



# Chemical Recycling Processes of Nylon 6 to Caprolactam: Review and Techno-Economic Assessment

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## ABSTRACT

Chemical recycling has increasingly gained attention in order to mitigate environmental pollution and facilitate the transition to a circular economy. Yet only a minor fraction of the polyamide 6 waste is chemically recycled to its monomer  $\epsilon$ -caprolactam. The present paper provides a systematic overview of chemical polyamide 6 re-monomerization pathways, an analysis of each pathway's reaction mechanism, a comprehensive simulative techno-economic process comparison of the alcoholysis and neutral, acidic, and alkaline hydrolysis as well as process opportunities for the chemical re-monomerization of polyamide 6. For this, a conceptual process design was carried out using a connected Aspen Plus and Python model. The results indicate that alkaline hydrolysis is the most energy-efficient process due to its simple integration of the reaction and purification section. In contrast, neutral hydrolysis using subcritical water generates by-products, which require energy-intensive separation, leading to the highest total annual costs. Although the conventional pathway using phosphoric acid requires less energy than the alcoholysis using supercritical isopropanol, the expensive hazardous waste treatment and raw material costs make it less economically attractive. Nevertheless, a cash flow analysis shows that both alkaline and acidic hydrolysis, as well as alcoholysis, become profitable within five years at the chosen scale of 12 kilotons of caprolactam per year. The results suggest that a non-volatile solvent or catalyst that catalyzes the chain-end back-biting depolymerization mechanism of polyamide 6 using an integrated reaction and separation zone with straight distillation or stripping of caprolactam would be the most economically and environmentally attractive process for chemical recycling of polyamide 6.

## 1. Introduction

The massive production of plastics caused undeniable issues, such as land and ocean pollution and depletion of petroleum-based resources. The global market of polyamides, also called Nylons, is expected to reach 10.4 million tons per annum by 2027. This market growth is a considerable constraint for sustainability since polyamide waste is non-biodegradable. Therefore, developing efficient and sustainable recycling technologies is indispensable [1].

To meet the recycling targets of the European Commission for 2025, several recycling options are being investigated and improved (see Fig. 1) [2]. Mechanical, chemical, and energy recycling are the three leading plastic recycling approaches. Mechanical recycling is the most applied material recycling strategy in Europe and involves sorting, washing, shredding, melting and remoulding without altering the basic polymer [3–6]. However, it causes severe degradation, decrease of

molar mass, and downcycling over several recycling cycles due to chain scission and oxidation reactions, especially for mixed or contaminated plastic waste and in the presence of moisture [7–9]. In contrast to mechanical recycling, chemical recycling, where the polymer chain is broken down to monomers, oligomers or other lower molecular weight compounds, enables the “re-cycling” and “up-cycling” of those plastic materials that are no longer suitable for mechanical recycling [10,11]. Therefore it has gained much attention, as shown by numerous reviews over the past two years [5,9,11,12]. Chemical recycling is usually classified by solvolysis/chemolysis in a mild-temperature environment and thermochemical pathways [8,10]. Thermochemical pathways such as pyrolysis, gasification, or catalytic cracking are widespread and investigated technologies which are often more tolerant towards mixed or contaminated plastic waste [8,13]. However, many of them involve high temperatures, complex mixtures of crude oils, waxes, chars and harmful gases [2,7,8,10]. In the so-called back-to-monomer, re-monomerization or monomer recycling approach of solvolysis or

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Nomenclature			
ACA	aminocaproic acid	iPrOH	isopropanol
ACAM	aminocaproamide	K	kinetics
ACAN	aminocapronitrile	k'	rate constant
CAPEX	capital investment expenditures	LP	low-pressure steam
CL	$\epsilon$ -caprolactam	MP	medium-pressure steam
C <sub>pi</sub>	equipment purchase costs	NaOH	sodium hydroxide
CSTR	continuous stirred tank reactor	NPV	net present value
CW	cooling water	OIL	No. 2 fuel oil
D	depreciation	OPEX	operational expenditures
EG	ethylene glycol	PA6	polyamide 6
F <sub>L</sub>	Lang factor	r	discount rate
G&A	general and administrative	S	sales
H <sub>3</sub> PO <sub>4</sub>	phosphoric acid	TAC	total annualized costs
HP	high-pressure steam	t <sub>f</sub>	final time
HPA	phosphotungstic heteropoly acid	VLE	vapor–liquid equilibrium
HTW	high-temperature water	X	conversion
I	chemical engineering plant cost index	Y	yield
IL	ionic liquid	[bmim][Cl]	1-butyl-3-methylimidazoliumchlorid
i <sub>min</sub>	minimum return on investment	[emim][BF <sub>4</sub> ]	1-ethyl-3-methylimidazolium tetrafluoroborate
		[PP13][TFSI]	1-methyl-1-propylpiperidinium bis (trifluoromethylsulfonyl)imide

chemolysis, the polymer chain is depolymerized into monomers using a solvent or catalyst in comparably milder conditions [7,10,14]. It, therefore, acts in favor of a circular economy with multiple polymerization–depolymerization cycles, especially if the mentioned approaches and recycling technologies complement each other based on the type of plastic waste and required products [10,14,15].

