

Development of New Sustainable Solvent and Antisolvent Systems for HDPE Recycling

Dissolution and Precipitation

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Declaration

I, Sofia Canteiro Aparício, student number 93488 of Instituto Superior Técnico, declare that this master thesis is the original work of my authorship, and it follows the requirements of the conduct code and good practices of the Universidade de Lisboa and of Instituto Superior Técnico.

Abstract

Plastic waste has been a topic of increasing interest in recent years, and the recycling technologies available are still far from reaching the required capacity. We are at a point that the end-product quality will dictate the real shift to a circular plastic economy. Polyolefins are one of the most abundant plastics, but their recycling faces various difficulties. This work focused on the recycling of HDPE through the dissolution-precipitation method. Although a few works have been published on this topic, there is an urgent need to use greener solvents and minimize energy usage for this kind of process so that it becomes a viable alternative for the years to come.

Several natural terpenes were screened based on COSMO-RS predictions for HDPE solubility, from which four were selected to carry out the experimental work: limonene, α -pinene, p-cymene, and squalane. Even though squalane showed little capacity for dissolving HDPE, the remaining solvents were suitable for the process. The dissolution and precipitation conditions were optimized based on the results for limonene, being fixed at 3wt%, 10 min at 110°C, and antisolvent/solvent ratio of (2/1). Comparing HDPE and solvent recoveries for the various solvents, the best results were obtained for α -pinene as solvent and ethanol as antisolvent. The recovered samples were analyzed through various techniques, showing little modifications between the recycled and the pristine materials.

The scale-up of the process and the solvent reuse were also investigated, as well as the separation of HDPE and PET, and the possibility of using the same solvent/antisolvent system for recovering PP.

Keywords: Polymer recycling, Physical recycling, HDPE, COSMO-RS, Green solvents

Resumo

Os resíduos plásticos e o seu tratamento em fim de vida são um dos grandes problemas dos dias de hoje. Urgem melhorias na capacidade de reciclagem instalada e na qualidade dos produtos reciclados, que ditarão a mudança para uma economia circular. Em particular, a reciclagem de poliolefinas, uma das categorias mais abundantes de polímeros, é ainda limitada. Neste trabalho, estudou-se a reciclagem de HDPE por dissolução-precipitação. Apesar de existirem estudos anteriores neste âmbito, é necessário tornar o processo mais verde, quer através da escolha de solventes, quer minimizando o consumo energético.

A solubilidade do HDPE em vários terpenos de origem natural foi prevista através do software COSMO-RS, de entre os quais quatro foram selecionados para o trabalho experimental: limoneno, α -pineno, p-cimeno e esqualano. Este último não proporcionou resultados satisfatórios, mas os restantes dissolveram adequadamente o polímero. As condições de dissolução foram otimizadas de acordo com os resultados referentes ao limoneno: 3wt%, 10 min, a 110°C, e rácio antisolvente/solvente 2/1. Comparando os solventes utilizados, os resultados mais promissores foram obtidos usando α -pineno como solvente e etanol como antisolvente.

As amostras de polímero recuperado foram analisadas com recurso a diferentes técnicas, mostrando-se semelhantes ao polímero virgem. O scale-up do processo e a reutilização do solvente foram também estudadas, assim como a separação de HDPE e PET, e a hipótese de utilizar o mesmo sistema para a recuperação de PP.

Palavras-chave: Reciclagem de polímeros, Reciclagem física. HDPE, COSMO-RS, Solventes verdes

Table of Contents

Acknowledgments	i.		
Declarationii			
Abstracti	ii		
Resumoi	v		
List of Figuresi	x		
List of Tables xi	ii		
List of Abbreviations and Symbolsx	v		
1. Introduction	1		
1.1. Global plastic waste scenario	1		
1.2. Polyolefins	4		
1.2.1. Properties	4		
1.2.2. Polymerization: Ziegler-Natta mechanism	4		
1.2.3. Processing	6		
1.2.4. Applications	7		
1.2.5. Impact in the plastic waste global scenario	7		
1.3. HDPE and PP disposal and recovery methods	8		
1.3.1. Landfill	8		
1.3.2. Biodegradation	Э		
1.3.3. Incineration and energy recovery	9		
1.3.4. Recycling	С		
1.3.4.1. Chemical recycling1	1		
1.3.4.2. Mechanical recycling1	3		
1.3.4.3. Physical recycling1	5		
1.4. Dissolution and precipitation processes for plastic recovery	7		
1.4.1. Background on polymer dissolution and solubility1	7		
1.4.1.1. Insights on polymer dissolution1	7		
1.4.1.2. Polymer dissolution models1	7		
1.4.1.3. Thermodynamic predictive models for polymer solubility	9		
1.4.2. Dissolution and precipitation of HDPE and PP2	1		
1.4.2.1. Solvents and antisolvents state of the art2	1		
1.4.2.2. Large-scale implementation	3		

	1.4	4.2.3.	Technical and economical bottlenecks	23
2.	Motiv	vatior	٦	24
3.	3. Materials and Methods			
÷	3.1.	Mate	erials	25
÷	3.2.	Exp	erimental methods	26
	3.2.1	۱.	Dissolution and reprecipitation	26
	3.2	2.1.1.	HDPE and PET separation	26
	3.2.2	2.	Solvent recovery	26
	3.2.3	3.	Fourier Transform Infrared spectroscopy	27
	3.2.4	1.	Differential Scanning Calorimetry	27
	3.2.5	5.	Thermogravimetric Analysis	27
	3.2.6	6.	Nuclear Magnetic Resonance spectroscopy	27
;	3.3.	Con	nputational methods	28
	3.3.1	۱.	Solvent screening on COSMO-RS	28
	3.3.2	2.	Aspen Plus simulation and economical assessment	30
4.	Resu	ults a	nd Discussion	31
4	4.1.	Solv	rent screening in COSMO-RS	31
4	4.2.	Limo	onene as HDPE solvent	35
	4.2.1.		Optimization of dissolution conditions	35
	4.2.2.		Antisolvent selection	36
4	4.3.	Squ	alane, α -pinene and p-cymene as HDPE solvents	41
4	4.4.	Solv	rent selection for HDPE dissolution and precipitation	43
4	4.5.	Mec	hanism of HDPE dissolution in α -pinene	44
4	4.6.	Rec	overed HDPE characterization	45
	4.6.1	۱.	Thermogravimetric Analysis	45
	4.6.2	2.	Differential Scanning Calorimetry	47
	4.6.1	۱.	Fourier Transform Infrared spectroscopy	48
4	4.7.	Rec	overed solvent characterization	49
4	4.8.	Sca	le-up	51
4	4.9.	Solv	rent reuse and cycling	52
4	4.10.	Proc	cess simulation and economical assessment	54

	4.	11.	Polypropylene – proof of concept	56
		4.11.	1. Solvent screening for PP in COSMO-RS	56
		4.11.	2. PP's dissolution and recovery	58
		4.11.	3. Recovered PP characterization	59
	4.	12.	HDPE and PET separation	61
		4.12.	1. Recovered PET characterization	63
5	•	Conc	lusions and Future Work	65
6		Refe	rences	66
7	•	Appe	ndix	81
	7.	1.	HDPE solvent screening	81
	7.	2.	Optimization of dissolution conditions in limonene	81
	7.	3.	Antisolvent study for HDPE dissolved in limonene	82
	7.	4.	Antisolvent study for HDPE dissolved in α -pinene	82
	7.	5.	Antisolvent study for HDPE dissolved in p-cymene	82
	7.	6.	Tukey Honestly Significant Difference (HSD) test	83
	7.	7.	Characteristic FTIR bands of HDPE and correspondence	83
	7.	8.	Characteristic FTIR bands of α -pinene and correspondence	84
	7.	9.	Differential thermogram of recovered HDPE	85
	7.	10.	FTIR analysis of recovered HDPE from different solvent/antisolvent systems	86
	7.	11.	FTIR analysis of recovered solvent from different solvent/ antisolvent systems	89
	7.	12.	NMR of pure α-pinene	92
	7.	13.	HDPE and α -pinene recovery at scale-up	93
	7.	14.	FTIR analysis of α -pinene recovered in the washing step	93
	7.	15.	HDPE and α -pinene recovery from 3 processing cycles	93
	7.	16.	FTIR analysis of α -pinene recovered from third cycle	94
	7.	17.	NMR analysis of α -pinene recovered from third cycle	94
	7.	18.	Aspen Plus simulation: stream description	95
	7.	19.	PP solvent screening	96
	7.	20.	PP and α -pinene recovery	97
	7.	21.	Differential thermogram of recovered PP	97
	7.	22.	Characteristic FTIR bands of isotactic PP and correspondence	98

7.23.	HDPE, PET, α -pinene and thymol:carvacrol (1:1) recovery	98
7.24.	FTIR spectra of pristine and recovered HDPE from HDPE/PET mixture	99
7.25.	Differential thermogram of recovered PET	99

List of Figures

Figure 1 - Number of scientific publications per year related to "Plastic recycling" 8
Figure 2 - Value chain of plastic products ¹⁰
Figure 3 – Worldwide share of plastics treated by waste management category, in 2019 (adapted from
OECD – Global Plastics Oultook, 2022 ⁴)
Figure 4 - Chemical structure of polyethylene and polypropylene
Figure 5 - Mechanism for Ziegler-Natta olefin polymerization ²⁵ 5
Figure 6 - Distribution of plastic use by polymer, in 2019 (data from OECD ¹⁷)7
Figure 7 - Cumulative distribution of the fate of polyolefins in Europe, between 1950 and 2016 (data
from Kawecki et al. ³⁷)
Figure 8 - Overview of recycling loops and technologies (adapted from Closed Loop Partners ⁵³) 10
Figure 9 - Mechanical recycling of plastic waste ²⁷ 14
Figure 10 - Scheme of a dissolution-precipitation process (Illustration built with BioRender)
Figure 11 - Number of publications related to "plastic recycling dissolution" per year found in the Web of
Science Core Collection up to July 2023 ⁸ 16
Figure 12 - Representation of the charge density distribution for the center monomer of an HDPE
oligomer, as simulated in COSMO-RS
Figure 13 - σ -profile and σ -potential of HDPE drawn in COSMO-RS
Figure 14 - Chemical structures of the solvents screened
Figure 15 - σ -profiles of the solvents screened drawn in COSMO-RS
Figure 16 - COSMO-RS solubility prediction of HDPE in several selected solvents at three different
temperatures (110°C, 120°C, 130°C)
Figure 17 - Recovery yield of HDPE according to concentration and dissolution temperature
Figure 18 - Recovery yield of limonene according to concentration and dissolution temperature 36
Figure 19 - Ternary liquid-liquid equilibrium of limonene, ethanol and water, drawn in COSMO-RS 37
Figure 20 - Ternary liquid-liquid equilibrium of limonene, 2-propanol and water, drawn in COSMO-RS.
Figure 21 - Ternary liquid-liquid equilibrium of limonene, 1-butanol and water, drawn in COSMO-RS.37
Figure 22 - Ternary liquid-liquid equilibrium of limonene, 1,2-propanediol and water, drawn in COSMO-
RS
Figure 23 - Ternary liquid-liquid equilibrium of limonene, 1,2-butanediol and water, drawn in COSMO-
RS
Figure 24 - Ternary liquid-liquid equilibrium of limonene, glycerol and water, drawn in COSMO-RS 38
Figure 25 - Ternary liquid-liquid equilibrium of limonene, ethylene glycol and water, drawn in COSMO-
RS
Figure 26 - Ternary liquid-liquid equilibrium of limonene, diethylene glycol and water, drawn in COSMO-
RS
Figure 27 - Ternary liquid-liquid equilibrium of limonene, triethylene glycol and water, drawn in COSMO-
RS

Figure 28 - Recovery of HDPE using different antisolvents and three antisolvent/solvent ratios (1/1, 2/1
and 3/1). (* represents values higher than 100wt%) 39
Figure 29 - Recovery of limonene using different antisolvents and three antisolvent/solvent ratios (1/1,
2/1 and 3/1). ((a) refers to the cases where it was not possible to attain pure limonene)
Figure 30 - Ternary liquid-liquid equilibrium of α -pinene, ethanol and water, drawn in COSMO-RS 42
Figure 31 - Ternary liquid-liquid equilibrium of α -pinene, 1,2-propanediol and water, drawn in COSMO-
RS
Figure 32 - Ternary liquid-liquid equilibrium of α -pinene, diethylene glycol and water, drawn in COSMO-
RS
Figure 33 - Ternary liquid-liquid equilibrium of p-cymene, ethanol and water, drawn in COSMO-RS 42
Figure 34 - Ternary liquid-liquid equilibrium of p-cymene, 1,2-propanediol and water, drawn in COSMO-
RS
Figure 35 - Ternary liquid-liquid equilibrium of p-cymene, diethylene glycol and water, drawn in COSMO-
RS
Figure 36 - HDPE and alpha-pinene recovery yields using three different antisolvents
Figure 37 - HDPE and p-cymene recovery yields using three different antisolvents
Figure 38 - FTIR spectra of pristine HDPE, pure α -pinene, and swollen HDPE in α -pinene
Figure 39 - Variation of the HDPE residual weight with temperature, from TGA analysis, for the different
limonene/antisolvent systems studied, and respective ampliation (on the right)
Figure 40 - Variation of the HDPE residual weight with temperature, from TGA analysis, for the different
α -pinene/antisolvent systems studied, and respective ampliation (on the right)
Figure 41 - Variation of the HDPE residual weight with temperature, from TGA analysis, for the different
p-cymene/antisolvent systems studied, and respective ampliation (on the right)
Figure 42 - FTIR spectra of pristine and recovered HDPE (using $\alpha\text{-pinene}$ as solvent and ethanol as
antisolvent) 49
Figure 43 - FTIR spectra of pure and recovered α -pinene
Figure 44 - ¹ H NMR spectra of recovered α-pinene
Figure 45 - ¹³ C NMR spectra of recovered α-pinene
Figure 46 - HDPE and α -pinene recovery from scale-up 5 times in mass of HDPE
Figure 47 - HDPE and α -pinene recovery considering three consecutive solvent reuses
Figure 48 - Flowsheet of the process as implemented on Aspen Plus for the dissolution and precipitation
process of HDPE, including solvent and antisolvent recycling
Figure 49 - PP molecule (with charge density points) used for the COSMO-RS calculations
Figure 50 - σ -profile and σ -potential of PP generated by COSMO-RS software
Figure 51 - COSMO-RS solubility prediction of PP in several selected solvents at three different
temperatures (160°C, 170°C, 180°C)
Figure 52 - PP and α -pinene recovery after dissolution at 110°C and precipitation with ethanol in the
antisolvent to solvent ratio of 2/1
Figure 53 - Variation of recovered PP's residual weight with temperature, resulting from TGA analysis.

Figure 54 - FTIR spectra of pristine and recovered PP61
Figure 55 - FTIR spectra of pure and recovered α -pinene used in PP dissolution61
Figure 56 - Schematic representation of the selective dissolution of HDPE and PET (Illustration built in
BioRender)
Figure 57 - Recoveries of selectively dissolved polymers, HDPE and PET, and respective solvents, α -
pinene and thymol:carvacrol (1:1)
Figure 58 - Variation of recovered PET's residual weight with temperature, resulting from TGA analysis.
Figure 59 - FTIR spectra of pristine and recovered PET
Figure 60 - FTIR spectra of pure and recovered thymol:carvacrol NaDES (1:1)
Figure 61 - Derivative thermogravimetric analysis of recovered HDPE samples from different
solvent/antisolvent systems
Figure 62 - FTIR spectra of pristine and recovered HDPE using limonene as solvent and water as
antisolvent
Figure 63 - FTIR spectra of pristine and recovered HDPE using limonene as solvent and ethanol as
antisolvent
Figure 64 - FTIR spectra of pristine and recovered HDPE using limonene as solvent and 2-propanol as
antisolvent
Figure 65 - FTIR spectra of pristine and recovered HDPE using limonene as solvent and 1-butanol as
antisolvent
Figure 66 - FTIR spectra of pristine and recovered HDPE using limonene as solvent and 1,2-propanediol
as antisolvent
Figure 67 - FTIR spectra of pristine and recovered HDPE using limonene as solvent and 1,2-butanediol
as antisolvent
Figure 68 - FTIR spectra of pristine and recovered HDPE using limonene as solvent and glycerol as
antisolvent
Figure 69 - FTIR spectra of pristine and recovered HDPE using limonene as solvent and ethylene glycol
as antisolvent
Figure 70 - FTIR spectra of pristine and recovered HDPE using limonene as solvent and diethylene
glycol as antisolvent
Figure 71 - FTIR spectra of pristine and recovered HDPE using limonene as solvent and triethylene
glycol as antisolvent
Figure 72 - FTIR spectra of pristine and recovered HDPE using α -pinene as solvent and 1,2-propanediol
as antisolvent
Figure 73 - FTIR spectra of pristine and recovered HDPE using α -pinene as solvent and diethylene
glycol as antisolvent
Figure 74 - FTIR spectra of pristine and recovered HDPE using p-cymene as solvent and ethanol as
antisolvent
Figure 75 - FTIR spectra of pristine and recovered HDPE using p-cymene as solvent and 1,2-
propanediol as antisolvent

Figure 76 - FTIR spectra of pristine and recovered HDPE using p-cymene as solvent and diethylene Figure 81 - FTIR spectra of pure and recovered limonene using 1,2-propanediol as antisolvent. 90 Figure 84 - FTIR spectra of pure and recovered limonene using ethylene glycol as antisolvent. 90 Figure 85 - FTIR spectra of pure and recovered limonene using diethylene glycol as antisolvent...... 90 Figure 86 - FTIR spectra of pure and recovered limonene using triethylene glycol as antisolvent. 90 Figure 88 - FTIR spectra of pure and recovered α -pinene using diethylene glycol as antisolvent. 91 Figure 90 - FTIR spectra of pure and recovered p cymene using 1,2-propanediol as antisolvent. 91 Figure 91 - FTIR spectra of pure and recovered p cymene using diethylene glycol as antisolvent...... 91 Figure 94 - FTIR spectra of pure and recovered α -pinene from the washing step, using ethanol as Figure 95 - FTIR spectra of pure and recovered α -pinene after 3 consecutive uses, using ethanol as

List of Tables

Table 1 - Comparison of chemical, mechanical, and physical recycling (adapted from Arena et al. ⁵⁴).11
Table 2 - Experimental dissolution and reprecipitation conditions reported for the recovery of HDPE and
PP. (NA stands for "not available")
Table 3 - Identification, purity, source, and indicative price of solvents used for HDPE dissolution and
precipitation
Table 4 - Polymer properties considered in COSMO calculations. 29
Table 5 - Solvent and antisolvent properties considered in COSMO calculations ^{158,159} . 29
Table 6 - Properties and cost of utilities 30
Table 7 - Average dissolution time of HDPE in limonene at different temperatures. 35
Table 8 - Solubility (wt%) of limonene, α -pinene, p-cymene and squalane in the antisolvents selected,
as calculated in COSMO-RS
Table 9 - Results obtained for three different solvents, using ethanol as antisolvent in (2/1)
antisolvent/solvent massic ratio
Table 10 - List of FTIR bands from HDPE and alfa-pinene that suffered wavelength deviations during
dissolution
Table 11 - Polymer content of HDPE samples, determined through TGA analysis
Table 12 - Thermal properties of the recovered HDPE samples for the solvent/antisolvent systems used
in this work. (T _c is the crystallization point, T _m the melting point, ΔH_f the enthalpy of fusion, and %C the
crystallinity percentage.)
Table 13 - Required raw materials and respective cost for the proposed Aspen process for HDPE
dissolution and precipitation
Table 14 - Utility usage and respective cost, as simulated in Aspen Plus. 55
Table 15 - Thermal properties of pristine and recovered PP. 60
Table 16 - Thermal properties of pristine and recovered PET. 64
Table 17 - Solubility (wt%) of HDPE in different solvents at 110°C, 120°C and 130°C, as calculated in
COSMO-RS
Table 18 – HDPE and limonene recovery at different dissolution temperatures and initial solid contents.
Table 19 - HDPE and limonene recovery for different antisolvents and antisolvent/solvent ratios, after
dissolution at 110°C for 10 min
Table 20 - HDPE and α -pinene recovery for different antisolvents, after dissolution at 110°C for 10 min.
Table 21 - HDPE and p-cymene recovery for different antisolvents, after dissolution at 110°C for 10 min.
Table 22 - Tukey HSD test regarding HDPE recovery with different solvents. 83
Table 23 - Tukey HSD test regarding solvent recovery after HDPE dissolution in different solvents and
Table 23 - Tukey HSD test regarding solvent recovery after HDPE dissolution in different solvents and precipitation. 83

