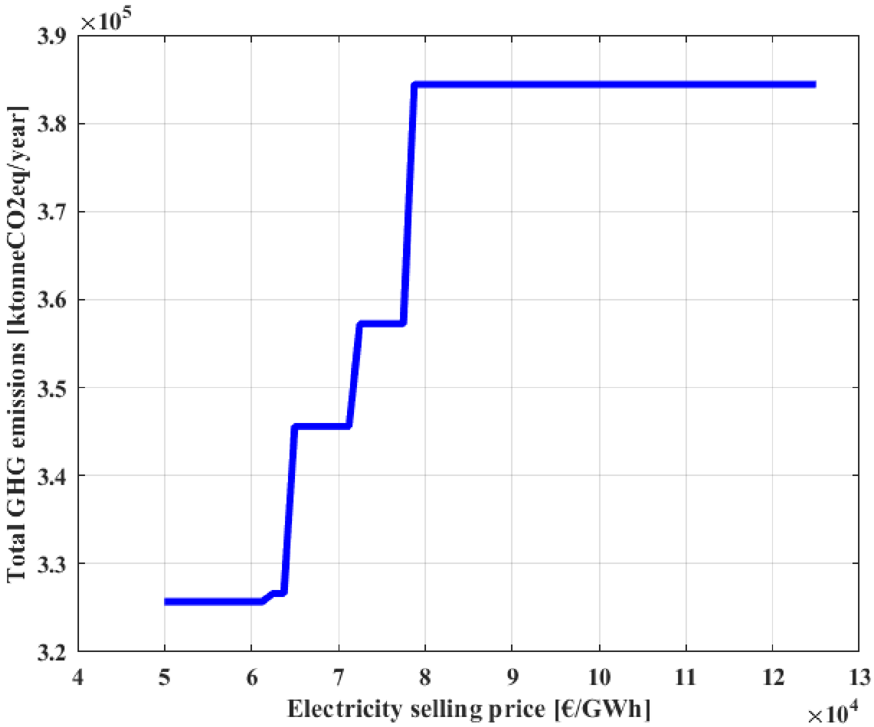


__Figure A.3:__ Change in supply chain total GHG emissions for economically optimized base case scenario when changing electricity selling price

As expected, some improvements in terms of GHG emissions are observed when lowering the electricity selling price, due to the selection of pyrolysis plants for MPW treatment. However, the GHG emissions of the entire supply chain when two pyrolysis plants (Trecate and Sannazzaro)

substitute two incineration plants (Granarolo and Milano) are only 15% less with respect to the initial case, stepping from 384411 ktonne of CO_2^{eq}/year to 325704 ktonne of CO_2^{eq}/year.
The reason for such a small change in GHG emissions is mostly due to the selection of PO_Pyrolysis plants, which are the most environmentally impactful, and also because the largest part (almost 65%) of MPW is still treated in incineration plants even when electricity price is lowered down to its minimum value.

A.3 Sensitivity analysis for electricity selling price – cracking scenario economic optimum

The sensitivity analysis is repeated also for the cracking scenario, changing the electricity selling price down to the 40% of its initial value, from 124989 €/GWh to 49995.6 €/GWh.
In this scenario, when pyrolysis plants are chosen by the supply chain, pyrolysis oil is treated as a fossil naphtha substitute. Therefore, the economic competition for supply chain revenues is between selling electricity obtained from incineration plants, and selling naphtha substitute, *i.e.* pyrolysis oil. If selling electricity becomes less attractive, then pyrolysis is a valuable economic option, with consequent benefits also from the environmental point of view.
Changes in Gross Profit for economically optimized cracking scenario (Figure A.4) and number and typology of MPW treatment plants chosen (Figure A.5, Tables A.4-A.8) will be tracked when decreasing electricity price. Finally, also change in total GHG emissions is followed as sensitivity analysis is developed (Figure A.6).