Table 25 - Characteristic FTIR bands of $\alpha\mbox{-pinene}$ and corresponding vibrations. (NA stands for not
available)
Table 26 - HDPE and α -pinene recovery using ethanol as antisolvent, in the antisolvent:solvent ratio
2:1, at two different scales: 50 mg HDPE and 250 mg HDPE
Table 27 – HDPE and α -pinene recovery using ethanol as antisolvent, in the antisolvent:solvent ratio
2:1, for 3 consecutive solvent utilizations
Table 28 - Stream characterization from Aspen plus simulation (part 1). 95
Table 29 - Stream characterization from Aspen plus simulation (part 2). 96
Table 30 - Solubility (wt%) of HDPE in different solvents at 110°C, 120°C and 130°C, as calculated in
COSMO-RS
Table 31 - PP and α -pinene recovery using ethanol as antisolvent, in the antisolvent/solvent ratio 2/1,
after dissolution at 110°C for 10 min
Table 32 - Characteristic FTIR bands of iPP and corresponding vibrations. 98
Table 33 - HDPE, PET, α -pinene and thymol:carvacrol (1:1) recovery from selective dissolution and
precipitation

List of Abbreviations and Symbols

%C	Percentage of crystallinity	
ABS	Acrylonitrile Butadiene Styrene	
ADF	Amsterdam Density Functional	
AMS	Amsterdam Modeling Suite	
ATR-FTIR	Attenuated Total Reflectance – Fourier Transform Infrared	
СО	Carbon monoxide	
COSMO-RS	COnductor-like Screening Models - Real Solvents	
DFT	Density Functional Theory	
DSC	Differential Scanning Calorimetry	
Е	Cohesive energy	
EtOH	Ethanol	
GGA	Generalized Gradient Approximation	
HBA	Hydrogen Bond Acceptor	
HBD	Hydrogen Bond Donnor	
HDPE	High Density Polyethylene	
HSD	Honestly Significant Difference	
iPP	Isotactic Polypropylene	
LDA	Local Density Approximations	
LDPE	Low Density Polyethylene	
LLDPE	Linear Low Density Polyethylene	
NA	Not Available	
NaDES	Natural Deep Eutectic Solvent	
NMR	Nuclear Magnetic Resonance	
OECD	Organization For Economic Cooperation And Development	
PA	Polyamide	
PC	Polycarbonate	
PE	Polyethylene	
PET	Polyethylene terephthalate	
PetE	Petroleum ether	
PP	Polypropylene	
PS	Polystyrene	
PUR	Polyurethane	
PVC	Polyvinyl chloride	
p(σ)	σ-profile	
R	Gas constant	
R₀	Radius of interaction sphere in Hansen parameters	
Ra	Radius between polymer and solvent (Hansen parameters)	
Т	Temperature	
T_m	Melting temperature	

TGA	Thermogravimetric Analysis
U.S.	United States
UFF	Universal Force Field
UV	Ultraviolet
V	Molar volume
XC	Exchange and Correlation Functional
x_i^{SOL}	Solubility of compound i in a solvent (molar fraction)
Υi	Activity coefficient of compound i in a liquid solution
γ_i^{crs}	Activity coefficient
γ_i^{fv}	Combinatorial term of activity coefficient
δ	Solubility parameter
δ_D	Nonpolar interactions factor for Hansen parameter
δ_P	Permanent dipole-dipole interactions factor for Hansen parameter
δ_H	Hydrogen bonding factor for Hansen parameter
ΔC_p	Heat capacity of fusion
ΔG_m	Free energy of mixing
ΔH_f	Enthalpy of fusion
$\Delta H_{f,c}$	Enthalpy of fusion of the crystalline polymer
ΔH_m	Enthalpy of mixing
ΔS_m	Entropy of mixing
μ_i^{pure}	Chemical potential of the pure compound in the liquid phase
μ_i^{solv}	Chemical potential of the pure compound in a liquid solution
μ(σ)	σ-potential
ρ	Density
ϕ_i^{fv}	Volume fraction

1. Introduction

1.1. Global plastic waste scenario

The production of synthetic plastics can be traced back to 1907, with the invention of Bakelite, a phenolic resin to be used as a strengthening additive for wood. This polymer was an example of high heat resistance, and it was insoluble in most common solvents, thus presenting a great durability that made it suitable for application in various sectors¹. This was the first impulse for the development of many of the synthetic plastics that are widely used today. Plastics ' durability, as well as their low weight, made them the top choice for many applications, and over the first half of the 20th century they came to replace other materials such as paper, glass, natural rubber, and metal in many applications, ranging from consumer packaging to electrical equipment and the automotive industry².

By 1950, synthetic plastics were being produced at industrial scale, globally resulting in 2 Mt that year³. From that point onwards, the demand for plastics has been raising sharply, with the global usage reaching 460 Mt in 2019, according to the most recent report from OECD (Organization for Economic Cooperation and Development)⁴. The largest usage share corresponds to the packaging sector, with 31% of the global demand, followed by the construction sector⁴. The most abundantly used materials, such as high- and low-density polyethylene (HDPE and LDPE), polyethylene terephthalate (PET), polyvinyl chloride (PVC) and polypropylene (PP), are primarily produced from fossil fuels², representing 6% of the global oil consumption, as of 2016. The most recent report from the Ellen MacArthur Foundation predicts that by 2050 this value will increase to 20%, and that virgin plastic production will account for 15% of the annual carbon emission budget defined for the same year⁵. In addition to this issue, the chemical properties that confer durability to these products also imply severe problems when it comes to their end-of-life, as they are not biodegradable, and thus accumulate in the environment if not properly recycled or thermally treated. The issue of plastic waste started to be noticeable during the first decades of plastics mass production, namely with the appearance of plastic debris in marine environments⁶, and their accumulation in the environment has reached the point where they are analyzed as a geological indicator of the Anthropocene era⁷.

Although the first scientific publication related with plastic waste is dated from 1950, it became a recurring topic only in the end of the 1960's. Soon the necessity of finding new ways to repurpose end-of-life plastic products started to be understood, as the first references on "plastic recycling" can be traced to 1971. The number of scientific publications on the subject started to increase more significantly in 1990, evolving exponentially from 2010 onwards, as shown in Figure 1. The data presented was based on the search for the terms "plastic recycling" in the Web of Science Core Collection and goes as far as July of 2023⁸.



Figure 1 - Number of scientific publications per year related to "Plastic recycling" 8.

The lifetime of plastic products can vary greatly depending on the application, ranging from 6 months, in the case of packaging, a sector that includes most of single use products widely used everyday, to 35 years, for construction materials³. This distribution plays a major role in the type of plastic waste generated. Accordingly, in 2019 the greatest amount of waste generated belonged to the packaging sector, with 142 Mt, while the global accounted for 353 Mt⁴. According to the recent evolution of the plastic waste scenario, OECD predicted that its global value will reach 1014 Mt by 2060⁹.

While there have been successive legislative attempts to limit plastic usage and thus lower its demand, it is likely that it will continue to increase as it is truly difficult to find adequate substitutes for many applications. Furthermore, a great share of the issue lays in the inadequate management of the plastic products reaching the end-of-life status, although there are other steps of the value chain, represented in Figure 2, that are source of concerns.



Figure 2 - Value chain of plastic products¹⁰.

The fate of plastics after consumption, in 2019, is broken down in Figure 3. First, it is possible to observe that 22% of plastic waste is lost to the environment even before entering treatment pathways, due to inefficient management⁴. Part of this can be related to accidental spillages, that happen throughout the entire value chain, including during manufacturing. Although difficult to quantify, some plastics materials are also lost through the degradation of products exposed to the environment, either through mechanical, biological, thermal or photodegradation processes⁷.

Globally, the most common option is still the deposit in landfills, while the collection rate for recycling is only 15%. Although there are some countries with higher collection rates, namely European OECD countries and China, these rates are not ideal, and this percentage lacks to take into account the subsequent material losses during the recycling processes themselves. In fact, in the same year, only 6% of all plastics produced were originated from recycling of the pristine materials^{4,11}.



Figure 3 – Worldwide share of plastics treated by waste management category, in 2019 (adapted from OECD – Global Plastics Oultook, 2022⁴).

This distribution needs severe improvement, namely to reach the goal set by the European Union of recycling 55% of plastic packaging, by 2030^{12,13}. This goal was set considering the 55% reduction in net greenhouse gas emissions that was targeted to 2030, through the European Green Deal and the circular economy action plan of the European Commission, as a prerequisite to the further transition actions that aim to achieve climate neutrality in Europe in 2050¹⁴.

The main courses of action include enhancing the usage of alternative feedstocks and the production of more sustainable plastics, improving key steps in the value chain, such as sorting and collection processes, in order to reduce leakages to the environment, and improving and developing closed-loop recycling processes^{15,16}, which are only applied to 2% of the plastic waste generated, according to the values reported by the Royal Society of Chemistry and the Ellen McArthur Foundation^{5,15}.

1.2. Polyolefins

Polyolefins are a class of polymers derived from alkenes, such as ethylene and propylene, thus being characterized by the general chemical formula (CH₂CHR)_n. They are the most produced type of polymer¹⁷, being the most abundant polyethylene (PE) and polypropylene (PP), each industrially produced in numerous different grades¹⁸. In general, these materials have a good chemical and thermal resistance, strength, and they are easily processed due to their thermoplastic behavior.



Figure 4 - Chemical structure of polyethylene and polypropylene.

1.2.1. Properties

Polyethylene is a semicrystalline polymer that follows the molecular formula (CH₂=CH₂)_n, but it can exist in different types, depending on the arrangement of the chains, each with different characteristics and properties, such as molecular weight distribution, degree of crystallinity, density and rheological behavior. The two main types of polyethylene are high-density polyethylene (HDPE), which is not branched, and low-density polyethylene (LDPE), with a branched structure. The processing properties of both vary significantly, as HDPE has a higher tensile strength and stiffness, while LDPE shows a high resistance to breakthrough impact. HDPE presents a higher melting point (130-140°C) and density between 0.96 and 0.98 g/cm³. LDPE has a melting point around 110°C and its density varies between 0.91 and 0.93 g/cm³. Due to its branched structure, the processing properties of LDPE are largely influenced by the branching degree, while the most influential variable in the case of HDPE is the molecular weight. Also common is the linear low-density polyethylene (LLDPE), which is a copolymer of ethylene with another linear monomer such as propylene, butene or pentene, among others¹⁹.

Polypropylene, on the other hand, is a homopolymer that contains only propylene as monomer. It exists as atactic, syndiotactic and isotactic PP (iPP), depending on the orientation of the methyl groups, but the last is the one usually commercialized¹⁹. Its melting point is above that of HDPE, varying between 165 and 179°C, and it has a higher tensile strength. Its density is around 0.90 to 0.91 g/cm^{3 19}.

1.2.2. Polymerization: Ziegler-Natta mechanism

In general, polyolefins are polymerized through addition or chain-growth mechanisms: the reaction starts by action of an initiator, that reacts with a first monomer, allowing the propagation of the

reaction. These reactions, however, can proceed very differently depending on the type of initiator and on the presence of a catalyst. In this sense, polymerization takes different paths for linear or branched polyolefins. While the polymerization of LDPE happens through free radical polymerization, resulting in a high branching degree, linear polyolefins, such as HDPE and PP, which are the focus of this work, are obtained through catalyzed processes using coordination catalysts, that on one hand suppresses the chain transfer that would otherwise cause branching, and, in the case of PP, also allows for regulation of the stereochemical configuration of the chains^{20–22}.

The most common catalysts used to produce HDPE and isotactic PP are Ziegler-Natta catalysts. These contain four different species: MgCl₂, used as catalyst support, TiCl₄, the active catalyst precursor, AlR₃ (where R is an alkyl group), responsible for activating the previous compound, and a donor, a Lewis base, such as ethyl benzoate, phthalate, or alkoxy silane. The catalyst is activated through the transference of one alkyl group in AlR₃ to the titanium center. The compound formed, Ti-R, allows the binding of the monomer to this complex, which leads to the propagation of the chain-growth reaction. The donor has the main function of regulating the support, either by stabilizing its surface and regulating the active area of the catalyst, in the case of internal donors, or by controlling the isospecificity of the active site, in the case of external donors. The second type has a major importance in the polymerization of propylene, influencing the isotactic content of the final PP. The termination of the reaction is usually performed by the insertion of hydrogen that is transferred to the monomer, ceasing its binding to the catalyst and thus the growth of the polymer chain^{23–25}. This mechanism is represented in Figure 5.



Figure 5 - Mechanism for Ziegler-Natta olefin polymerization²⁵.

Most industrial processes for the production of HDPE are based on this mechanism, but the technologies implemented at industrial scale differ widely in the conditions and types of reactors used. The most common option is the continuous production of HDPE at low pressure, in a liquid slurry phase, which requires the use of a heavy hydrocarbon as diluent. This type of process can take place in

stirred-tank, loop or pool reactors. As an alternative, in some processes the polymerization takes place in an adequate solvent, being the solution devolatilized to obtain the pure polymer. This commonly takes place in adiabatic reactors. HDPE can also be polymerized in the gas phase, in fluidized bed reactors. Most of these processes have also been used in the production of PP, but the focus lays in liquid pool slurry phase and gas phase processes¹⁹.

Other catalyst systems can also be applied for HDPE polymerization, although they are less common. These include chromium catalysts (Cr/SiO₂), which are of particular interest for obtaining broad molecular weight distributions, and metallocene catalysts, mainly used in gas phase reactors^{19,26}. Those last compounds are also an option for polypropylene polymerization²⁶.

1.2.3. Processing

The manufacturing of plastic products from the virgin materials includes a series of steps before the final assembly, such as the incorporation of additives, and the forming of the product's shape²⁷.

The incorporation of additives in polymers is a common procedure that can be performed through melt compounding, dispersion, or solution²⁷. Additives can have various functions, being subdivided in functional additives, colorants, fillers and reinforcements. The final application has a great influence on the most adequate additives, for example, packaging usually contains antioxidants, plasticizers, slip additives and antistatic agents, but flame retardants become essential for electronic devices and transportation-related products²⁸.

Regarding the forming step, there are various options suitable for HDPE and PP. These processes are not restricted to these polymers, but instead can be applied to all polymers with thermoplastic behavior, in general. The most common processes include extrusion, injection, rotational and blow molding and thermoforming^{19,29,30}. Extrusion is a continuous process that allows the production of rods or sheets of plastic. The equipment includes a screw-like form with three distinguishable zones: the solids conveying zone, where the plastic enters as solid pellets and is compressed along the screw; the transition zone, where the plastic is heated and begins to melt; and the metering zone, where the molten plastic is homogenized at the final intended temperature. A variation of this process is coextrusion, that allows the production of multilayer films through the simultaneous extrusion of different plastics in individual screws^{29,30}. In injection molding, the plastic is molten and injected into a cavity of the desired shape. After cooling, the final piece is ejected already in the solid state with the same shape as the mold used. Blow and rotational molding, on the other hand, do not require the complete melting of the plastic, and are very similar processes between them, where a sheet of plastic is pressurized against the walls of a mold, taking its form. Rotational molding is preferred for pieces of large dimensions. Thermoforming works nearly in the same way as blow molding, but it suits only simpler pieces, as the molds in this case are simple shaped surfaces, while blow molding allows the formation of bottles in one single step, for example^{29,30}.

1.2.4. Applications

Among common use plastics (considering PET, PVC, PS (polystyrene) and PC (polycarbonate)), polyolefins perform the best when it comes to environmental impacts, as they have high atom economy, low energy demand, and lead to little respiratory effects and ecotoxicity³¹. In addition, they are significantly cheaper than most other commercial plastics^{31,32}.

Polyolefins perform adequately as moisture barriers and heat seal films, and thus are commonly used in packaging applications. HDPE can be found in beverage bottles, stiff bottles, and chemical containers such as those used for cleaners and shampoos. It is also used in more flexible films in the form of plastic bags, an application where LDPE is also common. HDPE use is favored by its high resistance to UV radiation, which makes it a frequent option for other applications such as rigid toys and outdoor products^{21,33}. PP, due to its greater rigidity, is also a typical material for stiff food containers, but it is widely used in other materials as well, such as pipes and wire coatings^{2,7}.

The same properties make these materials a preferred option for multilayer packaging, where they are present in layers that function as barrier and that provide structure to the film. PE is also widely applied as the outer and inner layers, as it has good sealing capability³⁴. Most multilayer films found in packaging applications combine either polyolefins among them, or a polyolefin and PET³⁵.

1.2.5. Impact in the plastic waste global scenario

In 2019, polyolefins (PP, HDPE, LDPE and LLDPE) accounted for nearly 40% of the global plastic use¹⁷, which distribution is shown in Figure 6. Their role in the plastic waste scenario is even more relevant, as they are the major components used in packaging applications, which with their short lifetimes lead the global waste generation, as aforementioned⁴. In the figure, PUR refers to polyurethane, and ABS to acrylonitrile butadiene styrene.



Figure 6 - Distribution of plastic use by polymer, in 2019 (data from OECD¹⁷).

Although these plastics are considered possible to recycle, they are often found in waste streams in the form of multilayer films or present various additives that compromise the use of simple sorting and recycling processes^{12,15,34,35}. In fact, according to the U.S. Federal Trade Commission Green Guides, for example, these polymers are only considered recyclable in the form of HDPE rigid packages and bottles, PP rigid packaging, and LDPE flexible packaging³⁶. Even then, these products are not always recycled, and although their recycling rates have been improving in the last years, it was estimated that the total percentages that followed recycling pathways between 1950 and 2016, in Europe, were 12% for HDPE and 9% for PP, while more than half of each of these polymers was landfilled³⁷, as described in Figure 7. Although there is leakage of plastics into the waste waters, which presents a severe problem for the water quality and treatment, the respective fraction within the total amount of plastics in their end-of-life is lower than 0.06%, thus not being visible in the figure.



Figure 7 - Cumulative distribution of the fate of polyolefins in Europe, between 1950 and 2016 (data from Kawecki et al. ³⁷).

The low cycling rates mentioned are evidence that the recycling processes implemented so far still lack efficiency in post-consumer products, and that there are several areas where improvements are necessary, with the aim of reducing the amount of primary polyolefins produced. The feedstock for these materials is usually obtained from steam cracking of naphta, product of crude oil refining^{27,38}, a fossil fuel which consumption urges to be minimized. In this light, the different options for end-of-life treatment of plastic waste and polyolefins in particular, namely HDPE and PP, will be discussed in the next section, including their limitations and advantages.

1.3. HDPE and PP disposal and recovery methods

1.3.1. Landfill

According to the zero-waste hierarchy defined in the European Commission's waste framework directive, landfilling is the least preferred disposal method, after mismanaged disposal^{14,36}. Although landfills, as opposed to open dumps, are projected to allow the management of liquid and gas emissions, keeping them under regulated norms, these have several drawbacks in comparison with other end-of-life options. First, landfills are very demanding regarding land area⁷. Furthermore, plastic waste is not eliminated rapidly by being disposed of in a landfill, since its degradation is slow, especially in low-

oxygen environments³⁹. Polyolefins, in particular, are hydrophobic, and thus resistant to hydrolysis, and are often additivated with antioxidants and stabilizers, which increase their already high resistance to UV radiation and heat⁴⁰. Nevertheless, over long periods exposed to various environmental stimuli, such as light, heat and water exposure, degradation of polyolefins occurs, in the form of breakage and release of leachable compounds to some extent, generating small plastic waste particles that can be transferred to water streams³⁹. These leachates are collected by the intended circuits, but contain both organic and inorganic contaminants, which require specific treatment either in the landfill itself or in general wastewater treatment plants. Before treatment, the leachate is sometimes circulated through the landfill in order to promote degradation⁴¹. Furthermore, as stated before, food packaging is one of the main applications for plastics such as HDPE and PP. These products, if not properly washed and treated, may still contain organic matter that decomposes, emitting greenhouse gases⁴². The gases emitted also require treatment, either by a flare, or they can be used to generate electrical energy²⁷.

Considering this, while landfilling can be a suitable option to treat easily degradable materials, the most valuable advantage of landfilling plastic waste is to avoid water and soil contamination, as even the energy recovery regarding the plastic materials themselves is minimal.

1.3.2. Biodegradation

Biodegradation refers to the fragmentation of polymer chains by action of enzymes, followed by the assimilation of the resulting oligomers by microorganisms. By using the molecules as energy source, the microorganisms produce carbon dioxide, water, and methane through microbial respiration^{43,44}. Species whose capability to degrade polyethylene and propylene has been demonstrated include *Bjerkandera adusta, Brevibacillus sps.*, and *Aneurinibacillus sp.*^{45,46}. While biodegradation of polyolefins has been a topic of interest in the last years, it is important to note that this process does not lay within the recycling framework neither it is a suitable via for energy recovery, but rather is a way to destroy plastic waste, converting it to simple molecules rather than hydrocarbons that are used as feedstock, and avoid its uncontrolled leaking to the environment.

1.3.3. Incineration and energy recovery

Incineration belongs to the category of waste-to-energy technologies. It consists of the combustion of waste in aerobic atmospheres, at temperatures between 750 and 1000°C. This leads to the production of steam, which is then used for generating electricity, heat, or a combination of both⁴⁷. This technology is not applied to waste consisting exclusively of plastics, but rather to mixed municipal solid waste, that also contains textiles, paper, and organics. In this sense, the sorting requirements for the waste streams are low, but excessive moisture content can be a limiting factor for the efficiency of incineration, and a drying pretreatment may be necessary⁴⁷. This process can have a high energetic efficiency, if applied to the production of both heat and electricity and allows a substantial reduction in the volume of municipal solid waste, but leads to gas emissions containing dioxins and furans, while the

ashes also present high amounts of contaminants²⁷. Thus, to minimize the concern of toxic emissions, strict control and purification processes are required⁴⁸.

Regarding plastic waste, for example, additives may contain halogenated compounds associated with toxicity, that would also require specific pretreatment, increasing substantially the cost of this disposal method^{49,50}. In this case, also the ashes present further issues as they contain microplastics, estimated up to 102 000 particles per metric ton of waste incinerated, being PE and PP some of the most abundant⁵¹. If a mixed plastic waste stream is considered, it was assessed that the direct emissions from its incineration overcome the benefit that could be obtained from the energy generated, resulting in an overall negative impact in the environment⁵².

1.3.4. Recycling

Recycling is the preferred option in waste management, as it allows the production of new materials without requiring the use of primary feedstock, that in the case of HDPE and PP would mean an additional expense of fossil fuels.

Three different levels, or loops, of recycling can be distinguished, depending on the phase of plastics value chain where the recycled materials reenter the chain, as represented in Figure 8: the polymer loop, that includes separation/purification processes and mechanical recycling, in which the polymer is recovered with nearly the same characteristics of the pristine material, the monomer loop, in which the plastic is depolymerized through chemical recycling, and the monomers can be repolymerized to produce new plastics, and the molecular loop, in which the plastic is converted to feedstock for polymer production, which usually occurs through pyrolysis or gasification^{10,12,36}. The classification of the last processes can differ between authors, and they can also be included in chemical recycling.



Figure 8 - Overview of recycling loops and technologies (adapted from Closed Loop Partners⁵³).

Each of these technologies has its advantages, disadvantages, and ranges of application. A brief comparison regarding the most important parameters in a recycling process is presented in Table 1. Further details on the application of these technologies to HDPE and PP will be detailed ahead in the present section.

	Chemical recycling	Mechanical recycling	Physical recycling
Type of resources obtained	Monomers or chemical feedstock	Recycled plastics	Recycled plastics
Tolerance to feedstock contamination	Very low	Low	High
Possibility of multiple input valorization	Very low	Low	High
Quality of obtained resources	High	Medium	High
Complexity of technology required	High	Low	Medium
Cost	High	Low	Medium
Energy requirements	Medium	Low	Medium
GHG emissions	High	Low	High

Table 1 - Comparison of chemical, mechanical, and physical recycling (adapted from Arena et al.⁵⁴).

1.3.4.1. Chemical recycling

Chemical recycling refers to processes in which the polymer chains are destroyed. They can either be converted to the monomers, situation in which those can be repolymerized to new polymers, or converted to other molecules, that can be used as chemical feedstock for the production of monomers, thus requiring all the processing steps involved in the production of polymers from fossil feedstock.

Pyrolysis

Pyrolysis is a process of thermal degradation, usually conducted above 350°C, that allows the conversion of plastics to low molecular weight compounds, that can be used as fuels or feedstock to produce new polymers. These are distributed along gas, liquid and solid products. This process can be applied to a wide range of plastics, and thus can be used in mixed plastics streams without requiring complex sorting, although the heterogeneity of the feed stream influences that of the products, and thus the process can only be thoroughly optimized for application to each individual polymer^{27,42,54,55}.

The thermal degradation of HPDE occurs through random chain-scission, which originates free radicals that are stabilized through intermolecular hydrogen transfer, resulting in further break of carbon bonds⁵⁶. This leads to formation of multiple hydrocarbons, with chain lengths up to 40 carbon atoms, being the most common alkenes, alkanes and dienes⁵⁶, but their distribution was found to be sensitive to the temperature at which pyrolysis is conducted. A study carried out in a fluidized bed reactor at temperatures between 500 and 600°C found out that lower temperatures lead to an increased yield in

hydrocarbons with long chains (above 20 carbon atoms), while it is reduced at lower temperatures⁵⁷. The content of ethylene in the gaseous product increases with temperature, reaching 34.6 vol% at 600°C, but the gas yield corresponds 10% of the products at maximum⁵⁸.

Pyrolysis of PP happens trough similar routes, resulting mainly in alkenes and alkadienes⁵⁹. Its monomer, polypropylene, is usually the major component from the gaseous products, but these correspond to a maximum of 14wt% of the total products obtained. In the liquid fraction, the trimer of polypropylene is the most abundant compound⁵⁸. Pyrolysis can also be performed as a catalyzed process, which was shown to allow the minimization of the temperature and the reaction time in comparison to the uncatalyzed process^{55,60,61}.

In conclusion, the pyrolysis of polyolefins results in a small yield of the respective monomers, while the main products are large hydrocarbons. The oils obtained can be used as fuels, as their lower heating values are comparable to those of gasoline and diesel, for example⁵⁸, or they can be further treated through steam cracking, converting the hydrocarbons to lower olefins, that can be used as chemical feedstock to produce these polymers⁴².

When considering mixed plastic waste streams, pyrolysis represents about half the climate change impact of incineration with energy recovery. This technology also presents a significant reduction in the impact of plastic production from the secondary feedstock, in comparison to virgin plastic, despite the fact that pyrolysis products require complex treatment by steam cracking to be converted to the monomers⁶².

Gasification

Gasification allows the conversion of plastics to syngas or producer gas, via thermo-chemical conversion in a reducing atmosphere, at temperatures usually above 700°C⁶³. The composition of the gas product depends on the atmosphere or gasifying agent, that can be air, steam, or oxygen⁶⁴.

The process itself comprises four steps: i) drying, which eliminates excess water; ii) pyrolysis, that was described above; iii) oxidation, where the presence of oxygen leads the hydrocarbons resulting from the previous step to be oxidized do carbon monoxide and water steam; and iv) a reduction step, in the absence of oxygen, that leads to the formation of hydrogen^{65,66}. Gasification can take place in different kinds of reactors and with various configurations, but most studies of PE and PP gasification were performed in fluidized, spouted, or fixed bed reactors, using air or steam as gasification medium⁶⁴. In steam gasification, some general findings include the fact that HDPE gasification leads to higher gas yields than that of PP⁶⁷, and while PE results in higher H₂ and CO contents, PP products have a higher methane content. When a mixture of the two is used, H₂ represents almost half the volume of gas products⁶⁸.

After gasification, the resulting volatiles are subject to a sequence of cleaning operations and treatments to remove solid fractions and contaminants. The clean product can be used for power generation or can be catalytically upgraded to alcohols, such as methanol, that can then be used to

synthetize ethylene and propylene, monomers of the polyolefins studied^{27,69}. There are a few technologies implemented that are capable of converting methanol to a mixture of ethylene and polypropylene through acid catalysis⁶⁹.

Gasification presents an improved flexibility regarding the suitable feedstocks, but it is also a very complex process, mainly regarding the subsequent treatment operations that are required to obtain an uncontaminated gas product and convert it to the monomers for secondary polyolefin production, making it an expensive and uncompetitive technology, when comparing to pyrolysis for example^{42,54}.

There are other technologies suitable for converting polyolefins to chemical feedstock, but are further away from large-scale implementation, due to high implementation costs. These include hydrocracking, liquefaction, microwave, and ultrasound assisted cracking^{27,44,54}.

Depolymerization

While depolymerization is widely used through various mechanisms in polymers such as PET, depolymerization of polyolefins is not a commonly used or even a viable process, in most cases, because they are characterized by being chemically inert apolar polymers with extremely high activation energies to be depolymerized into their monomers^{70,71}.

Attempts were made to depolymerize PE through thermolysis in an induced coupled plasma reactor, reaching only 25% selectivity towards ethylene, while propylene selectivity reached up to 92% under certain conditions, using an induced coupled plasma reactor⁷². The same type of apparatus was used for PP depolymerization with a 94% yield⁷³, but the economic feasibility of the process was not demonstrated. More recently, PE was also treated through a cold plasma process using a zeolite catalyst but resulted in similar ethylene recovery to that of coupled plasma thermolysis⁷⁴.

Other approach researched is cross-alkane metathesis using a tandem catalyst, leading to the conversion of HDPE to small alkanes, liquid fuels, and waxes⁷⁵, being a form of downcycling rather than recycling. As an alternative, *Arroyave et al.* proposed the use of an Iridium based catalyst to partially dehydrogenize HDPE, which would then go through cross metathesis. The resulting oligomers can be hydrogenated to allow for repolymerization. Nevertheless, the repolymerization to a linear polymer, which would be the case of HDPE, showed poor mechanical properties⁷⁶.

1.3.4.2. Mechanical recycling

Mechanical recycling is the recycling process with higher readiness level, and it allows the recovery of the polymer itself rather than its degradation into polymer precursors. Polyolefins from packaging waste are widely treated through this method, but other products are rarely mechanically recoverable due to the presence of additives that compromise the process^{54,77}.

In general, mechanical recycling includes various steps: i) separation and sorting, that can be done according to multiple properties, with the aim of obtaining single polymer streams; ii) washing, for contaminant removal, and iii) compounding and/or pelletizing^{27,77}. After this, the polymers can usually be reprocessed through the same technologies used for the virgin materials, as described in section 1.2.3. A simple schematization of the overall mechanical recycling process is shown in Figure 9.



Figure 9 - Mechanical recycling of plastic waste²⁷.

This technology, however, faces multiple challenges regarding the quality of the recycled plastics. On the one hand, the input material, even if consisting of only one polymer, can have a wide range of properties such as molecular weight and crystallinity, and may contain various additives that are not possible to be removed with the common pretreatments implemented. Thus, the final product will be a recyclate with the average properties and additives contained in the feed stream^{16,36,42}. Furthermore, plastics will be subject of some degradation over reprocessing cycles. In the case of polyolefins, degradation happens when the polymer suffers radical attack, and can lead either to cross-linking, chain-scission or formation of alcohols, aldehydes and ketones through reactions with oxygen-based radicals⁷⁸. These mechanisms often lead to modifications in the properties of the polymers, affecting its molecular weight and thus its melt flow index and viscosity, as well as their mechanical properties.

In the reprocessing of iPP through injection moulding, it was observed that although the chemical structure was not compromised over 10 cycles, the melt flow index increased, implying a reduction in the molecular weight of the polymer. Other properties such as the melting temperature, the crystallinity, the elastic modulus and the yield stress saw an increase in their values⁷⁹. HDPE seems to be more prone to chain branching, leading to an increase in molecular weight and decrease in melt flow index over reprocessing cycles, while the mechanical properties change to a stronger and less ductile material⁸⁰. The secondary materials can be tuned to some extent by blending them with virgin materials of different grades, but this approach has limitations. For example, the melt flow index has a high impact on the processability of the polymers, and its increase can ultimately make it impossible to continue to reprocess the polymer⁸¹.

Mechanical recycling also has severe limitations when it is not possible to completely sort the different polymers, as in the case of multilayer materials. These are only treatable by mechanical recycling if the different polymers are miscible between them, which is rarely the case. Regarding polyolefins, for example, PE is not significantly miscible common polymers other than itself, and the same is true in the case of PP³⁴. Although this process is suitable only for high purity streams and the recyclates may have some limitations regarding their end uses, it allows to eliminate the polymerization step, as opposed to chemical recycling, and leads to a significant reduction in the energy usage and greenhouse gas emissions, comparing to the production of virgin HDPE or PP⁸².

1.3.4.3. Physical recycling

Physical recycling includes solvent-based processes where the polymers are recovered without suffering degradation or structural modifications, resulting in a recycled plastic with essentially the same properties as the pristine material. This can either be accomplished through supercritical fluid extraction or selective dissolution and precipitation^{54,83}.

Supercritical fluid extraction

This process aims at the removal of contaminants or impurities from post-consumer plastics, taking advantage of the improved mass transfer allowed by the use of solvents in their supercritical state to efficiently penetrate the polymer matrixes⁵⁴. Its overall readiness level is still low, and there are few examples of its application to polyolefins recycling, but it was recently patented by The Procter & Gamble Company the purification of PP or PE with supercritical butane or pentane⁸⁴.

Dissolution/precipitation

The concept of dissolution and precipitation processes relies on the separation of a target polymer from a mixture of plastics through its selective dissolution. When the target polymer is dissolved, the solution can be filtered, thus separating it from the other polymers or compounds that are not soluble in the chosen solvent. A second step consists of the precipitation of the polymer, converting it back to a solid plastic, through the addition of an antisolvent that lowers its solubility, or by lowering the temperature to the point where the polymer is no longer soluble. Furthermore, it allows the removal of certain additives or impurities, in one of two ways: either the polymer is solubilized, and the additive remains solid, allowing it to be removed through filtration, along with other solid polymers, or the additive is also soluble, but the antisolvent causes the precipitation of the pure polymer^{27,54,85}. By successively employing this process to different target polymers of a mixed stream, it is possible to efficiently recover each one, which can be particularly important in cases where typical sorting is not possible, such as multilayer films³⁴. Figure 10 presents a general scheme of a dissolution-precipitation process.



Figure 10 - Scheme of a dissolution-precipitation process (Illustration built with BioRender).

This technology results in the recovery of plastic materials without prejudice to its pristine quality and can be applied to a wide range of polymers, as long as suitable solvents are used. In this sense, it has the potential to fulfill a gap within the available techniques for polyolefin recycling, eliminating the need for feedstock conversion and further repolymerization, and resulting in materials of better quality that those produced by mechanical recycling. In fact, the interest in these processes has increased exponentially in the last decade, as the number of publications referring to "plastic recycling dissolution" in the Web of Science Core Collection⁸, shown in Figure 11, reflects.



Figure 11 - Number of publications related to "plastic recycling dissolution" per year found in the Web of Science Core Collection up to July 2023⁸.

Being the focus of the present work, a more detailed analysis of dissolution-precipitation treatment for HDPE and PP will be conducted in the next section, as well as some theoretical background and other useful considerations.

1.4. Dissolution and precipitation processes for plastic recovery

1.4.1. Background on polymer dissolution and solubility

1.4.1.1. Insights on polymer dissolution

The dissolution of polymers is greatly different from that of other materials, and it is consensual that the process is led by two main transport phenomena: the diffusion of the solvent and the disentanglement of polymer chains. Normal polymer dissolution involves a prior formation of a gel layer, caused by the diffusion of the solvent into the polymer and its consequent swelling. When this layer is not formed but the polymer is dissolved, it is considered that it happened trough cracking of the polymer structure^{86,87}.

During normal dissolution, a more detailed division of layers with different characteristics can be made. Adjacent to the solid polymer, an infiltration layer is formed, by the penetration of the solvent in the gaps of the polymer structure. With the increased diffusion, the polymer chains are pushed to the solvent, and a second adjacent layer is formed, the solid swollen layer. The swollen polymer then changes to a rubbery consistency, forming the gel layer, closest to the solvent. Over time, an equilibrium is attained, ceasing the growth of the swollen and gel layers, and the polymer is dissolved⁸⁸.

Several experimental studies were conducted regarding which parameters influence the dissolution of polymers and their rate, besides the solvent-polymer affinity. Although no specific information was found regarding the dissolution mechanism of polyolefins, the influence of certain parameters is often taken as universal for all polymers. Molecular weight was found to be an important property, with its increase improving the degree of chain disentanglement, and thus, the dissolution rate⁸⁹. Other factors include polydispersity⁹⁰, the stereochemical conformation of the polymer⁹¹, the size of solvent molecules⁹², and the stirring speed of dissolution process⁸⁸.

1.4.1.2. Polymer dissolution models

Various models attempted to describe the behavior that is experimentally observed during polymer dissolution. Nevertheless, this is a complex process, sometimes difficult to analyze due to the inherent complexity of polymeric structures, and no universal, completely satisfactory model has been proposed so far. Overall, these models can be divided in five main approaches: phenomenological models based on Fickian equations, external mass transfer models, stress relaxation models, anomalous transport and scaling laws models, and continuum framework models⁸⁶.

Phenomenological models use Fickian equations and representative boundary conditions to physically describe the dissolution of polymers. The first of these models was proposed by Tu and Oano⁹³. It assumed one-dimensional diffusion and considered two boundaries: liquid-gel and gel-glass, leading to the conclusion that the dissolution process could be controlled either by diffusion of the solvent in the polymer matrix or by the dissociation rate of the polymeric chains, although this last step was not studied. This model lacks to consider the reptation time, the time required for the polymer chains to

disentangle and that can be responsible for a certain offset in the dissolution time⁹³. Posterior phenomenological models started to take into account the reptation time, as well as the dynamics of disengaging polymer chains from the gel layer into the liquid layer, which was found to be a possible controlling factor for dissolution. Further studies included considerations on the impact of particle size and on the presence of residual solvent on the polymeric structure^{94,95}. Only recently the specific situation of semicrystalline polymers was addressed, adding a step related to the decrystallization of the polymer, and modeling polymer particles as non-uniform structures with different properties⁹⁶.

External mass transfer models are based on the assumption that the resistance to mass transfer of the layer closest to the polymer is the controlling parameter in dissolution. Different studies conducted on this subject reached the conclusion that the thickness of the gel layer increases with time, not in a linear way but as a function of its square root^{86,97}. These models did not include an explanation of the offset time necessary before swelling⁸⁷.

Stress relaxation models, as the name indicates, focus on the relaxation of polymer chains as response to solvent uptake. These assume the solvent flux can be described by the polymer concentration, the stress in the system, and the osmotic pressure, and that the dissolution happens in two steps: the swelling of the polymer and its disengagement, associated with the reptation time. Nevertheless, there is no evidence of experimental validation of these models, that were mostly abandoned^{86,87}.