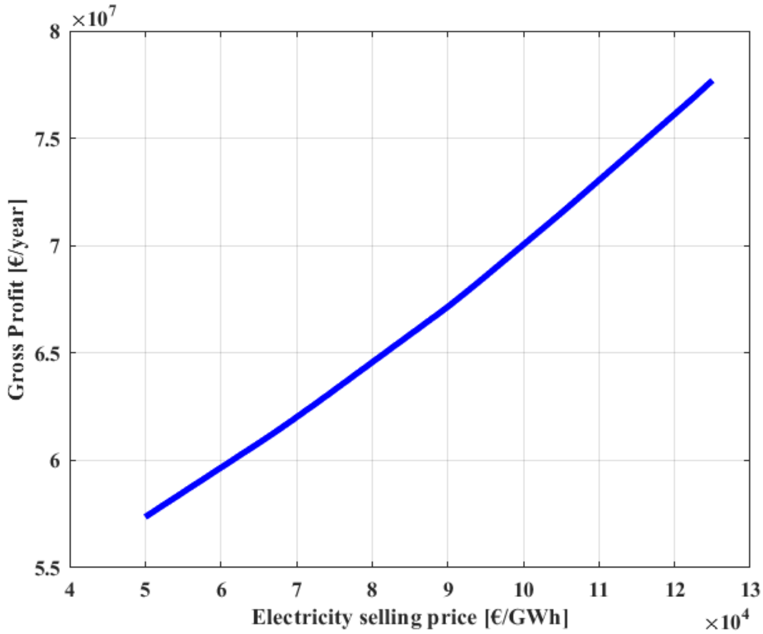


Figure A.4: *Change in Gross Profit for the economically optimized cracking scenario when changing electricity selling price*

Also for cracking scenario, Gross Profit changes almost linearly as electricity selling price decreases. If for base case Gross Profit witnessed a decrease of 45%, this time the drop is more restrained, a decrease of about 25% with respect to the initial value is observed, from 77.7 M€/year to 57.4 M€/year. This means that alternative configurations of the supply chain can be found in order to limit the losses due to drop in electricity selling price, finding alternative sources of revenues, which in this case is selling pyrolysis oil as fossil naphtha.

In Figure A.5 (a) and (b) it is shown how the number of pyrolysis plants and the total number of MPW treatment plants vary when changing the electricity selling price.