Scaling laws have been used to describe the reptation of polymers, by considering that the disentanglement happens at a rate given by the ratio between a characteristic dimension and the reptation time, which depends on the solvents diffusion coefficient. This model takes the solvent concentration on the polymers surface as a critical parameter for its effective penetration⁹⁸. Another approach is to consider a "dissolution clock", initially set to zero, and that starts counting when the critical solvent concentration is reached in a certain point of the polymer. When the clock reaches the reptation time, the respective polymer point is dissolved⁹⁹. Although these models are intuitive, they lack to consider viscoelastic effects during polymer dissolution⁸⁷.

Continuum framework models have the advantage of considering that the viscoelastic behavior of the polymer, and thus the conformation and mobility of its chains varies between the different steps of dissolution. Narasimhan and Peppas developed a model for polymer dissolution, both for glassy and rubbery polymers, by considering three different regimes^{100,101}. On a first step, the solvent penetrates the polymer matrix, causing its swelling and transition from glassy to rubbery state, if it is the case. This was considered the concentrated regime, being described by Fickian laws, which account for the variation in the viscosity depending on the concentration of solvent in the polymer. When the concentration increases to a critical value, the polymer chains begin to disentangle, in the semi-dilute regime described by transport laws, based on diffusion phenomena. When disentanglement is complete, the polymer is dissolved, passing to a dilute regime, where its chains move freely in the solution^{100,101}. This is the most complete model for polymer dissolution, but it still faces some limitations, mainly considering that few of the polymer's properties are taken into account, and that other factors known to influence dissolution time, such as stirring, are not considered.
Although the modelling of the dissolution itself has not been in the research priorities in the last years, the focus has been on understanding the viscoelastic properties of the solutions attained. In plastic recycling applications, that include operations such as filtration and centrifugation, the viscosity of polymer solutions plays a major role on the processes. The higher the concentration of the polymer in the solution, the higher the degree of entanglement observed in its chains, thus leading to an increase in viscosity. But the polymer conformation and solutions' viscosity can also vary with the shear rate applied to the solution, which increase leads to stretching of the chains, the molecular weight of the polymer, and the affinity towards the solvent^{102,103}.

1.4.1.3. Thermodynamic predictive models for polymer solubility

The solubility of a polymer widely depends on its affinity towards the solvent. The most common rule of thumb is that "like dissolves like", as compounds with similar structures tend to interact similarly regarding intermolecular forces^{86,87,104}.

The thermodynamics of polymer dissolution relies on the free energy of mixing, ΔG_m , given by equation (1), where ΔH_m is the enthalpy of mixing, ΔS_m the entropy of mixing, and T the temperature.

$$\Delta G_m = \Delta H_m - T \Delta S_m \tag{1}$$

For a mixing process, inherent to dissolution, to happen spontaneously, the free energy of mixing must take a negative value. In these processes, the entropy of mixing is usually positive but low, due to the low mobility of polymer chains, meaning that the enthalpy will be the most determining parameter, and should be negative or lower than the entropy term^{86,105}. This term is commonly positive, corresponding to a comparative measure of the intermolecular interactions between polymer molecules and between a polymer and a solvent molecule¹⁰⁵. Thus, the solubility of polymers is often greatly impacted by temperature⁸⁶.

Solubility parameters

Aiming to describe and predict the enthalpy of mixing of two substances, various solubility parameters have been defined. The first of those was proposed by Hildebrand, which is defined based on the ratio between the cohesive energy, directly related to the energy of vaporization (E), and the molar volume (V), as described in equation (2)¹⁰⁶. According to this definition, the enthalpy of mixing is proportional to the square of the difference between the Hildebrand solubility parameters of the solvent and the polymer, meaning that those values must be similar for a polymer to be soluble in the considered solvent¹⁰⁶. Nevertheless, this parameter does not consider the hydrogen bond interactions that the compounds can establish, the volume change during mixing, as well as temperature and crystallinity effects¹⁰⁷.

$$\delta = \sqrt{\frac{E}{V}}$$
(2)

Hansen solubility parameters were proposed as an extension and improvement of the Hildebrand solubility parameter, and divide the cohesive energy in three different factors, representing nonpolar interactions, δ_D , permanent dipole-dipole interactions, δ_P , and hydrogen bonding, δ_H . These values are reported for the most common compounds, but they are commonly estimated for other substances according to group-contribution methods, especially for polymers, which experimental determination of vaporization energy is not possible. In this case, a solvent can dissolve a polymer if its solubility parameters, placed in a three dimensional referential, are within a sphere centered in the polymer's Hansen parameters and with radius R₀, tabulated in literature. This is described by equation (3), and it is important to note that the dispersion or non-polar interactions have twice the impact of the remaining terms^{108,109}. Although these are more accurate than the Hildebrand parameter, often show significant deviations from reality. The hydrogen bonding ability description is still insufficient, as there is no differentiation between donor and acceptor compounds, and are estimated for ambient temperature, requiring sometimes complex correction for higher temperatures. It also lacks to consider the structure of the polymer^{87,110}.

$$R_a^2 = 4(\delta_{D,p} - \delta_{D,s})^2 + (\delta_{P,p} - \delta_{P,s})^2 + (\delta_{H,p} - \delta_{H,s})^2 < R_0^2$$
(3)

Conductor-like screening model for realistic solvents (COSMO-RS)

In light of the severe limitations faced by the previous models, the use of computational strategies for more accurate estimations of polymer solubility has been receiving increased interest. COSMO-RS (Conductor-like screening model for realistic solvents) allows to approach this issue based on statistical thermodynamics while taking into account the temperature effect and has been successfully applied to polymer-solvent systems in various recent works. Two main approaches are used: activity coefficient at infinite dilution and iterative calculation of the maximum solubility. On one hand, the ability of a solvent to dissolve a certain polymer can be assessed based on the activity coefficient at infinite dilution^{111,112}. for which values lower than 1 indicate that dissolution may occur. This model also allows the quantitative calculation of the polymer's solubility in a given solvent. Although these values may show deviations from reality, because the calculations are sensitive to input parameters such as the enthalpy of melting, the melting temperature, the density, and the molecular weight of the polymer, which are not common to all grades of the same polymer, it has been shown to provide good estimations by different works¹¹³⁻ ¹¹⁶. These calculations can either be performed with the COSMO-RS model or the COSMO-SAC model, which shares the principles but consists of a variation that accounts for the indistinguishability of surface segments between molecules of the same species¹¹⁷. Nevertheless, both follow the same general methodology for the calculation of properties. All properties are calculated based on the chemical potentials of the molecules involved. For pure components, these are obtained from the respective σ profiles, that represents the probability of a surface point having a certain charge density^{118–120}. From the chemical potentials, it is possible to calculate also the activity coefficient, γ_i^{crs} , defined as shown in (4), where μ_i^{pure} is the chemical potential of the pure compound in the liquid phase and μ_i^{solv} in a liquid solution, R is the gas constant and T the temperature¹²¹. In the case of solutions, a combinatorial term is necessary to correct the activity coefficient according to the entropy of the solution. This term is of increased importance for polymer calculations, given their large volumes, and the specific combinatorial term γ_i^{fv} is given by (5), where ϕ_i^{fv} is the volume fraction. The activity coefficient, in this case, is given by the sum of both contributions, as in equation (6)¹²².

Below the melting temperature of the polymer, its solubility is given by equation (7), depending from the enthalpy of fusion ΔH_{fus} , the melting temperature T_m , the dissolution temperature T, and the heat capacity ΔC_p . To reach a final estimation of the solubility, in molar fraction, its value is calculated iteratively, along with the activity coefficient, given their interdependence¹²¹.

$$\gamma_i^{crs} = \exp\left(\frac{\mu_i^{solv} - \mu_i^{pure}}{RT}\right)$$
(4)

$$\ln(\gamma_i^{fv}) = \ln\left(\frac{\phi_i^{fv}}{x_i}\right) + 1 - \frac{\phi_i^{fv}}{x_i}$$
(5)

$$\ln(\gamma_i) = \ln(\gamma_i^{crs}) + \ln(\gamma_i^{fv})$$
(6)

$$x_i^{SOL} = \frac{1}{\gamma_i} \exp\left(\Delta H_{fus} \frac{\frac{1}{T_m} - \frac{1}{T}}{R} - \Delta C_p \frac{\ln\left(\frac{T_m}{T}\right) - \frac{T_m}{T} + 1}{R}\right)$$
(7)

1.4.2. Dissolution and precipitation of HDPE and PP

1.4.2.1. Solvents and antisolvents state of the art

The dissolution and precipitation of HDPE and PP has been studied in previous works with resource to various solvents and antisolvents. These, as well as the significant conditions used in the process, are summarized in Table 2.

$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	Reference	Year	Polymer	Solvent	Temperature	Concentration	Time	Antisolvent	Antisolvent/
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$\begin{array}{ c c c c c c } \hline PP & 135^{\circ}C \\ \hline 127 & 2007 & HDPE \\ PP & Xylene & 110^{\circ}C & 5-20 wt% & 30 & n-hexane & 3/1 & min \\ \hline 178 & 2008 & HDPE & Toluene & 110^{\circ}C & 0.05 kg/L & 30 & n-hexane & 3/1 (vol) & min \\ \hline 179 & 2012 & HDPE & Toluene & 100^{\circ}C & 7 wt% & NA & n-hexane & NA & \hline Toluene/ & 98^{\circ}C & Petroleum Ether & C (PetE C) & \hline PP & Toluene / 105^{\circ}C & \hline Toluene/ & 98^{\circ}C & Petroleum Ether & C (PetE C) & \hline PP & Toluene / 100^{\circ}C & 0.5 - 25\% & 15 & n-hexane; & 1/1 & \hline Turpentine & 100^{\circ}C & 0.5 - 25\% & 15 & n-hexane; & 1/1 & \hline Turpentine & 100^{\circ}C & 0.5 - 25\% & 15 & n-hexane; & 1/1 & \hline Turpentine & 118^{\circ}C & \hline & & & & & \hline & & & & \hline & & & & & \hline & & & & & \hline & & & & & & & & \hline & & & & & & & & \hline & & & & & & & & \hline & & & & & & & & \hline & & & & & & & & \hline & & & & & & & & & \hline & & & & & & & & \hline & & & & & & & & \hline & & & & & & & & \hline & & & & & & & & \hline & & & & & & & & \hline & & & & & & & & & \hline & & & & & & & & & \hline & & & & & & & & & \hline & & & & & & & & & \hline & & & & & & & & \hline & & & & & & & & & \hline & & & & & & & & & \hline & & & & & & & & & \hline & & & & & & & & & \hline & & & & & & & & & \hline & & & & & & & & & \hline & & & & & & & & & \hline & & & & & & & & & \hline & & & & & & & & & \hline & & & & & & & & & \hline & & & & & & & & & & \hline & & & & & & & & & & & \hline & & & & & & & & & & \hline & & & & & & & & & & & \hline & & & & & & & & & & & & & \hline & & & & & & & & & & & & & \hline & & & & & & & & & & & & & & & & & \hline & & & & & & & & & & & & & & & & & & \hline & & & & & & & & & & & & & & \hline &$	126	2001	LDPE	Xylene	100°C	10% w/v	1 hr	1-propanol	3/1 (vol)
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min ¹¹⁶ 2023 LDPE Dodecane 120°C NA 1 hr 2-propanol NA PP Tetrahydropyran 88°C Evaporation	135	2022	HDPE	D-limonene	110°C	0.02 kg/L	30	Glycerol	3/1
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PP Tetrahydropyran 88°C Evaporation	116	2023	LDPE	Dodecane	120°C	NA	1 hr	2-propanol	NA
			PP	Tetrahydropyran	88°C			Evaporation	

 Table 2 - Experimental dissolution and reprecipitation conditions reported for the recovery of HDPE and PP.

 (NA stands for "not available").

Toluene^{113,114,124,127–129,134} and xylene^{125–128,131,132} are the most commonly used solvents for such processes, although a set of studies from *Hadi et al.*^{129–131} focused on the use of petroleum ether-based solvents. Further deviation from the traditional solvents was only found in 2022, in the work of *Ferreira*

*et al.*¹³⁵, that used d-limonene, a biobased solvent. Nevertheless, this study focused on the dissolution of HDPE to recover colorants from plastic, while the extent to which the plastic was recovered was not extensively accounted for. In another study, p-cymene, was found to be a solvent for LDPE and PP, but was not studied for HDPE dissolution¹³³. Acetone^{113,114,124,132–134} and n-hexane^{127–131} are the usual choices for antisolvents.

1.4.2.2. Large-scale implementation

The suitability of dissolution-precipitation processes for large-scale implementation has been proved by various companies.

Creacycle GmbH is responsible for the *CreaSolv* process, which has been applied to different plastics in various projects and pilot units¹³⁶. Projects treating polyolefins include the Unilever pilot plant, for PE sachets¹³⁷, the *Multicycle* project, for separating PE, PP, PA (polyamide) and PET from both packaging and end-of-life vehicles¹³⁸, and the *Circular Packaging* plant, for recycling of PE and PP from multilayer films¹³⁹. Additionally, the *NONTOX* project focus on the recycling of hazardous waste from electronics, vehicles and construction¹⁴⁰. The composition of the solvents and antisolvents used is not publicly available.

*Newcycling*¹⁴¹ and *PureCycle*¹⁴² detain two similar processes for recycling of LDPE and PP, respectively.

1.4.2.3. Technical and economical bottlenecks

Although dissolution-precipitation seems to be a promising option for treating various types of plastic waste, mainly polyolefins, whose chemical recycling is especially difficult, it would greatly benefit from improvement in certain aspects.

Firstly, most reported works on the recovery of HDPE through this process make use of toluene or xylene. Both are produced by refining fossil fuels¹⁴³, are considered hazardous air pollutants¹⁴⁴, and harmful to the human health and aquatic life^{145,146}. Thus, they are considered problematic solvents according to solvent selection metrics based on environmental, health and social impact¹⁴⁷, and there is an increasing need to replace them by greener, natural, and less hazardous solvents. Also, acetone, one of the most common antisolvents, is considered problematic by some associations, and thus the shift to other compounds would be preferred, such as alcohols¹⁴⁷.

From the economical point of view, the employment of this technology may be limited, since the estimations of the minimum selling price point to a higher value than that of the virgin polymer, which in the case of HDPE is greatly influenced by the yield of recycled solvent. Both from the economic and energetic point of view, the major contributions come from the solvent and antisolvent, and from the energy required to separate both compounds⁸². Greenhouse gas emissions are also mostly related to the recovery of the solvent^{82,138}.

2. Motivation

Plastic waste has become a topic of serious concern, especially over the last decades, and strict ambitious targets to reduce its generation and limit the consequential environmental impact have been defined to 2030 and 2050. Thus, a shift towards a circular value chain is urgent, which requires a steep increase in recycling rates, articulated with more efficient collection and sorting of mixed waste streams, ultimately leading to the minimization of virgin plastic production from fossil fuels derivatives.

Within the global plastic scenario, polyolefins are one of the most concerning types of plastic. They represent the largest share of plastic consumption and plastic waste generation, are often used in consumer goods such as packaging applications, but their recycling options are particularly limited. Chemical recycling processes for these plastics are very complex and energy demanding, and require further treatment, as it is not possible to depolymerize PE and PP to their monomers with good yields. Mechanical recycling has been the preferred option, but it is not suitable for complex mixed streams that do not allow efficient sorting, such as multilayer films, and this type of reprocessing is unable to eliminate certain additives and impurities that lead to a final product with lower quality than the pristine.

Dissolution-precipitation seems to be one of the most promising options for recycling polyolefins, however current processes and studies still face some issues, such as the use of hazardous and fossil fuel-based solvents, that may inclusively hinder the use of the recycled plastics for some applications, and the high energy requirements of solvent recovery.

This work aims to contribute to fill in some of these gaps, by screening and testing natural and greener solvents for the dissolution of HDPE and approaching the influence of the antisolvent selected on the quality of the recovered polymer as well as on the simplicity of solvent recovery and respective quantitative yield. The suitability of the optimized system for PP dissolution-precipitation will also be assessed, as well as the hypothesis of using this process to separate HDPE and PET from a mixed stream.

3. Materials and Methods

3.1. Materials

HDPE was used in the form of commercial clear fruit bags, obtained from *Continente* supermarkets. Isotactic PP was used in the form of clear punched pockets from *Note*, and PET as clear water bottles from *Luso*.

The compounds used as solvents and antisolvents for the dissolution and precipitation of HDPE (and PP) are listed in Table 3. They were all purchased from commercial sources, with exception of limonene rich extract, which was provided by *Sumol-Compal*, as a subproduct of mechanical processing of orange peels and subject to purification through steam distillation, followed by fractioned distillation, thus obtaining pure limonene; and bidistilled water, which was attained from the purification system *BioSan Labaqua Trace*, with a resistivity of 18.2 M Ω /cm. Table 3 also presents an indicative price of each compound, as retrieved from the *Merck* website¹⁴⁸.

For the separation of HDPE and PET, PET was dissolved with a thymol:carvacrol NaDES (Natural Deep Eutectic Solvent), compounds also listed in Table 3.

	Solvent	C 4 S	Purity (mass	Sourco	Price (f/kg)
	Solvent	CAS	fraction)	Source	Fille (e/kg)
	Limonene			Sumol-Compal	78.04
	(1S)-(-)-α-pinene	7785-26-4	98%	Thermo scientific	64.5
/ent	p-cymene	99-87-6	>95%	Fluka	61.5
Solv	Squalane	111-01-3	>98%	TCI	406
	Thymol	89-83-8	99%	Sigma-Aldrich	426
_	Carvacrol	499-75-2	NA	Thermo scientific	352
	Ethanol	64-17-5	96%	LABCHEM	2.82
	2-propanol	67-63-0	>99.9%	Carlo Erba	66.24
	1-butanol	71-36-3	99.5%	Sigma-Aldrich	51.36
ť	1-octanol	111-87-5	99%	Alfa Aesar	154.78
Ive	1,2-propanediol	57-55-6	>99%	Fischer scientific	31.57
ntisc	1,2-butanediol	584-03-2	>98%	Sigma-Aldrich	65.71
- A	Glycerol	56-81-5	>99%	Alfa aesar	36.80
	Ethylene glycol	203-473-3	>99.5%	Carlo Erba	57.86
	Diethylene glycol	11-46-6	99%	Sigma-Aldrich	34.78
	Triethylene glycol	112-27-6	99%	Sigma-Aldrich	34.31

 Table 3 - Identification, purity, source, and indicative price of solvents used for HDPE dissolution and precipitation.

3.2. Experimental methods

3.2.1. Dissolution and reprecipitation

The polymers used were previously cut into quadrangular pieces, with a side length of approximately 0.5 cm. Polymer dissolution was carried out at different concentrations by heating the mixture in an oil bath at a controlled temperature, and a stirring speed of 400 rpm. After complete dissolution, the clear solution was removed from the heating bath, the antisolvent was added and the flask was vortexed, promoting the precipitation of the polymer. The obtained mixture was then filtered under vacuum, and the resulting polymer flakes were dried in an oven at 80°C for 48 hours.

The dry polymer was then grinded, washed with ethanol (in the case of HDPE and PP), and dried for 48 hours. After that time, the percentual recovery of polymer was determined through gravimetric measurements.

3.2.1.1. HDPE and PET separation

The separation of HDPE and PET was performed from a solid mixture containing equal mass of both polymers. HDPE was selectively dissolved first, at the optimized conditions studied in this work, following the same procedure as described above. The mixture was then filtered through a 2 mm mesh filter, retaining the solid PET, and allowing the solubilized HDPE to pass. Afterwards, the anti-solvent was used to precipitate and recover HDPE.

PET was washed and dried at 40°C. It was then dissolved and recovered following the procedure described by *Pestana et al.*¹⁴⁹. The solvent, a NaDES composed of thymol and carvacrol in equimolar proportions, was prepared by heating the mixture of the two compounds up to 80°C for 1 hour, after which the obtained clear solution was slowly cooled. The PET dissolution was done at the 1/10 mass ratio between polymer and solvent, at 150°C for 7 min., and a mixture of ethanol (60 v/v%) and water was used as antisolvent. The drying steps were performed at the same conditions used for HDPE (80°C for 24 hours), but the washing agent used was water.

3.2.2. Solvent recovery

For the solvent's recovery, water was added to facilitate the phase separation, according to the ternary liquid-liquid equilibrium diagrams estimated in COSMO-RS. The resulting mixtures were centrifuged at 5000 rpm for 20 minutes, on a *VWR CompactStar CS 4* centrifuge. The percentual recovery was calculated by weighting.

3.2.3. Fourier Transform Infrared spectroscopy

Attenuated total reflectance – Fourier transform infrared (ATR-FTIR) spectroscopy was used to evaluate the integrity of the recovered polymers and solvents, in comparison with the pristine materials. A *PerkinElmer UATR Two* spectrometer with a diamond crystal was used, and the analysis was carried out in the range between 4000 and 400 cm⁻¹, based on the accumulation of 8 scans with a resolution of 4 cm⁻¹.

3.2.4. Differential Scanning Calorimetry

Samples of the recovered polymers were analyzed through differential scanning calorimetry (DSC), to assess changes in the main thermal properties of the polymer due to the dissolution and precipitation process. The equipment used was *DSC 200 F3* from *NETZSCH*, in which two sequential heating-cooling cycles were performed, between 20 and 250°C, at a heating/cooling rate of 10°C/min, and with a nitrogen flow rate of 50 mL/min. In the case of PET, the temperature range was 20 to 300°C. The melting and crystallization points and the enthalpy of fusion were determined based on the second cycle, as the first cycle had the function of eliminating the thermal memory of the polymer and removing possible impurities.

While the melting and crystallization points correspond to the temperature at which the heat flow reaches its minimum or maximum value, respectively, the enthalpy of fusion is the area of the melting peak, observed in the heating cycle. This value was used to estimate the percentage of crystallinity of the polymers, according to equation (8), where ΔH_f is the enthalpy of fusion measured, and $\Delta H_{f,c}$ is the enthalpy of fusion of the completely crystalline polymer. This value is reported as 293 J/g for PE, 165 J/g for PP and 140 J/g for PET¹⁵⁰.

$$\%C = \frac{\Delta H_f}{\Delta H_{f,C}} \times 100 \tag{8}$$

3.2.5. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was used to quantify solvent residues present in the recovered polymers. The weight loss of the samples was analyzed in *HITACHI's* thermal analysis system of the model *STA7200*, between 35 and 600°C, at the heat rate of 10°C/min, in a nitrogen atmosphere (with a flow rate of 200 mL/min).

3.2.6. Nuclear Magnetic Resonance spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy was used to conclude the recovered solvent integrity and purity. ¹H and ¹³C spectra were recorded in a *400 Ultrashield*TM spectrometer, by *Bruker*, at 25°C, using deuterated chloroform as solvent.

3.3. Computational methods

3.3.1. Solvent screening on COSMO-RS

The software COSMO-RS, from *Amsterdam Modelling Suit 2023* (AMS), was used to calculate the predicted solubilities of HDPE and PP in various solvents, as well as the solubility of the solvents in the antisolvents, and the ternary liquid-liquid diagrams relative to solvent recovery. Each compound or molecule used is represented by a file containing data on the respective charge density distribution. These files are available in the COSMO-RS database for some molecules, but otherwise the molecule can be built and optimized using the ADF (Amsterdam Density Functional) environment, as was the case of HDPE, PP, and some of the solvents screened (3-carene, β -caryophyllene, farnesane, farnesene, sabinene and squalene).

ADF is based on the Kohn-Sham density functional theory (DFT), using a fragment-oriented approach to compute the electronic configuration of molecules, which analysis can provide accurate estimations of various chemical properties^{151,152}. ADF calculations are made through various basis functions, which need to be carefully chosen. On one hand, the basis functions are Slater-type orbitals, which quality ranges from single to quadruple zeta (exponential factors that are included in the function) and have various polarization functions. In this work, TZP86 was selected as basis-set, a triple-zeta function in the valence region and double-zeta in the core region, that includes an additional polarization function¹⁵³. In addition to the basis-set, the density functional, or exchange and correlation functional (XC), also needs to be selected. These can either correspond to local density approximations (LDA), depending only on the spin density in each surface point, or can contain an additional generalized gradient approximation (GGA), which depends also on the derivatives of the charge density¹⁵². GGA:BP86 was used as density functional, comprising an exchange correction developed by Becke¹⁵⁴, and a correlation correction by Perdew¹⁵⁵. The parameters used correspond to those suggested for the simulation of PE by the AMS tutorials¹⁵⁶.

After inputting the chemical structure of the intended compound in the ADF environment, the Geometry Optimization of the structure is performed, using the parameterization described above. The optimized geometry will be that which results in the minimum total energy of the system. In the case of the polymers, to facilitate the convergence of the geometry optimization task, a pre-optimization was performed through the Universal Force Field (UFF) engine.

COSMO-RS allows to define a compound as polymer, with a certain molecular weight, and thus there is no need to simulate the molecule as a large polymeric chain. Instead, a trimer was built, with two additional methyl groups at the ends. In this case, the calculations are performed based solely on the most central monomer, as a way to minimize the influence of the end groups on the charge distribution considered.

The simulated molecules were then added to the COSMO-RS calculation environment by generating the respective COSMO-RS files. To improve the accuracy of the calculations, some known

properties were given as input: the melting temperature, T_m , the enthalpy of melting, ΔH_f , and the density, ρ . For HDPE and PP, the properties of a 100% crystalline polymer were used, to account for the worst-case scenario, the situation where dissolution would be the least favorable, and a default molecular weight of 10 kg/mol was considered. The properties considered for the polymers are described in Table 4, and the solvents and antisolvents properties in Table 5.

	ρ (g/cm³) ¹⁵⁷	T _m (°C) ¹⁵⁰	ΔH _f (kcal/mol) ¹⁵⁰
HDPE	1.00	141.4	701.0
PP	0.95	220.0	334.9

Table 4 - Polymer properties considered in COSMO calculations.

		ρ (g/cm³)	T _m (°C)	ΔH _f (kcal/mol)
	Toluene	0.862	-94.9	1.59
	p-xylene	0.861	13.3	4.09
	d-limonene	0.841	-95.5	2.72
	α-pinene	0.858	-62.0	2.73
	p-cymene	0.857	-68.9	2.31
nts	Terpinolene	0.863	-93.3	NA
lvel	γ-terpinene	0.843	-10.0	NA
So	3-carene	0.860	NA	NA
	β-caryophyllene	0.908	NA	NA
	Squalane	0.810	-38.0	12.52
	Squalene	0.858	-75.0	15.98
	Farnesane	NA	NA	NA
	Farnesene	0.834	NA	NA
	Water	0.995	0.0	1.44
	Ethanol	0.790	-114.1	1.19
	1-butanol	0.810	-88.6	2.22
ŝ	2-propanol	0.786	-90	1.62
'eni	1,2-propanediol	1.036	-60	2.01
	1,2-butanediol	1.002	-50.0	NA
ntis	Glycerol	1.260	16.9	4.37
A	Ethylene glycol	1.114	-12.7	2.38
	Diethylene glycol	1.120	-10,2	NA
	Triethylene glycol	1.125	-7.0	NA
_	Octanol	0.826	-14.7	6.04

Table 5 - Solvent and antisolvent properties considered in COSMO calculations^{158,159}.

For further calculations, both the COSMO-RS and COSMO-SAC activity coefficient models are available, each with various sets of parameters resulting from different optimization works. COSMO-SAC DHB¹⁶⁰ was chosen for this work, since it showed good accuracy in the prediction of solubility of apolar compounds, in comparison with the other options. This comparison was made by

calculating the solubility of the solvents used in the screening in water and comparing the respective values with reported experimental values.

3.3.2. Aspen Plus simulation and economical assessment

The dissolution precipitation process developed for HDPE was simulated in *Aspen Plus V11*, in order to estimate the energy requirement and the cost associated with each step, to better evaluate the optimization of the overall process.

The polymer, HDPE, was defined as an oligomer, using C_2H_4 -R as repeating segment. The polymer molecular weight is a required input parameter, which was fixed to the value of 100 kg/mol. The necessary phase equilibria properties for the simulation were estimated using the method POLYUF, which is a modification of the activity coefficient's group contribution method UNIFAC, specifically improved for polymers. The distillation column used to separate water and ethanol was simulated also using the UNIFAC method. Group contribution methods were used due to the lack of adequate data in the available Aspen databases for α -pinene.

The required utilities were defined according to the Aspen templates and attributed to each equipment in a way that the minimum temperature difference of 10°C between streams is respected¹⁶¹. The utilities used were heated air, low pressure steam, cooling water and refrigerating water, being the respective properties defined as presented in Table 6. For estimating the costs associated with utilities, also shown in Table 6, the cost per unit was used as tabulated in literature¹⁶², and the values were actualized to the year of 2023 according to the inflation¹⁶³.

The prices associated with the raw materials were retrieved from the Sigma Aldrich website¹⁴⁸, as presented before in Table 3. The price considered for water was 3 €/kg¹⁴⁸. The conversion between U.S. dollars and euros was done according to the values of July 8th, 2023¹⁶⁴.

	Inlet temperature (°C)	Outlet temperature (°C)	Cost
Air	100	95	0.96 €/m³
Low pressure steam	125	124	5.08 €/GJ
Cooling water	20	25	0.42 €/GJ
Refrigeration water	5	15	5.34 €/GJ

4. Results and Discussion

4.1. Solvent screening in COSMO-RS

The COSMO-RS predictions performed regarding HDPE were based on the simulation of an oligomer with 8 carbon atoms, where only the most central monomer weights in for the charge density distribution calculations, as represented in Figure 12. In this way, it is possible to discard the effect of the end-groups, which represent a negligible weight of a long HDPE chain, thus aiming to minimize errors associated with the different charge density distribution in these groups. Only one conformation of the oligomer was considered, since it was already reported that the benefit attained from taking into account several oligomers is small in comparison with the increase of computational power and time required¹¹⁵.



Figure 12 - Representation of the charge density distribution for the center monomer of an HDPE oligomer, as simulated in COSMO-RS.

The charge density distribution of the molecule can be further analyzed by drawing the respective σ -profile (p(σ)), which defines the probability of finding a surface point with polarity σ , and σ -potential ($\mu(\sigma)$), which can explain the affinity of the molecule towards segments or compounds of different polarity. Both functions regarding HDPE are represented in Figure 13.



Figure 13 - σ -profile and σ -potential of HDPE drawn in COSMO-RS.

The polarity scale used can be subdivided into three different regions: the non-polar region, between -0.01 and 0.01 $e/Å^2$, the hydrogen bond-donor (HBD) region on the most negative range, and

the hydrogen bond-acceptor (HBA) region on the positive (right) end. The σ -profile of HDPE only takes non-null values in the apolar range, revealing the absence of polar segments in the molecule. Furthermore, the σ -potential forms an upwards parabola with minimum on 0 e/Å². The positive and increasing potential values towards the extremes of the polarity range indicate that the establishment of polar interactions is not favorable, either towards HBD's or HBA's¹¹².

Based on the information retrieved from the analysis of HDPE's σ -profile and σ -potential, and in line with the solubility rule of thumb "like dissolves like", a set of apolar solvents were screened by calculating their capability to dissolve HDPE. The selected compounds include several natural and widely available terpenes that are commercialized at prices below 100 €/kg, according to the values available in the Sigma Aldrich website¹⁴⁸. Nevertheless, above this price range, four other compounds, squalane and farnesane, as well as their saturated precursors, squalene and farnesene were added to this screening, given the great similarity between their chemical structures and that of HDPE. The structures of all solvents included in the screening are represented in Figure 14, and their respective σ -profiles in Figure 15. The calculations were also performed for toluene and p-xylene, for comparison purposes, given the fact that they are the most common solvents for HDPE dissolution reported in literature^{113,114,124,127–129,134}.



Figure 14 - Chemical structures of the solvents screened.



Figure 15 - σ -profiles of the solvents screened drawn in COSMO-RS.

From the σ -profiles, it is possible to confirm that the solvents selected are completely non-polar, although HDPE has the narrowest distribution from all the compounds. The solvents whose profile is the most similar to the polymer's are squalane and farnesane, showing only two distinguishable peaks, nearly symmetrical, around 0.001-0.002 E/A² and –(0.001-0.002) E/A². This is consistent with the chemical structure of the compounds, being the only unsaturated solvents considered. Squalene and farnesene show a different distribution, slightly shifted to the left and with a shoulder in the upper region. The remaining solvents, that not only present double bonds, but also have a cyclic structure, have broader probability distributions, in particular in the upper region, closer to the hydrogen bond acceptor range. In comparison with the conventional solvents, toluene and xylene, the most similar profile belongs to p-cymene, which is also an aromatic compound, presenting a sharp peak around 0.006 E/A².

Although the similarities between σ -profiles can provide a first idea on the affinity between compounds, it is based solely on the electronic distribution of the molecules, without considering other physical and thermal properties, nor temperature dependance. Thus, the quantitative solubility of crystalline HDPE in the aforementioned solvents was calculated, at different temperatures below its melting point, leading to the results shown in Figure 16 (and Table 17 in appendix 7.1).

The first observation is that no solvent, including the conventional, was predicted to dissolve HDPE below 120°C. Nevertheless, it was previously reported that HDPE could be dissolved in toluene, xylene, and d-limonene at lower temperatures. This inaccuracy of COSMO-RS may be caused by the dependence between solubility and the melting point and enthalpy of fusion, values which are lower for a semicrystalline polymer, the case of commonly available HDPE samples.

At 120°C, the solubility predicted for toluene and xylene is 12wt% and 1wt%, respectively. The only green solvent studied in this work that approaches these results is α -pinene (1wt%). At 130°C, nevertheless, HDPE was predicted to be soluble in all the screened compounds, except for squalane, squalene, and farnesene. Farnesane was predicted to solubilize HDPE up to 16wt%, and

 β -caryophylene up to 32wt%, while the predictions for all the other terpenes lay between 50 and 60wt%. The fact that the estimated solubility increased steeply between 120°C and 130°C may be due to the proximity to the HDPE melting point defined (140°C), as the calculations depend on the quotient between the two (equation (7)), but it was not possible to infer if any other factors contribute to this predicted behavior.



Figure 16 - COSMO-RS solubility prediction of HDPE in several selected solvents at three different temperatures (110°C, 120°C, 130°C).

The solvents d-limonene, α -pinene, and p-cymene were selected to proceed with the experimental study, based on the promising predicted solubility of HDPE, low price, and wide availability, namely as waste byproducts of existing industries. Limonene is abundantly present in citrus essential oils, that are extracted by mechanical processing of citrus fruits for food products¹⁶⁵, while α -pinene is a by-product of paper pulping and also found in numerous plants and trees¹⁶⁶. p-cymene can be found in essential oils from various natural sources, such as eucalyptus and carrots¹⁶⁷. It was also taken into account that these compounds have similar properties to those of toluene and p-xylene, such as melting and boiling points, density and viscosity. Considering the similarity between the σ -profile of HDPE and squalane, the use of this solvent was also attempted.

4.2. Limonene as HDPE solvent

4.2.1. Optimization of dissolution conditions

The dissolution of HDPE in limonene was already reported by *Ferreira et al.*¹³⁵, up to 2wt%, and under the typical conditions used with toluene, at 110°C and with a minimum dissolution time of 30 minutes. These experimental dissolution conditions were taken as a starting point, but the process still ought to be optimized, namely regarding the polymer content, the temperature, and the dissolution time. Thus, HDPE was dissolved in limonene at temperatures between 100°C and 120°C and starting from different HDPE solid contents, up to 5wt%. The precipitation of the polymer was carried out using ethanol as antisolvent, in a mass ratio of antisolvent to solvent of 2/1.

The use of limonene afforded the complete dissolution of HDPE in the entire range of concentrations selected. The 5wt% HDPE concentration limit was selected since the viscosity of the solutions greatly increased with polymer concentration, causing difficulties in its handling, which would possibly compromise the reliability of the results obtained above this point. The time required for the polymer to be completely dissolved showed no dependence on the initial solid content used, implying that the solvent was far from saturation. Moreover, the dissolution time decreased with temperature increase, taking the average values described in Table 7. In the worst-case scenario, this value did not surpass 7min 30s, which represents a considerable decrease in relation to previously reported works, either using limonene or other solvents, where the mixture is heated during a time period between 30 minutes and 4 hours^{113,114,116,126–128,131,132,134,135}.

Temperature (°C)	Dissolution time (min)
100	7
110	4
120	3

Table 7 - Average dissolution time of HDPE in limonene at different temperatures.

Furthermore, the effects of temperature and concentration were analyzed through the percentual recoveries of the polymer and the solvent, results which are shown in Figure 17 and Figure 18, respectively. The exact values are described in Table 18 in appendix 7.2.





Figure 17 - Recovery yield of HDPE according to concentration and dissolution temperature.

Figure 18 - Recovery yield of limonene according to concentration and dissolution temperature.

Up to 3wt% of HDPE, the polymer recovery was lower at when dissolution takes place at 100°C than at higher temperatures but reaches a plateau at 110°C and 120°C. Above this content, the opposite occurs, and the recovery only increased at the temperature of 120°C. However, regarding limonene recovery, it was reduced when the temperature increases from 110°C to 120°C, except for the lowest concentration tested. Furthermore, above 2wt% of HDPE, the solvent recovery decreased with the increase of the solid content, for all temperatures studied. One probable cause for this steep variation is the fact that at high concentrations the polymer precipitates in visibly larger particles, in which the solvent can be entrapped, hindering its solubilization in the antisolvent. This leads not only to a decrease in the solvent recovery efficiency, but also to a less pure form of recovered HDPE.

Overall, more solvent was recovered at 110°C, temperature at which the polymer yield does not have a significant improvement with the increase of the concentration of HDPE. Taking this into account, the compromise between polymer and solvent recovery yields was found at 110°C and 3 wt%, conditions at which 80.5wt% of the HDPE and 47.3wt% of the limonene are recovered, for an average dissolution time of 4 min.

4.2.2. Antisolvent selection

The influence of the antisolvent used and its ratio to the solvent was studied at the selected dissolution conditions: temperature of 110°C and 3wt% HDPE in limonene. To avoid inconsistencies due to small variations in the time required for complete dissolution between experiments, the dissolution time was fixed at 10 min. Several alcohols were selected for this antisolvent study, with varying chain length, number of OH groups and position of these groups in the molecule. Water was also added to the antisolvents screening.

The recovery of the solvent was achieved by adding water to the solvent-antisolvent mixture, which in most cases allows for the nearly complete recovery of limonene with a high purity, according to the ternary liquid-liquid diagrams calculated by COSMO-RS, and shown in Figure 19 to Figure 27. Two exceptions are the systems composed of 2-propanol (Figure 20) and 1-butanol (Figure 21), in which the addition of water leads to phase separation, but the limonene-rich phase does not have high purity. Limonene is not soluble in water, so no further purification step was needed for its recovery.



Figure 19 - Ternary liquid-liquid equilibrium of limonene, ethanol and water, drawn in COSMO-RS.



Figure 21 - Ternary liquid-liquid equilibrium of limonene, 1-butanol and water, drawn in COSMO-RS.



Figure 20 - Ternary liquid-liquid equilibrium of limonene, 2-propanol and water, drawn in COSMO-RS.



Figure 22 - Ternary liquid-liquid equilibrium of limonene, 1,2-propanediol and water, drawn in COSMO-RS.



Figure 23 - Ternary liquid-liquid equilibrium of limonene, 1,2-butanediol and water, drawn in COSMO-RS.





Figure 24 - Ternary liquid-liquid equilibrium of limonene, glycerol and water, drawn in COSMO-RS.