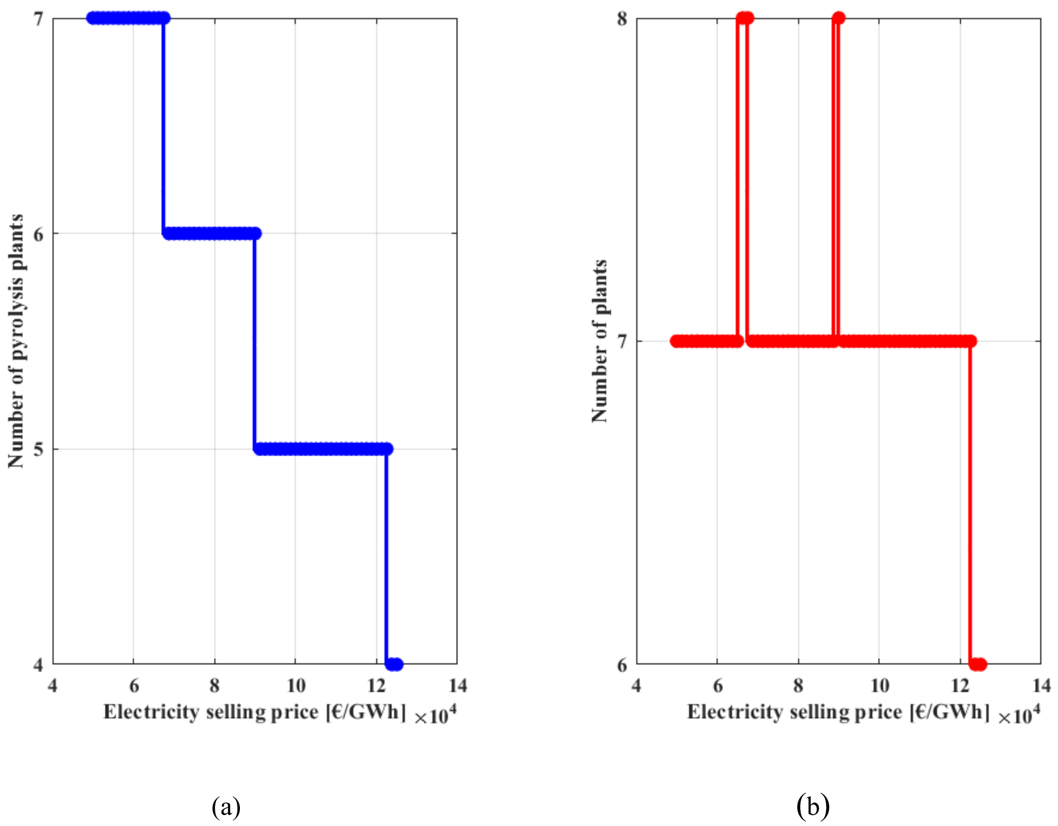


Figure A.5: *Economically optimized cracking scenario change in MPW treatment plants: number of pyrolysis plants (a) chosen by supply chain and total number of treatment plants (b) in the supply chain*

The results presented in Table 4.3 are taken as the reference, and they show the technology type for MPW treatment and their number, before performing any sensitivity analysis. They include 4 pyrolysis plants and 2 incineration plants. A first change in the supply chain configuration is observed when the electricity selling price was decreased by 2% (from 1249898 €/GWh to 122490 €/GWh): one pyrolysis plant is selected, and the total number of treatment plants rise to 7.

When electricity selling price is lowered by 28% with respect to its initial value, reaching a value of 89990€/GWh, another pyrolysis plant is added to the supply chain. Therefore, the number of pyrolysis plants becomes 6 and the total number of plants are 8. However, this situation is rapidly overcome, because when electricity price reaches 88740 €/GWh, namely the 29% of the initial market price, the total number of treatment plants returns to be 7.

An analogue situation is repeated when electricity selling price reaches the value of 67495 €/GWh, namely the 46% of its initial value: one pyrolysis plants is added to the other treatment plants, so that the number of pyrolysis plants become 7 and the total number of plants becomes 8. After a small further change in electricity price, reaching the value of 64995 €/GWh (48% less of the initial electricity market price), supply chain consists of only pyrolysis plants and no incineration plants are left.

This is a more dynamic scenario with respect to the base case sensitivity analysis. In fact, not only the number and typology of plants is continuously changing when electricity price goes down, but also the flowrates of MPW treated by each plant changes. For sake of simplicity, it is reported the cases when there is some actual modification to the supply chain treatment plants, *i.e.* when a plant is added or removed. The frequent changes in MPW flowrate treated by each plant are anyway visible in Figure A.6, which shows how supply chain GHG emissions are affected by the change in electricity selling price.

Table A.4: *Change in typology and number of MPW treatment plants when electricity selling price is lowered of 2% of its initial value*

Treatment location		**Technology**	**Amount of MPW treated [ktonne/year]**
Torino	TO	Incineration	39.1
Brescia	BS	Incineration	102.3
Sannazzaro	PV	PO_PS_Pyrolysis	55.2
Trecate	NO	PO_PS_Pyrolysis	77.2
Granarolo	BO	PO_PS_Pyrolysis	55.2
Trieste	TS	PO_PS_Pyrolysis	55.2
Busalla	GE	PO_PS_Pyrolysis	55.2

The first pyrolysis plant which is added to the initial configuration is Busalla plant, which is a pyrolysis plant very close to the Genoa port, so that pyrolysis oil can immediately be shipped to a cracking plant.