Figure 25 - Ternary liquid-liquid equilibrium of limonene, ethylene glycol and water, drawn in COSMO-RS.





Figure 27 - Ternary liquid-liquid equilibrium of limonene, triethylene glycol and water, drawn in COSMO-RS.

Figure 28 and Figure 29 present the experimental yields for the recovery of HDPE and limonene, respectively, according to the antisolvent used and the antisolvent/solvent mass ratio. These results are

also described in Table 19 in appendix 7.3. Overall, it is clear that the mass ratio between the antisolvent and the solvent did not have a considerable impact in the recovery of the polymer, causing variations lower than 6wt% in HDPE recovery in most cases. Conversely, the solvent's recovery was much more influenced by this parameter, except for 1,2-butanediol and 1,2-propanediol, in which the average values were nearly constant for all ratios. For the remaining antisolvents, the 2/1 ratio led to the best results, with no significant improvement being observed with the further increase of this parameter. Exception to this was diethylene glycol, for which the 3/1 ratio resulted in a limonene recovery nearly 20wt% above the same value for the 2/1 ratio.



Figure 28 - Recovery of HDPE using different antisolvents and three antisolvent/solvent ratios (1/1, 2/1 and 3/1). (* represents values higher than 100wt%)



Figure 29 - Recovery of limonene using different antisolvents and three antisolvent/solvent ratios (1/1, 2/1 and 3/1). ((a) refers to the cases where it was not possible to attain pure limonene)

However, different antisolvents led to significantly different results, which can be further understood by analyzing the solubility of limonene in each one of these compounds, as estimated at 25°C using COSMO-RS and listed in Table 8. In fact, the highest limonene recovery, above 50wt%, was obtained using ethanol as antisolvent, one of the compounds in which it is most soluble. The HDPE recovery in this case was slightly lower than that for other systems, possibly due to the fact that the affinity of the polymer is higher for the limonene-ethanol mixture than for other systems, eventually limiting the amount that actually precipitates. On the other extreme, for water and glycerol, polymer recoveries above 100wt% were obtained, leading to the conclusion that the solvent was not efficiently removed, due to its lower affinity towards the antisolvent. Coherently, the limonene recovery for these systems was low or even null. As for the 1,2-propanediol antisolvent, intermediate limonene results were obtained, which again is coherent with the partial solubility of 16wt%. For the antisolvents in which limonene is less soluble than in 1,2-propanediol, the relation between the solvent recovery and the solubility is less clear, which may be influenced by slight inaccuracies in the COSMO-RS predictions, given that the values are low and within the same order of magnitude. Nevertheless, the only true exception to the trend is ethylene glycol, in which limonene has a very low solubility according to COSMO-RS calculations but the experimental results are closer to those obtained for 1,2-propanediol.

	Limonene	α-pinene	p-cymene	Squalane
Water	1.5E-03	6.1E-04	1.9E-03	9.9E-16
Ethanol	high	high	high	7.08
2-propanol	high	high	high	high
1-butanol	high	high	high	high
1,2-propanediol	16.19	9.15	21.51	0.05
1,2-butanediol	10.20	6.81	12.77	0.03
Glycerol	1.27	0.71	1.70	0.00
Ethylene glycol	1.02	0.60	1.31	0.00
Diethylene glycol	3.91	2.38	5.05	0.00
Triethylene glycol	7.59	4.62	9.92	0.01
1-octanol	high	high	high	high

Table 8 - Solubility (wt%) of limonene, α-pinene, p-cymene and squalane in the antisolvents selected, as calculated in COSMO-RS.

Overall, it can be concluded that a high solubility of the solvent in the antisolvent used enables a high recovery of the solvent and facilitates its exclusion from the polymer in the precipitation step, allowing for high polymer purity.

4.3. Squalane, α-pinene and p-cymene as HDPE solvents

With a deeper understanding of the parameters that influence the recovery of the polymer and solvent, three other solvents were tested and their performance in HDPE dissolution and precipitation compared: α -pinene and p-cymene, that COSMO-RS calculations predicted to be suitable solvents for HDPE, as seen in section 4.1, and squalane, a compound which structure and σ -profile is similar to that of HDPE.

At 110°C, the temperature used for the dissolution of HDPE in limonene, both α -pinene and p-cymene allowed the complete dissolution of at least 3wt% of HDPE, in around 4 minutes, the same time used for limonene as solvent. Squalane, on the other hand, was not able to dissolve even small quantities of HDPE at the same temperature. At 120°C, the dissolution of 3wt% of HDPE took 6 hours, but this time decreased steeply at 125°C, to 15 min. Thus, although squalane showed capability to dissolve HDPE to a small extent, contrarily to what had been predicted in COSMO-RS, the dissolution only occurred very close to the melting point of the polymer, and thus the observed results may be due to the conjugation of dissolution and melting phenomena.

For HDPE precipitation, in each case the antisolvents used were selected according to the solubility of the solvent in them, to confirm the relationship that was inferred in the case of limonene. The solubilities of each solvent in the antisolvents are presented in Table 8.

Squalane's solubility in any of the compounds screened is much lower than that of the other solvents. In this case, the first experiments were made with ethanol or 1-butanol as antisolvent, but it was observed that the polymer was not dry even after being in the oven for long periods of time, making it clear that the solvent had not been efficiently removed from the polymer particles. Also quantitatively, the mass of the recovered polymer was much higher than the pristine. To find a better solution, 1-octanol was added to the antisolvents tested, since its larger carbonated chain leads to a higher squalane solubility. Nevertheless, the results obtained were not better than for ethanol and 1-butanol, and thus the use of squalane for HDPE dissolution and recovery was discarded. Besides the fact that squalane and limonene are structurally different, and so are the possible interactions between these compounds and the polymer, one more parameter that could lead to additional difficulties in this process is the viscosity of the squalane, which is much higher than that of all the compounds commonly used to dissolve this polymer, and may ultimately compromise the efficiency of the filtration operations and consequently of the solvent's removal¹⁰³.

The solvents α-pinene and p-cymene, on the other hand, have similar properties to limonene, including their solubility in the antisolvents. Here, three different antisolvents were selected for experimental testing, ranging from high to low solubility values: ethanol, in which all three solvents are highly soluble, diethylene glycol, in the opposite extreme, and 1,2-propanediol, as an intermediate case. The addition of water was again found to be a good way to recover the pure solvent, according to the ternary liquid-liquid equilibrium diagrams drawn in COSMO-RS (Figure 30 to Figure 35).



Figure 30 - Ternary liquid-liquid equilibrium of α-pinene, ethanol and water, drawn in COSMO-RS.



Figure 32 - Ternary liquid-liquid equilibrium of α-pinene, diethylene glycol and water, drawn in COSMO-RS.



Figure 34 - Ternary liquid-liquid equilibrium of p-cymene, 1,2-propanediol and water, drawn in COSMO-RS.



Figure 31 - Ternary liquid-liquid equilibrium of α-pinene, 1,2-propanediol and water, drawn in COSMO-RS.



Figure 33 - Ternary liquid-liquid equilibrium of p-cymene, ethanol and water, drawn in COSMO-RS.



Figure 35 - Ternary liquid-liquid equilibrium of p-cymene, diethylene glycol and water, drawn in COSMO-RS.

The experimental results obtained for the solvents α -pinene and p-cymene, using different antisolvents at an antisolvent/solvent ratio of 2/1, are represented in Figure 36 and Figure 37, respectively. The description of the values represented can be found in Table 20 in appendix 7.4, for α -pinene, and in Table 21 in 7.5, for p-cymene. In what concerns the solvent recovery, and for both cases, it was possible to conclude that the solubility of the solvent in the antisolvent seems to govern its recovery, in agreement to what was observed for limonene. For α -pinene, the average HDPE recovery slightly increased when diethylene glycol and 1,2-propanediol, the antisolvents with the lowest solvent solubility, were used, reaching 90wt%. However, this value is not significantly different from that obtained for ethanol, of 87wt%. In the case of p-cymene, the HDPE recovery also increased for 1,2-propanediol (82wt%), but the value obtained for diethylene glycol (75wt%) is set between this and ethanol (72wt%), despite it being the compound in which p-cymene is less soluble.





Figure 36 - HDPE and alpha-pinene recovery yields using three different antisolvents.

Figure 37 - HDPE and p-cymene recovery yields using three different antisolvents.

Independently of the solvent considered, the use of ethanol as antisolvent showed to be the most promising compromise between the recoveries of polymer and solvent, as the HDPE yield is only slightly lower than that obtained for other antisolvents, while the solvent's recovery increased more than 30wt% in comparison with the remaining antisolvents. The recovery of the solvent is a crucial aspect in the economic prospects of the process, as it also corresponds to the amount of solvent that can potentially be reused. Furthermore, ethanol at 96 v/v% is the cheapest of the antisolvents studied, as shown in Table 3.

4.4. Solvent selection for HDPE dissolution and precipitation

A comparison of the results obtained for the 3 different solvents is depicted in Table 9, fixing the dissolution conditions at 3wt%, 110° C, 10 minutes, and an ethanol/solvent ratio of 2/1. The solvent α -pinene showed the most promising results, allowing an increase on the polymer recovery of nearly 10wt%, when compared to the other solvents, while p-cymene yielded the lowest amount of recovered polymer (72wt%). Regarding the solvents' recovery, the differences between solvents were less

significant, ranging between 48wt% for p-cymene and 57wt% for limonene, where α -pinene represents an intermediate scenario.

To better evaluate these results, a Tukey test was employed, to determine if the results were statistically different between solvents. The solvent recovery showed no significant differences, while the results for HDPE recovery can be subdivided in two sets: limonene and p-cymene are not significantly different between themselves, but α -pinene yields significantly higher polymer recoveries. A brief context into this type of statistical test is provided in 7.6, as well as the specific results for the set of data present in Table 9.

 Table 9 - Results obtained for three different solvents, using ethanol as antisolvent in (2/1) antisolvent/solvent

 massic ratio.

	HDPE recovery (wt%)	Solvent recovery (wt%)	
Limonene	77.73 ± 3.09	56.99 ± 5.67	
α-pinene	86.84 ± 2.47	50.52 ± 3.95	
p-cymene	72.09 ± 1.94	48.17 ± 1.92	

4.5. Mechanism of HDPE dissolution in α-pinene

The mechanism through which HDPE is dissolved in α -pinene, the solvent selected to proceed with this work, was investigated by comparing the FTIR spectra of the pristine polymer, the solvent, and the polymer swollen in α -pinene, thus corresponding to the dissolution stage where the solvent has diffused into the polymer matrix, but the HDPE was not yet dissolved. The obtained spectra are presented in Figure 38.



Figure 38 - FTIR spectra of pristine HDPE, pure α -pinene, and swollen HDPE in α -pinene.

Overall, it was observed that the spectrum of the swollen sample shows the characteristic bands of both the polymer and the solvent. Nevertheless, a more detailed analysis shows that some bands were slightly deviated to lower energies (higher wavenumbers), which is an indication that the corresponding groups took part in the interactions established in the dissolution of the polymer. Regarding the characteristic polymer peaks, those associated with CH₂ bending (719/730 cm⁻¹ and 1463/1473 cm⁻¹) and CH₂ stretching (2848/2916 cm⁻¹), suffered slight deviations, and the same was observed in several bands of the solvent, that are characteristic of C-H bonds. α -pinene also contains double carbon bonds (C=C), but the respective FTIR bands showed no modification, implying that the interactions between C-H fragments contributed the most to the dissolution process. Table 10 lists the peaks that suffered deviations to lower energies and the corresponding groups^{168,169}. The complete lists of characteristic bands of HDPE and α -pinene is presented in Table 24 in appendix 7.7 and in Table 25 in appendix 7.8, respectively.

HDPE bands	Correspondence	α-pinene	Correspondence
(cm ⁻¹)		bands (cm ⁻¹)	
719	CH ₂ bending	772	C-H bending
730	CH ₂ bending	886	C-H bending
1463	CH ₂ bending	1446	C-H bending
1473	CH ₂ bending	2725	C-H bending
2848	CH ₂ symmetric stretching	2916	C-H stretching
2916	CH ₂ asymmetric stretching		

Table 10 - List of FTIR bands from HDPE and alfa-pinene that suffered wavelength deviations during dissolution.

4.6. Recovered HDPE characterization

4.6.1. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was used to assess if the solvent removal from the polymer's matrix was successful. Figure 39 to Figure 41 show the thermograms, corresponding to the variation of the residual weight of the samples analyzed through TGA, for the solvent/antisolvent systems studied in this work. The respective differential thermograms are presented in Figure 61 in appendix 7.9. Thermal degradation of pristine HDPE happens above 400°C, corresponding to a single peak in the differential thermogram¹⁷⁰. This corresponds to the same behavior observed in most samples analyzed, pointing towards the polymer's integrity and the absence of solvent residues. Nevertheless, when using limonene as solvent, the HDPE samples precipitated using water or glycerol showed considerable weight loss before this temperature. When water is used as antisolvent, a loss of 10wt% over a broader range of temperatures, above 150°C, is observed, which is coherent with the reported limonene thermograms¹⁷¹, thus indicating an incomplete removal of the solvent. Glycerol led to a sharp weight loss peak of nearly 25wt% at around 200°C. This temperature can be associated with the decomposition of glycerol residues¹⁷², rather than limonene's. Both situations are in agreement with the aforementioned results, as HDPE recoveries above 100wt% were obtained for these systems. The sample obtained after dissolution with α -pinene and precipitation with diethylene glycol showed a sharp weight loss peak around 150°C, corresponding to 5wt%, signaling the presence of solvent residues in the recovered

polymer. These observations can be further confirmed through the analysis of the polymer content in the samples, which was determined graphically. The polymer content, listed in Table 11, is above 98wt% in most samples, reaching the maximum of 99.8wt% for α -pinene/ethanol and α -pinene/1,2-propanediol, but is significantly lower for the aforementioned abnormal systems: limonene/water, limonene/glycerol, and α -pinene/diethylene glycol.



Figure 39 - Variation of the HDPE residual weight with temperature, from TGA analysis, for the different limonene/antisolvent systems studied, and respective ampliation (on the right).



Figure 40 - Variation of the HDPE residual weight with temperature, from TGA analysis, for the different α -pinene/antisolvent systems studied, and respective ampliation (on the right).



Figure 41 - Variation of the HDPE residual weight with temperature, from TGA analysis, for the different p-cymene/antisolvent systems studied, and respective ampliation (on the right).

Solvent	Antisolvent	HDPE content (<i>wt</i> %)
Limonene	Water	91.0
	Ethanol	99.4
	2-Propanol	99.4
	1-Butanol	99.4
	1,2-propanediol	99.0
	1,2-butanediol	99.4
	Glycerol	69.8
	Ethylene glycol	97.9
	Diethylene glycol	98.0
	Triethylene glycol	98.3
α-pinene	Ethanol	99.8
	1,2-propanediol	99.8
	Diethylene glycol	94.3
p-cymene	Ethanol	99.0
	1,2-propanediol	98.4
	Diethylene glycol	98.0

Table 11 - Polymer content of HDPE samples, determined through TGA analysis.

4.6.2. Differential Scanning Calorimetry

The thermal properties of the recovered HDPE, assessed through DSC, showed small deviations regarding the pristine material, maintaining approximately the same melting and crystallization temperatures, each varying in a range of about 5°C, as presented in Table 12. The estimated crystallinity

percentage varied in a small range, between 55% and 63%, indicating that the dissolution and recovery processes do not lead to significant structural changes in the polymer.

Solvent	Antisolvent	Tc (°C)	Tm (°C)	ΔH _f	%C
Pristine HDPE		111.3	131.5	177.4	60.42
	Ethanol	109.4	133.8	161.9	55.14
	2-propanol	112.0	130.6	186.8	63.62
	1-butanol	110.9	130.8	168.1	57.25
Limonono	1,2-propanediol	110.0	134.1	179.1	61.00
Limonene	1,2-butanediol	110.3	133.4	173.4	59.06
	Ethylene glycol	110.6	133.3	172.2	58.65
	Diethylene glycol	112.3	131.8	170.9	58.21
	Triethylene glycol	109.1	134.9	169.0	57.56
	Ethanol	108.9	135.5	182.2	62.06
α-pinene	1,2-propanediol	109.8	133.0	185.7	63.25
	Diethylene glycol	113.6	130.6	185.6	63.22
	Ethanol	109.8	132.8	162.8	55.45
p-cymene	1,2-propanediol	109.4	129.8	161.3	54.94
	Diethylene glycol	113.1	129.3	184.3	62.77

Table 12 - Thermal properties of the recovered HDPE samples for the solvent/antisolvent systems used in this work. (T_c is the crystallization point, T_m the melting point, ΔH_i the enthalpy of fusion, and %C the crystallinity percentage.)

4.6.1. Fourier Transform Infrared spectroscopy

FTIR spectroscopy was performed to assess if the process led to any modifications in the structure of the polymer. The FTIR spectrum of the pristine HDPE, in Figure 42, shows the characteristic bands of PE, at 2916 and 2848 cm⁻¹, corresponding to the asymmetric and symmetric CH₂ stretch, and two bifurcated bands characteristic of CH₂ bending, at 1475/1463 cm⁻¹ and 730/720 cm⁻¹. In the region between 1380 and 1300 cm⁻¹, the spectra also has the characteristic peaks of HDPE, showing no individual peak at 1377 cm^{-1 168}.

The recovered polymer's spectrum, from the different systems, maintained the characteristic bands found in the pristine polymer, but presented some additional peaks. The spectrum of the recovered polymer using the most promising system (α -pinene as solvent and ethanol as antisolvent) is presented in Figure 42, while the spectra of the remaining systems is shown in Figure 62 to Figure 76, in appendix 7.10. All recovered samples showed some modifications in the region between 800 and 1200 cm⁻¹, although these additional bands do not have a clear correspondence with either the solvents or the antisolvents, and are not associated with any weight loss, as thermogravimetric analysis had confirmed. In some cases, bands representative of OH groups were also present, between 3000 and 4000 cm⁻¹ ¹⁶⁹, these being prominent in some cases where abnormalities were found in TGA (limonene/glycerol and α -pinene/diethylene glycol).



Figure 42 - FTIR spectra of pristine and recovered HDPE (using α-pinene as solvent and ethanol as antisolvent).

4.7. Recovered solvent characterization

Samples of the solvents used in all solvent/antisolvent systems were analyzed through FTIR spectroscopy, to conclude about the efficiency of its recovery with high purity. First, the inability to efficiently separate limonene from both 2-propanol and 1-butanol through the addition of water, which was predicted by the liquid-liquid equilibrium diagrams drawn in COSMO-RS (Figure 20 and Figure 21, respectively), was confirmed, as the spectra of the isolated phases showed the coexistence of the solvent and the antisolvent. From all other systems, the solvents were efficiently recovered, showing only a slight decrease of transmittance that may indicate the presence of traces of compounds with OH bands, probably water. The spectra referring to the α -pinene/ethanol system is shown in Figure 43, while the remaining are presented in Figure 77 to Figure 91 in appendix 7.11.



Figure 43 - FTIR spectra of pure and recovered α -pinene.

For the selected system, which uses α -pinene as solvent and ethanol as antisolvent, the integrity of the recovered solvent was also checked by ¹H and ¹³C NMR spectroscopy. The spectra obtained are shown in Figure 44 and Figure 45, respectively, and the correspondence between the peaks and the functional groups assigned. The peak integration was done using the peak at 1.68 ppm as reference, corresponding to the methyl group (10). This confirmed the presence of a small amount of water in the solvent, identified by a peak in the ¹H spectra, at 1.56 ppm, corresponding to 7% in molar composition, or 1wt%. Comparing to the pure solvent's NMR (presented in Figure 92 and Figure 93, in appendix 7.12), in which the molar composition of water was around 4%, it was observed that the water content increased slightly in the recovered solvent.



Figure 44 - ¹H NMR spectra of recovered α-pinene.



Figure 45 - ¹³C NMR spectra of recovered α-pinene.

4.8. Scale-up

Having concluded that the dissolution of HDPE in α -pinene and subsequent precipitation with ethanol allows to recover both the polymer and the solvent with adequate purity, the variation of the results obtained was investigated at a larger scale, to determine the feasibility of the process scale-up. The scale at which the experiments were conducted was increased 5 times, from 50 mg to 250 mg of HDPE, while keeping constant the dissolution temperature (110°C), the initial solid polymer content (3wt%) and the antisolvent to solvent ratio (2/1). First, it was verified that the polymer was completely dissolved in around 4 min., the same as observed in the small scale, and thus the dissolution time was also kept constant at 10 min. The attained results are present in Figure 46 (and in Table 26 in appendix 7.13). The possibility to improve the total solvent recovery was also assessed, by adding water and centrifuging the washing solution. The integrity of the solvent recovered in this step was assessed through FTIR, which spectra is presented in Figure 94 in appendix 7.14.



Figure 46 - HDPE and α -pinene recovery from scale-up 5 times in mass of HDPE.

Regarding the recovery of HDPE, an increase of nearly 10wt% was attained by scaling-up the process, from 84wt% to 93wt%. The most probable cause for this is the fact that eventual accidental losses related to the experimental procedure became less significant. On the other hand, the increase in the scale did not lead to significant changes in the recovery of the solvent. From the washing step mixture, it was possible to recover roughly an additional 17wt% of α -pinene in both cases, resulting a total α -pinene recovery of 73wt%, at the larger scale, similarly to the small scale (72wt%).

These results point to the viability of the process, as the scale-up did not lead to any decrease in the final yields, but rather to some improvement regarding the polymer recovery.

4.9. Solvent reuse and cycling

The viability of a large-scale dissolution-precipitation process highly depends on the possibility of reusing the solvent recovered multiple times. Starting from the larger scale tested (250 mg), the recovered solvent was reused twice, and the recovery yield regarding both the polymer and the α -pinene was analyzed. The 2nd and 3rd cycle were performed at the scales of 125 mg and 50 mg, respectively, in order to allow the exclusive use of recovered solvent from the previous experiment, instead of adding pure α -pinene. The results are represented in Figure 47 (and in Table 27 in appendix 7.15).

Figure 47 - HDPE and α -pinene recovery considering three consecutive solvent reuses.

The polymer recovery only varied around 3wt%, taking the values of 93wt%, 92wt%, and reaching the lowest value in the 3rd cycle, with a value of 90wt%. This value corresponds to that obtained for the experiments done at the original scale of 50 mg of HDPE, meaning that the recovery increased around 6wt% by reusing the solvent, with no other modifications to the experimental conditions. Some small residues of unprecipitated HDPE might exist in the solvent, which could play an important role in facilitating the precipitation of the polymer, thus the increase observed in its recovery.

Regarding the solvent, the global trend shows that the recovery decreases over reuse cycles, having been recovered 73wt% in the 1st cycle, 70wt% in the 2nd and 65wt% in the 3rd. One possible cause for this decrease may be the presence of water in the recovered α -pinene, as was proven by NMR analysis (section 4.7), meaning that the amount of solvent accounted for in the next cycles slightly deviated from the actual quantity. No clear trend was observed in the two recovery steps separately, but rather one step seems to compensate the other, as the results for the total amount recovered are coherent between experiments.

The integrity of the solvent recovered at the end of the third cycle (Figure 95 in appendix 7.16) was investigated through FTIR analysis, showing no signs of impurities other than a slight OH band, similar to what was observed in the sample that had undergone only one dissolution-precipitation cycle. NMR analysis of the recovered solvent after 3 dissolution cycles (Figure 96 and Figure 97 in appendix 7.17) pointed that the water content was the same as in the recovered solvent after only one dissolution, 7% molar.

4.10. Process simulation and economical assessment

The dissolution-precipitation process of HDPE was simulated in Aspen Plus as a continuous process, mimicking the aforementioned results, in order to assess the relative impact of each step of the process in its economic scenario. For this purpose, a calculation base of 1 kg HDPE/hr was used, and the flowsheet representing the simulated process is shown in Figure 48. Appendix 7.18 contains the description of the streams' properties and composition.

Figure 48 - Flowsheet of the process as implemented on Aspen Plus for the dissolution and precipitation process of HDPE, including solvent and antisolvent recycling.

The dissolution and precipitation operations were performed in RSTOIC models (**DISSOL** and **PRECIP**, respectively), assuming both steps are complete, and thus 100% of the polymer leaves the precipitation vessel in the solid state. For these steps, the amounts of α -pinene and ethanol entering the system were specified according to the experimental conditions chosen: 3wt% of HDPE in the dissolution, 10 minutes of residence time in the dissolution vessel, at 110°C, and a mass ratio of 2/1 between the antisolvent and the solvent. A heat exchanger (**HEAT-PIN**) was added before the dissolution vessel, with the function of heating the solvent to the desired temperature.

The stream resulting from the precipitation step (8) is then filtered, in **FILTER**, and it was defined that only 55% of the liquid phase is separated from the polymer, mimicking the solvent recovery attained for this step in the laboratory, in section 4.9. Two outlet streams were considered: stream 9 that contains the polymer and residual solvent, and stream 10 composed of α -pinene and ethanol.

The polymer stream is washed using 2 kg/hr of ethanol, in the equipment **WASH**, removing the remaining solvent, and the polymer (in stream 13) is finally dried at 80°C (**DRIER**). Both the liquid outlet of the filter (10) and the washing solution (14) are mixed with water and decanted (**DECANTER**). The amount of water was defined so that it corresponds to 50wt% of the mixed stream. According to the liquid-liquid equilibrium estimated in the decanter model, it is possible to recover α -pinene with a mass
purity of 98.5%, in stream 18. A purge was inserted in the simulation to mimic the loss of solvent observed experimentally, and thus only 70% of the α -pinene is recycled back to the dissolution vessel (stream 21).

The second liquid phase composed mainly of ethanol and water is distillated at atmospheric pressure (**DIST COLUMN**), allowing the recovery of ethanol with 95% massic purity (stream 24), and water with 99.4% purity (stream 22). Both streams can be recycled back to the respective operations, after cooling to 25°C, to match their temperature. Taking this into account, the required raw inlet of each solvent was determined as shown in Table 13, as well as the respective cost. It is clear that the cost associated with ethanol and water is negligible in comparison to that of α -pinene. On one hand, the unitary cost of this last compound is one order of magnitude above the remaining compounds, but on the other hand, its cost is mostly caused by the inefficiency of its recovery.

	Price (€/kg)	Raw inlet (kg/hr)	Cost (€/hr)
α-pinene	64.50	9.74	628.03
Ethanol 96%	2.82	0.10	0.28
Water	3.00	0.01	0.03

Table 13 - Required raw materials and respective cost for the proposed Aspen process for HDPE dissolution and
precipitation.

Regarding the necessary utilities, low pressure steam was used to heat the solvent, the dissolution vessel and the reboiler of the distillation column, while hot air was used in the convective drier. Cooling water was used in the condenser, and refrigerated water performed the remaining cooling operations. The energy requirements of each equipment and respective cost were estimated by Aspen Plus, for which the results are summarized in Table 14.

Utility	Equipment	Energy (kw)	Cost (€/hr)
	Heater for α-pinene	1.46	0.03
Low pressure	DC reboiler	336.51	6.15
	Dissolution	0.09	0.00
Cooling water	DC condenser	324.96	0.49
	Cooler for EtOH	2.88	0.06
Refrigerated water	Cooler for water	8.79	0.17
	Precipitation	1.42	0.03
Air	Drier	0.03	0.00

Table 14 - Utility usage and respective cost, as simulated in Aspen Plus.

Globally, most of the required energy is used in the distillation operation, both in the reboiler and the condenser, while the remaining operations represent only 2.2% of the total energy requirement of

the process. Nevertheless, since low pressure steam has a significantly high cost, the energy used in the reboiler corresponds to 88.9% of the total energy cost. To view these values in relative terms, the total energy usage requirement is of 676 kW, or 2.4 kJ/g of HDPE, which represents only 70% of the theoretical energy demand for the polymerization of the same polymer, 3.5 kJ/g⁴², while allowing the recovery of the polymer itself in a pure form.

A more detailed economic evaluation would require further optimization of the energy expenditure, namely by improving the configuration of the distillation column. Nevertheless, even with the implemented configuration, the total cost of utilities was estimated in 6.9 \in /hr, while raw materials correspond to 628.3 \in /hr, representing 99% of the operating costs estimated. Thus, α -pinene plays the major role in the economic viability of the process. In this sense, the main focus of improvement in this process should be the optimization of the solvent recovery. Possible influential factors that could not be optimized at the laboratorial scale are the stirring parameters during the precipitation step, the control of the particle dimensions after this step, and the possibility of recovering the solvent evaporated during the drying step.

Furthermore, it is important to keep in mind that the demand for natural alternative solvents, as is the case of α -pinene, has been increasing, and its global market size is expected to continue increasing in the next years¹⁷³. This trend has also been a driving force for the search for novel extraction and purification methods, which may play an important role in the future price decrease of this compound¹⁶⁶.

4.11. Polypropylene – proof of concept

The molecular structure of polypropylene is very close to the one of polyethylene, and thus it is likely that a solvent that successfully dissolves one of them can also be used for the other. In fact, there are several publications that use the same solvent/antisolvent system to dissolve both polypropylene and high-density polyethylene^{127–131}, sometimes at different temperatures, as presented in Table 2.

4.11.1. Solvent screening for PP in COSMO-RS

Similarly to what was described for HDPE in section 4.1, a molecule consisting of a trimer of PP was simulated in COSMO-RS, in order to calculate the representative density charge distribution of the polymer, as shown in Figure 49, and perform further calculations on its solubility in the solvents considered for HDPE.



Figure 49 - PP molecule (with charge density points) used for the COSMO-RS calculations.

The σ -profile and σ -potential of the polymer were drawn, as represented in Figure 50. It is not surprising to observe that also PP is a completely apolar polymer, unfavorable towards polar interactions with either HBDs or HBAs, and shows a very similar distribution to that of HDPE.



Figure 50 - σ -profile and σ -potential of PP generated by COSMO-RS software.

The solubility of PP in the solvents considered throughout this work was calculated in COSMO-RS, which results are present in Figure 51. These are also described in Table 30 in appendix 7.19. Although no solvent was predicted to dissolve PP below 160°C, it must be taken into account that the melting temperature of commercial PP samples is much lower than that of the completely crystalline polymer, value which was given as input for the COSMO-RS calculations. Furthermore, the results attained should be critically evaluated, since at those high temperatures some of the solvents screened are no longer in liquid phase but rather in the gas phase. Besides these considerations, α -pinene was predicted to be the best solvent for PP.



Figure 51 - COSMO-RS solubility prediction of PP in several selected solvents at three different temperatures (160°C, 170°C, 180°C).

4.11.2. PP's dissolution and recovery

Using α -pinene and the same stirring speed as for the dissolution of HDPE (400 rpm), below 100°C, no dissolution was observed, up to 6 hours. At 110°C and above, it was possible to completely dissolve 3wt% of PP under 10 minutes. Consequently, the hypothesis of separating the two polymers by means of selective dissolution in α -pinene at different temperatures was discarded. However, it was observed that both polymers can be dissolved simultaneously, which could allow their separation from other polymers in a mixed stream, and thus, after adequate grinding, PP and HDPE can be separated through flotation, as referred by *Quelal et al.*¹⁷⁴. The dissolution of PP in α -pinene was also achieved at higher temperatures, up to 140°C, but these conditions were no further pursued since there was no interest in increasing the operating temperature as it came with no additional benefits.

In order to understand if the recovery of the PP can be performed efficiently, allowing to maintain its integrity, experiments were carried out using ethanol as antisolvent, in the antisolvent/solvent mass ratio 2/1. The obtained results showed that it was possible to recover 98wt% of the initial PP, while the total solvent recovery layed around 62wt%, as demonstrated in Figure 52 (Table 31 in appendix 7.20). While the polymer recovery is much higher than the attained for HDPE, less α -pinene was recovered.



Figure 52 - PP and α -pinene recovery after dissolution at 110°C and precipitation with ethanol in the antisolvent to solvent ratio of 2/1.

The hypothesis of simultaneously dissolving and precipitating HDPE and PP was also investigated, using equal masses of both polymers. The dissolution of a total solid content of 3wt% in α -pinene was achieved in under 10 min at 110° C, and the cumulative recovery of the polymers was 99wt%. The separation was then attempted by flotation, by varying the content of a mixture of ethanol and water until a clear separation was achieved. It was not possible to depart from a mixture with a specific composition because the exact density of the polymer samples used was unknown. Although a clear separation was achieved, the yields obtained for the individual polymers were contradictory: 95wt% for PP and 103wt% for HDPE. It is possible that the complete separation of the polymer was hindered by limitations in the grinding step, which could lead to the existence of mixed-polymer particles within the mixture. Although this separation would require further optimization, these results do not deem it as unfeasible.

4.11.3. Recovered PP characterization

The presence of solvent in the recovered polymer was quantified through TGA analysis. According to the results, represented in Figure 53, a weight loss of around 5% was observed between 150°C and 200°C, before the characteristic loss caused by the polymer degradation (which happens above 400°C), meaning that the solvent was not efficiently removed from the polymer matrix, and the actual polymer content in the sample corresponds to 91.4wt%. This implies that the actual amount of polymer recovered is lower than presented in the previous section. In this case, the incomplete removal of the solvent from the polymer's matrix cannot be associated with low affinity between the solvent and the antisolvent, as α -pinene is highly soluble in ethanol. Nevertheless, in the experimental work, it was observed that the visible structure in which PP first precipitates differs from what was common in HDPE. In the case of PP, the polymer precipitated in a single matrix of net-like chains, and so this quick and complete aggregation could cause difficulties in the solvent removal. Furthermore, after drying, PP

presented a "textile-like" texture, which hindered its grinding to small particles. Figure 98 in appendix 7.21 shows the differential thermogram of the recovered PP.



Figure 53 - Variation of recovered PP's residual weight with temperature, resulting from TGA analysis.

DSC was again used to evaluate the thermal properties of the polymer, which showed no significant modifications compared to the pristine material, as present in Table 15. Although the melting point was reduced only by 2°C, the recovered polymer shows a shoulder in the left side of the peak, implying that two different types of crystalline structures were formed. This was not reflected in the estimated crystalline fraction.

	Tc (°C)	<i>T_m</i> (°C)	ΔH _m (J/g)	%C	-
Pristine	114.4	165.6	105.5	26.7	
Recovered	115.9	163.6	105.9	26.8	

Table 15 - Thermal properties of pristine and recovered PP.

FTIR analysis also showed some differences regarding the pristine material, as shown in Figure 54. Firstly, the pristine material showed the typical spectra of isotactic polypropylene (which bands are listed in Table 32 in appendix 7.22), and three additional bands: at 3358 and 3182 cm⁻¹, which are characteristic of OH groups, and one at 1633 cm⁻¹, possibly associated with double carbon bonds¹⁶⁹. These bands are not present in the recovered PP's spectra, thus indicating that the sample could possibly include an additive, that was removed in the dissolution process. In the recovered PP, a broad OH band was identified, as well as a band in the double bond (C=C) region, although at a higher frequency number than observed before, which could be associated with solvent residues. The characteristic isotactic bands, at 1167, 998, 899 and 842 cm⁻¹, also showed some modifications in absorbance, which can be caused by changes in the crystalline structure¹⁶⁸. The integrity of the recovered solvent was assessed through FTIR analysis, as shown in Figure 55, showing the same results that had been observed in the HDPE case.



Figure 54 - FTIR spectra of pristine and recovered PP.



Figure 55 - FTIR spectra of pure and recovered α -pinene used in PP dissolution.

4.12. HDPE and PET separation

The main advantage of dissolution-precipitation processes is, as referred previously, the possibility to recover the individual polymers from mixed streams, and thus this scenario was studied using a mixed sample of HDPE and PET, this last polymer being one of the most consumed besides polyolefins. As described in section 3.2.1.1, HDPE was first dissolved and recovered at the conditions defined throughout this work (3wt% of HDPE, using α -pinene as solvent and the dissolution at 110°C for 10 min, and using ethanol as antisolvent in the antisolvent/solvent ratio of 2/1), while the methodology used for PET dissolution was based on a previous work¹⁴⁹.

First, HDPE was dissolved in α -pinene, and the solution was filtered, thus recovering the solid PET particles. These were washed with ethanol and water, and showed no visible modification in comparison with their pristine form. The PET weight was the same before and after the process of HDPE dissolution. A simple schematic representation of the whole experimental process is shown in Figure 56, along with some pictures that illustrate the form of the polymers in each phase of the process.



Figure 56 - Schematic representation of the selective dissolution of HDPE and PET (Illustration built in BioRender).

The experimental recovery results obtained concerning both polymers and respective solvents are described in Figure 57 (and in Table 33 in appendix 7.23). 80wt% of HDPE was recovered, a value which is in agreement with the previous results obtained for the single polymer. The average recovery of α -pinene was 55wt%, although the replicates are less coherent than for the previous experiments done with the individual HDPE. This value is significantly lower than that observed for the individual studies, suggesting that the additional intermediate filtration step may have led to difficulties in the solvent removal during the precipitation step. In fact, it was observed that in general, HDPE solutions start to turn more viscous and solidify as soon as the heat source is removed, and the intermediate filtration step to recover solid PET implies a larger amount of time spent between the finish of the dissolution step and the addition of the antisolvent, which was not possible to mitigate with the laboratorial set-up used. This way, it is possible that more solvent got entrapped in the polymer during precipitation, but the drying steps before and after grinding were still efficient, as FTIR analysis showed similar results to the individually dissolved samples (Figure 99 in appendix 7.24). Regarding PET, it was possible to recover 84wt% of the initial amount of polymer, as well as 68wt% of the NaDES.



Figure 57 - Recoveries of selectively dissolved polymers, HDPE and PET, and respective solvents, α -pinene and thymol:carvacrol (1:1).

4.12.1. Recovered PET characterization

TGA was performed to a recovered PET sample, showing a weight loss of around 1wt% with the differential peak at 150°C (Figure 58), corresponding to a polymer content of 98.4wt%. The differential thermogram is presented in Figure 100 in appendix 7.25. It is possible that this behavior corresponds to the evaporation of solvent residues, but it is not known if the temperature corresponds to the boiling temperature of thymol:carvacrol (1:1), as it was not reported in literature so far.



Figure 58 - Variation of recovered PET's residual weight with temperature, resulting from TGA analysis.

Both the recovered PET and thymol:carvacrol (1:1) were evaluated through FTIR analysis, as presented in Figure 59 and Figure 60, respectively, showing an adequate correspondence with the spectra of the pristine materials.



Figure 59 - FTIR spectra of pristine and recovered PET.

Figure 60 - FTIR spectra of pure and recovered thymol:carvacrol NaDES (1:1).

The melting point of PET, evaluated through DSC, showed a small deviation between the pristine and the recovered samples. The crystallization point, on the other hand, increased around 10°C. The estimated crystallinity was reduced around 7% with the recovery process, which could be caused by the quick crystallization during precipitation. These values are described in Table 16.

	T _c (°C)	T _m (°C)	ΔH _f (J/g)	% C
Pristine	192.9	250.1	51.9	37.0
Recovered	203.1	252.1	41.5	29.7

Table 16 - Thermal properties of pristine and recovered PET.

This way, it was possible to selectively dissolve each polymer, efficiently separate them, and both were recovered while maintaining their integrity and without causing significant changes to the pristine materials.

5. Conclusions and Future Work

The urge to shift the plastics sector to a more circular paradigm comes hand in hand with the need for greener and more sustainable recycling processes, that allow the recycling of plastic streams that have been mostly discarded so far due to separation and purification difficulties inherent to the most common recycling technologies implemented. This work focused on the selective dissolution and precipitation of polymers, one of the most promising technologies to fill in this gap.