Table A.5: *Change in typology and number of MPW treatment plants when electricity selling price is lowered of 28% of its initial value*

Treatment location		Technology	Amount of MPW treated [ktonne/year]
Torino	TO	Incineration	6.8
Brescia	BS	Incineration	54.0
Sannazzaro	PV	PO_PS_Pyrolysis	78.8
Trecate	NO	PO_PS_Pyrolysis	78.8
Trieste	TS	PO_PS_Pyrolysis	55.3
Busalla	GE	PO_PS_Pyrolysis	55.2
Modena	MO	PO_PS_Pyrolysis	55.2
Cassana	FE	PO_PS_Pyrolysis	55.2

When electricity price decreases by 28% compared to its initial price, supply chain finds convenient to replace Granarolo pyrolysis plants with two new pyrolysis plants, located close to the previous one, Modena and Cassana. At the same time, MPW flowrate treated by incineration plants decreases more and more.

Table A.6: *Change in typology and number of MPW treatment plants when electricity selling price is lowered of 29% of its initial value*

Treatment location		Technology	Amount of MPW treated [ktonne/year]
Brescia	BS	Incineration	54.0
Sannazzaro	PV	PO_PS_Pyrolysis	78.8
Trecate	NO	PO_PS_Pyrolysis	78.8
Trieste	TS	PO_PS_Pyrolysis	55.3
Busalla	GE	PO_PS_Pyrolysis	61.9
Modena	MO	PO_PS_Pyrolysis	55.2
Cassana	FE	PO_PS_Pyrolysis	55.2

When electricity selling price decreases even more (29% less than its initial price), Torino incineration plants is removed from the supply chain, and all its MPW flowrate is moved South and treated in the pyrolysis plant of Busalla. Only Brescia, which is located in the middle of Northern Italy and far away from ports, remains as an incineration facility.

Table A.7: *Change in typology and number of MPW treatment plants when electricity selling price is lowered of 46% of its initial value*

Treatment location		Technology	Amount of MPW treated [ktonne/year]
Brescia	BS	Incineration	15.3
Sannazzaro	PV	PO_PS_Pyrolysis	69.3
Trecate	NO	PO_PS_Pyrolysis	78.8
Trieste	TS	PO_PS_Pyrolysis	55.2
Busalla	GE	PO_PS_Pyrolysis	55.2
Modena	MO	PO_PS_Pyrolysis	55.2
Cassana	FE	PO_PS_Pyrolysis	55.2
Bergamo	BG	PO_PS_Pyrolysis	55.2

As electricity price continues to decrease (46% less of its initial price), Brescia MPW flowrate is almost totally transferred to an additional pyrolysis plant, which is located in Bergamo. Only a small amount of MPW is left to incineration.

Table A.8: *Change in typology and number of MPW treatment plants when electricity selling price is lowered of 48% of its initial value*

Treatment location		Technology	Amount of MPW treated [ktonne/year]
Brescia	BS	PO_PS_Pyrolysis	55.2
Sannazzaro	PV	PO_PS_Pyrolysis	78.8
Trecate	NO	PO_PS_Pyrolysis	78.8
Trieste	TS	PO_PS_Pyrolysis	55.3
Busalla	GE	PO_PS_Pyrolysis	60.8
Modena	MO	PO_PS_Pyrolysis	55.2
Cassana	FE	PO_PS_Pyrolysis	55.2

Final configuration of supply chain is reached when electricity market price is lowered of 48% compared to its initial value. Only PO_PS_Pyrolysis plants are selected. Brescia incineration plants has turned into a pyrolysis plants, and consequentially Bergamo plant is removed.

As anticipated, also changes in supply chain GHG emissions are shown in Figure A.6.