Several natural solvents were screened for the dissolution of HDPE using COSMO-RS, and the experiments performed showed good qualitative agreement with the predictions. COSMO calculations were an adequate prediction tool, although the quantitative results need to be critically analyzed due to the high dependance on polymer properties that can vary substantially between different samples of the same polymer, such as density, melting point, and enthalpy of fusion.

Among the solvents and antisolvents tested experimentally, α -pinene and ethanol was considered the most promising combination for recovering both HDPE and the solvent, with similar properties and composition to the pristine materials. During this work, it was not possible to evaluate the variation of the molecular weight of the polymer caused by the dissolution process, which would be an important assessment. The dissolution was achieved in a short period of time (lower than 10 min), which comprises a significant reduction in comparison with most reported works on HDPE dissolution. In addition, α -pinene is an adequate option regarding its greenness, as it is a natural compound abundantly found as a by-product of the paper pulp industry. Furthermore, it was concluded that the affinity between the solvent and antisolvent used can have a significant influence on the recovery yields and quality of the recovered product.

The α -pinene/ethanol system and the dissolution and precipitation conditions that resulted from the optimization of HDPE solid content, dissolution temperature and antisolvent/solvent ratio led to robust results when increasing the scale of the experiments and also when reusing the solvent multiple times. These facts point to the suitability of the process for implementation at large scales. Nevertheless, it was estimated that the greatest bottleneck for the economic viability of the process would be the recovery of the solvent. Thus, further optimizations would be needed to increase the recovery of this compound, namely at large scale. The solution could include more controlled precipitation and grinding processes, or the modification of the drying steps in order to recover possible evaporated compounds.

The dissolution of PP was also achieved with the same solvent and dissolution conditions, but TGA showed that its recovery was not completely efficient due to incomplete solvent removal. Further studies shall be performed on PP precipitation to understand and possibly eliminate this issue.

Finally, the α -pinene/ethanol system was proved suitable for the selective dissolution of HDPE from a mixture containing PET. Nevertheless, the recovery yield of α -pinene was reduced when the mixture was separated, a situation which would require further study and improvement. From experimental observations, a possible improvement would be to attempt the filtration of the dissolved HDPE while maintaining the heating.

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7. Appendix

7.1. HDPE solvent screening

Solubility (wt%)	110°C	120°C	130°C
Toluene	0.00	11.89	71.98
p-Xylene	0.00	0.93	66.88
d-Limonene	0.00	0.00	54.47
α-Pinene	0.00	1.06	58.01
p-Cymene	0.00	0.00	55.05
Terpinolene	0.00	0.07	57.22
γ-Terpinene	0.00	0.01	55.46
3-Carene	0.00	0.02	56.35
β-Caryophyllene	0.00	0.00	32.11
Squalane	0.00	0.00	0.00
Squalene	0.00	0.00	0.00
Farnesane	0.00	0.00	16.33
Farnesene	0.00	0.00	0.25

Table 17 - Solubility (wt%) of HDPE in different solvents at 110°C, 120°C and 130°C, as calculated in COSMO-RS.

7.2. Optimization of dissolution conditions in limonene

Table 18 – HDPE and limonene recovery at different dissolution temperatures and initial solid contents.

	HDPE recovery (wt%)			Limonene recovery (wt%)		
HDPE content (wt%)	100ºC	110ºC	120ºC	100ºC	110ºC	120ºC
1	56.53 ± 0.40	70.00 ± 2.83	59.57 ± 13.88	47.35 ± 4.46	46.70 ± 10.73	54.11 ± 11.00
2	62.50 ± 11.79	75.13 ± 8.27	73.69 ± 1.10	48.74 ± 6.47	53.60 ± 0.94	48.75 ± 16.74
3	72.87 ± 3.02	80.51 ± 3.55	80.71 ± 0.51	42.76 ± 2.44	47.26 ± 4.96	37.59 ± 7.61
4	81.13 ± 2.67	81.23 ± 5.48	89.14 ± 1.95	23.92 ± 3.28	41.58 ± 2.32	34.25 ± 14.74
5	81.34 ± 5.76	83.08 ± 1.68	90.55 ± 4.32	18.48 ± 0.38	33.44 ± 6.21	13.58 ± 4.32

7.3. Antisolvent study for HDPE dissolved in limonene

	HDPE recovery (wt%)			Limonene recovery (wt%)		t%)
Ratio	1/1	2/1	3/1	1/1	2/1	3/1
Water	92.87 ± 7.15	88.39 ± 13.45	98.72 ± 4.29	9.30 ± 12.51	7.07 ± 6.69	2.64 ± 4.58
Ethanol	76.76 ± 1.58	77.73 ± 3.09	79.11 ± 1.35	43.09 ± 5.21	56.99 ± 5.67	53.56 ± 6.58
2-propanol	74.09 ± 8.42	61.75 ± 6.57	72.96 ± 2.13			
1-butanol	79.44 ± 5.15	72.80 ± 7.89	70.16 ± 2.67			
1,2-butanediol	82.69 ± 2.53	84.47 ± 1.27	86.37 ± 0.85	16.87 ± 5.24	12.93 ± 11.05	13.85 ± 2.06
1,2-propanediol	82.60 ± 7.21	84.45 ± 4.49	85.52 ± 1.49	19.83 ± 5.05	20.58 ± 8.46	20.50 ± 9.11
Glycerol	102.72 ± 8.25	116.25 ± 14.24	102.18 ± 14.44	0.00	14.82 ± 10.02	19.20 ± 4.17
Ethylene glycol	90.47 ± 4.26	86.63 ± 8.00	86.75 ± 3.63	21.89 ± 5.32	31.95 ± 5.82	19.59 ± 6.10
Diethylene glycol	83.92 ± 2.62	86.59 ± 5.79	83.69 ± 3.12	7.00 ± 5.61	9.72 ± 4.81	27.52 ± 3.78
Triethylene glycol	89.80 ± 3.03	84.03 ± 3.21	87.50 ± 4.44	5.45 ± 2.47	20.40 ± 5.26	13.78 ± 6.79

Table 19 - HDPE and limonene recovery for different antisolvents and antisolvent/solvent ratios, after dissolutionat 110°C for 10 min

7.4. Antisolvent study for HDPE dissolved in α-pinene

Table 20 - HDPE and α -pinene recovery for different antisolvents, after dissolution at 110°C for 10 min.

Recovery (wt%)	HDPE	α-pinene
Ethanol	86.84 ± 2.47	50.52 ± 3.95
1,2-propanediol	90.09 ± 5.72	16.19 ± 2.04
Diethylene glycol	89.97 ± 6.83	7.59 ± 1.68

7.5. Antisolvent study for HDPE dissolved in p-cymene

Table 21 - HDPE and p-cymene recovery for different antisolvents, after dissolution at 110°C for 10 min.

	HDPE recovery (wt%)	α-pinene recovery (wt%)
Ethanol	72.09 ± 1.94	48.17 ± 1.92
1,2-propanediol	81.75 ± 0.78	8.38 ± 10.47
Diethylene glycol	75.29 ± 0.33	7.64 ± 7.22

7.6. Tukey Honestly Significant Difference (HSD) test

Tukey HSD tests were performed in the software IBM SPSS Statistics 27, through a univariate analysis. This test is suitable for a wide range of situations, namely for pair-wise comparisons¹⁷⁵. The solvent was defined as fixed factor and the recovery as dependent variable. The degree of significance was set at 95%.

		Sub	Subset		
solvent	N	1	2		
p-cymene	2	72.0900			
Limonene	3	77.7300			
α-pinene	3		86.8433		
Significance		0.079	1.000		

Table 22 - Tukey HSD test regarding HDPE recovery with different solvents.

Table 23 - Tukey HSD test regarding solvent recovery after HDPE dissolution in different solvents and
precipitation.

		Subset
Solvent	Ν	1
p-cymene	3	46.0633
α-pinene	3	50.5267
Limonene	3	56.9900
Significance		0.060

7.7. Characteristic FTIR bands of HDPE and correspondence

Table 24 - Characteristic FTIR bands of HDPE and corresponding vibrations.

HDPE bands	Correspondence	
(cm ⁻¹)		
719	CH ₂ bending	
730	CH ₂ bending	
1368	methyl C-H bend	
1463	CH ₂ bending	
1473	CH ₂ bending	
2848	C-H symmetric stretching	
2916	CH2 asymmetric stretching	

7.8. Characteristic FTIR bands of α -pinene and correspondence

α-pinene	Correspondence	α-pinene	Correspondence
band (cm-1)		band (cm-1)	
564	NA	1329	C-H bending
619	NA	1335	C-H bending
772	C-H bending	1365	C-H bending
787	C=C bending	1375	C-H bending
886	C-H bending	1381	C-H bending
928	NA	1437	C-H bending
953	NA	1446	C-H bending
1015	NA	1470	C-H bending
1063	NA	1659	C=C stretching
1084	NA	2725	C-H stretching
1101	NA	2835	C-H stretching
1125	NA	2880	C-H stretching
1166	NA	2916	C-H stretching
1182	NA	2949	C-H stretching
1204	NA	2986	C-H stretching
1220	NA	3026	C-H stretching
1265	NA		(alkene)

Table 25 - Characteristic FTIR bands of α -pinene and corresponding vibrations. (NA stands for not available)

7.9. Differential thermogram of recovered HDPE



Figure 61 - Derivative thermogravimetric analysis of recovered HDPE samples from different solvent/antisolvent systems.

7.10. FTIR analysis of recovered HDPE from different solvent/antisolvent

systems



Figure 62 - FTIR spectra of pristine and recovered HDPE using limonene as solvent and water as antisolvent.



Figure 64 - FTIR spectra of pristine and recovered HDPE using limonene as solvent and 2-propanol as antisolvent.



Figure 63 - FTIR spectra of pristine and recovered HDPE using limonene as solvent and ethanol as antisolvent.



Figure 65 - FTIR spectra of pristine and recovered HDPE using limonene as solvent and 1-butanol as antisolvent.



Figure 67 - FTIR spectra of pristine and recovered HDPE using limonene as solvent and 1,2-butanediol as antisolvent.



Figure 69 - FTIR spectra of pristine and recovered HDPE using limonene as solvent and ethylene glycol as antisolvent.



Figure 71 - FTIR spectra of pristine and recovered HDPE using limonene as solvent and triethylene glycol as antisolvent.



Figure 66 - FTIR spectra of pristine and recovered HDPE using limonene as solvent and 1,2-propanediol as antisolvent.



Figure 68 - FTIR spectra of pristine and recovered HDPE using limonene as solvent and glycerol as antisolvent.



Figure 70 - FTIR spectra of pristine and recovered HDPE using limonene as solvent and diethylene glycol as antisolvent.



Figure 72 - FTIR spectra of pristine and recovered HDPE using α-pinene as solvent and 1,2-propanediol as antisolvent.



Figure 74 - FTIR spectra of pristine and recovered HDPE using p-cymene as solvent and ethanol as antisolvent.



Figure 73 - FTIR spectra of pristine and recovered HDPE using α-pinene as solvent and diethylene glycol as antisolvent.



Figure 75 - FTIR spectra of pristine and recovered HDPE using p-cymene as solvent and 1,2-propanediol as antisolvent.



Figure 76 - FTIR spectra of pristine and recovered HDPE using p-cymene as solvent and diethylene glycol as antisolvent.

7.11. FTIR analysis of recovered solvent from different solvent/ antisolvent systems



Figure 77 - FTIR spectra of pure and recovered limonene using water as antisolvent.



Figure 79 - FTIR spectra of pure and recovered limonene using 2-propanol as antisolvent.



Figure 78 - FTIR spectra of pure and recovered limonene using ethanol as antisolvent.



Figure 80 - FTIR spectra of pure and recovered limonene using 1-butanol as antisolvent.



Figure 81 - FTIR spectra of pure and recovered limonene using 1,2-propanediol as antisolvent.



Figure 83 - FTIR spectra of pure and recovered limonene using glycerol as antisolvent.



Figure 85 - FTIR spectra of pure and recovered limonene using diethylene glycol as antisolvent.



Figure 82 - FTIR spectra of pure and recovered limonene using 1,2-butanediol as antisolvent.



Figure 84 - FTIR spectra of pure and recovered limonene using ethylene glycol as antisolvent.



Figure 86 - FTIR spectra of pure and recovered limonene using triethylene glycol as antisolvent.


Figure 87 - FTIR spectra of pure and recovered α-pinene using 1,2-propanediol as antisolvent.



Figure 89 - FTIR spectra of pure and recovered p-cymene using ethanol as antisolvent.



Figure 88 - FTIR spectra of pure and recovered α-pinene using diethylene glycol as antisolvent.



Figure 90 - FTIR spectra of pure and recovered p cymene using 1,2-propanediol as antisolvent.



Figure 91 - FTIR spectra of pure and recovered p cymene using diethylene glycol as antisolvent.

7.12. NMR of pure α -pinene



Figure 92 - ¹H NMR spectra of pure α -pinene.



Figure 93 - ¹³C NMR spectra of pure α -pinene.

7.13. HDPE and α -pinene recovery at scale-up

Recovery (wt%)	Initial scale (50 mg)	Scale-up (250 mg)
HDPE	83.85 ± 3.00	93.21 ± 0.13
α -pinene from precipitation step	53.96 <u>+</u> 2.93	56.85 <u>+</u> 6.91
α -pinene from washing step	17.62 ± 1.75	16.48 ± 2.29
α-pinene total	71.58 ± 1.18	73.32 ± 4.62

Table 26 - HDPE and α -pinene recovery using ethanol as antisolvent, in the antisolvent:solvent ratio 2:1, at two different scales: 50 mg HDPE and 250 mg HDPE.

7.14. FTIR analysis of α -pinene recovered in the washing step



Figure 94 - FTIR spectra of pure and recovered α -pinene from the washing step, using ethanol as antisolvent.

7.15. HDPE and α -pinene recovery from 3 processing cycles

Table 27 – HDPE and α -pinene recovery using ethanol as antisolvent, in the antisolvent:solvent ratio 2:1, for 3 consecutive solvent utilizations

Recovery (wt%)	1 st cycle	2 nd cycle	3 rd cycle
HDPE	93.21 ± 0.13	92.10 ± 0.22	89.74 ± 0.59
α -pinene from precipitation step	56.85 ± 6.91	58.39 ± 5.43	45.68 ± 2.15
α -pinene from washing step	16.48 ± 2.29	11.96 ± 0.38	19.44 ± 1.21
α-pinene total	73.32 ± 4.62	70.36 ± 5.05	65.12 ± 3.36

7.16. FTIR analysis of α -pinene recovered from third cycle



Figure 95 - FTIR spectra of pure and recovered α-pinene after 3 consecutive uses, using ethanol as antisolvent.

7.17. NMR analysis of α -pinene recovered from third cycle



Figure 96 - ¹H NMR spectra of recovered α -pinene after 3 consecutive uses.



Figure 97 - ¹³C NMR spectra of recovered α -pinene after 3 consecutive uses.

7.18. Aspen Plus simulation: stream description

Stream	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Pressure (atm)	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Temperature (ºC)	25.0	24.9	110.0	25.0	110.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Solid stream														
Mass flow (kg/hr)	0.00	0.00	0.00	1.00	0.00	0.00	0.00	1	1.00	0.00	0.00	0.00	1.00	0.00
HDPE	0.00	0.00	0.00	1.00	0.00	0.00	0.00	1	1.00	0.00	0.00	0.00	1.00	0.00
Liquid stream														
Mass flow (kg/hr)	9.74	32.76	32.76	0.00	33.76	0.10	64.90	97.65	43.94	53.71	0.00	2.00	0.00	45.94
α-pinene	9.74	32.43	32.43	0.00	32.43	0.00	0.36	32.79	14.76	18.03	0.00	0.00	0.00	14.76
Ethanol	0.00	0.29	0.29	0.00	0.29	0.09	61.33	61.62	27.73	33.89	0.00	1.90	0.00	29.63
Water	0.00	0.04	0.04	0.00	0.04	0.00	3.20	3.24	1.46	1.78	0.00	0.10	0.00	1.56
HDPE	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 28 - Stream characterization from Aspen plus simulation (part 1).

Stream	15	16	17	18	19	20	21	22	23	24	25	26	27
Pressure (atm)	1	1	1	1	1	1	1	1	1	1	1	1	1
Temperature (⁰C)	80.0	25.0	25.0	25.0	25.0	25.0	25.0	99.2	25.0	78.0	25.0	25.0	25.0
Solid stream													
Mass flow (kg/hr)	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HDPE	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Liquid stream													
Mass flow (kg/hr)	0.00	0.01	100.23	32.88	167.03	9.87	23.02	100.22	100.22	66.81	66.81	2.01	64.80
α-pinene	0.00	0.00	0.00	32.42	0.37	9.73	22.69	0.00	0.00	0.37	0.37	0.01	0.36
Ethanol	0.00	0.00	0.58	0.41	63.72	0.12	0.29	0.58	0.58	63.15	63.15	1.90	61.24
Water	0.00	0.01	99.65	0.05	102.94	0.02	0.04	99.64	99.64	3.30	3.30	0.10	3.20
HDPE	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table 29 - Stream characterization from Aspen plus simulation (part 2).

7.19. PP solvent screening

Table 30 - Solubility (wt%) of HDPE in different solvents at 110°C, 120°C and 130°C, as calculated in COSMO-RS.

Solubility (wt%)	160°C	170°C	180°C
Toluene	27.44	45.74	60.41
p-xylene	14.86	36.30	53.73
d-limonene	0.02	13.53	37.65
α-pinene	2.10	21.80	41.88
p-cymene	0.04	14.91	38.85
Terpinolene	1.11	20.69	41.49
γ-terpinene	0.09	15.89	38.82
3-carene	0.30	18.26	40.17
β-caryophyllene	0.00	0.04	13.77
Squalane	0.00	0.00	0.00
Squalene	0.00	0.00	0.00
Farnesane	0.00	0.00	0.50
Farnesene	0.00	0.00	0.08

7.20. PP and α -pinene recovery

	Recovery (wt%)
PP	97.96 ± 0.61
α -pinene from precipitation step	47.15 ± 8.59
α -pinene from washing step	15.27 ± 4.86
α-pinene total	62.43 + 3.73

Table 31 - PP and α -pinene recovery using ethanol as antisolvent, in the antisolvent/solvent ratio 2/1, after dissolution at 110°C for 10 min.

7.21. Differential thermogram of recovered PP



Figure 98 - Derivative thermogravimetric analysis of recoverd PP, at different scales.

7.22. Characteristic FTIR bands of isotactic PP and correspondence

iPP band	Correspondence	iPP band	Correspondence
(cm⁻¹)		(cm⁻¹)	
809	C-C stretching	1376	C-H bending
841	C-H bending	1456	C-H bending
	(isotactic PP)		
899	C-H bending	2838	C-H asymetric
	(isotactic PP)		bending
973	C-C stretching	2868	C-H asymetric
			bending
998	C-H bending	2877	C-H asymetric
	(isotactic PP)		bending
1168	C-H bending	2918	C-H asymetric
	(isotactic PP)		bending
1359	C-H bending	2951	C-H asymetric
			bending
		1	

Table 32 - Characteristic FTIR bands of iPP and corresponding vibrations.

7.23. HDPE, PET, α-pinene and thymol:carvacrol (1:1) recovery

Table 33 - HDPE, PET, α -pinene and thymol:carvacrol (1:1) recovery from selective dissolution and precipitation.

	HDPE	PET
Polymer	79.77 ± 1.27	84.16 ± 5.26
Solvent from precipitation step	34.47 ± 12.39	68.11 ± 8.70
Solvent from washing step	20.38 ± 12.81	
Total solvent	54.85 ± 7.60	68.11 ± 8.70

7.24. FTIR spectra of pristine and recovered HDPE from HDPE/PET

mixture



Figure 99 - FTIR spectra of pristine and recovered HDPE from HDPE/PET mixture.

7.25. Differential thermogram of recovered PET



Figure 100 - Derivative thermogravimetric analysis of recovered PET, at different scales.