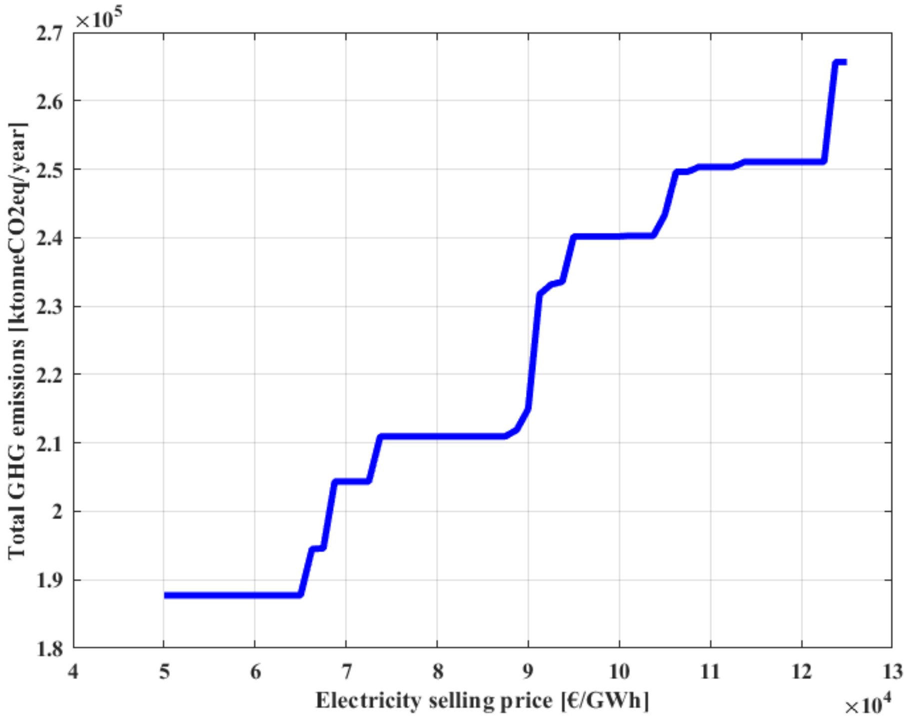


Figure A.6: *Change in supply chain total GHG emissions for economically optimized cracking scenario when changing electricity selling price*

GHG net emissions witness a substantial drop as electricity price decreases, stepping from 265677 ktonne of CO_2^{eq}/year in the initial configuration, *i.e.* the cracking scenario economic optimum when electricity price reported is the 2021 average value, to 187735 ktonne of CO_2^{eq}/year at the end of sensitivity analysis, meaning a decrease of 30% in the GHG emissions. The final configuration is reached before that electricity selling price drops by 40%. Only pyrolysis plants are chosen when electricity price is 48% less than its initial market value, *i.e.* 64995 €/GWh.

A.4 Sensitivity analysis conclusions

A sensitivity analysis concerning the economic optimization of both base case and cracking scenario was performed. The economic parameter that has been changed is the electricity selling price, analysing the consequences over the supply chain when it is decreased down to 40% of its initial value.

Base case scenario economic optimum is negatively affected by the drop in electricity market price, as Gross Profit decreases by 45%, from 75.3 M€/year to 41.4 M€/year, and no substantial benefit is reported from the environmental point of view, because GHG emissions decrease only by 15%, stepping from 384411 ktonne of CO_2^{eq}/year to 325704 ktonne of CO_2^{eq}/year.

Cracking scenario is instead more resilient to drop in electricity price, because Gross Profit changes only by 25%, from 77.7 M€/year to 57.4 M€/year, whereas GHG emissions drop by 30%, from

265677 ktonne of CO_2^{eq}/year to 187735 ktonne of CO_2^{eq}/year, which is very close to 186348 ktonne of CO_2^{eq}/year, the GHG emissions registered for the cracking scenario environmental optimum. Therefore, the cracking scenario might obtain some advantages from a decrease in electricity selling price: Gross Profit losses are restrained, but it allows to save a lot of GHG emissions, so that economic and environmental optima come to an agreement.

The major drawback of these results, especially for the cracking scenario, is that supply chain is very sensitive to electricity selling price, and its optimum configurations might change significantly if the electricity price fluctuates. It could be a good option to maintain flexible the supply chain number and typology of treatment plants even if the electricity market price is sufficiently low, not excluding *a priori* that a share of MPW might be treated in an incineration plant to preserve economic advantages.

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