The chemical recycling of polyamides has been investigated since the early 1960s. According to Coates' and Getzler's (2020) review of chemical recycling, polyamide 6 (PA6) is an ideal candidate for chemical depolymerization as it is neither thermodynamically nor kinetically limited [16]. Nonetheless, only two reviews specialize in the depolymerization of PA6. These reviews, authored by Datye (1991) and Mihut et al. (2001), were primarily centered on patents related to carpet or oligomeric manufacturing waste recycling [17,18]. Depending on the chemical agent, different chemical depolymerization pathways can be identified: hydrolysis, ammonolysis, glycolysis, and alcoholysis, all of which have been applied to polyamides [8,9]. In recent years, research studies have shifted their focus toward determining pseudo first-order reaction kinetics and exploring new solvents, such as supercritical fluids or ionic liquids (ILs). Despite those advances, only a minor fraction of the annual PA6 production is chemically recycled [13,16]. Reportedly, the reason for this is the weak economic competitiveness of depolymerization processes [19–21]. Therefore, a techno-economic analysis of the chemical recycling of PA6 that is not yet available in the literature needs to be performed [22].

With the aim of identifying the most promising monomer recycling

pathway and possible opportunities for its process optimization with regard to economic competitiveness, this paper presents a comprehensive literature review as well as a simulative techno-economic comparison of chemical PA6 re-monomerization processes, both of which have not been done yet. This is tackled in [section 2](#) by summarizing all chemical re-monomerization studies and their reaction mechanisms and selecting four pathways for the simulation and assessment, namely acidic hydrolysis with phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), alkaline hydrolysis with sodium hydroxide (NaOH), neutral hydrolysis with high-temperature water (HTW), and alcoholysis with isopropanol (iPrOH). Subsequently, the processes' flow sheets, conditions, particularities, and bottlenecks are analyzed ([section 4.1](#)). Starting with the discussion of the energy requirements for each pathway, the processes are compared with each other ([section 4.2.1](#)). The total annualized costs (TAC) as a standard measure for comparing different process scenarios are used to identify the most economically viable pathway ([section 4.2.2](#)). Furthermore, within a cash flow analysis, the profitability of the processes is evaluated using their net present values (NPVs). With those assessments, all advantages and disadvantages of different re-monomerization pathways are outlined and tabulated ([section 4.2.3](#)). Ultimately, this work tries to contribute to an overall improved understanding of the back-to-monomer pathways, which enables the environment of an ideal process and solvent for the chemical recycling of PA6 in [section 4.3](#).

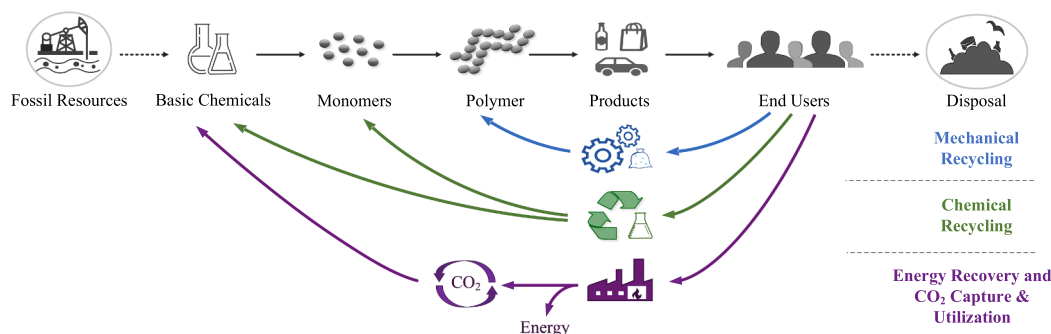


Fig. 1. Schematic representation of possible circular economies for polymers: mechanical recycling, chemical recycling, and energy recovery.

## 2. Literature study, reaction mechanisms & selection of re-monomerization pathways

The challenge of depolymerizing PA6 back to its monomer  $\epsilon$ -caprolactam/azepan-2-one (CL) is three-folded. Firstly, the semicrystalline PA6 exhibits strong intermolecular interactions through hydrogen bonding between the amide groups of different polymer chains, increasing its dissolution temperature [23,24]. The depolymerization of PA6 is only energetically favorable at elevated temperatures. The so-called ceiling temperature of 277 °C can be lowered by adding a chemical agent [16,25]. Secondly, the potential nucleophilic attack of any chemical agent on the carbonyl group of the amide is hindered by its resonance effect with a nitrogen-carbon double bond. Thirdly, secondary amines, as strong bases, are not a good leaving group, inhibiting successful amide cleavage [26]. To accomplish this endothermic reaction, different chemical recycling pathways have been investigated based on their chemical agent and depolymerization mechanism, as shown in Fig. 2. Depending on the pathway, the chemical agent can act as a solvent, catalyst, or both. In regular solvolysis, a substitution or elimination reaction occurs in which the solvent acts as a nucleophile

and interacts with the polar amide group. However, depending on the pathway, other mechanisms exist, e.g. the back-biting mechanism, also called end-biting or chain-end scission [27], where the primary amine at the end of the polymer chain attacks the adjacent carbonyl group [28]. In the following, each pathway shown in Fig. 2 is first described with respect to the reaction mechanisms, then tabulated by all conducted research studies and lastly, summarized by the most important findings. This section excludes the advantages and disadvantages of each pathway, as those are addressed in detail, along with the simulation results in section 4.2.

### 2.1. Hydrolysis

There are three different types of PA6 hydrolysis, namely acidic, neutral, and alkaline hydrolysis. The neutral hydrolysis of PA6 can be seen as the reverse reaction of the typical hydrolytic ring-opening polymerization process, in which CL is first hydrolyzed to its linear version aminocaproic acid/ $\epsilon$ -aminohexanoic acid (ACA) with subsequent polycondensation and addition reactions [29]. Adding an acidic or alkaline solvent considerably decreases the ceiling temperature [8].

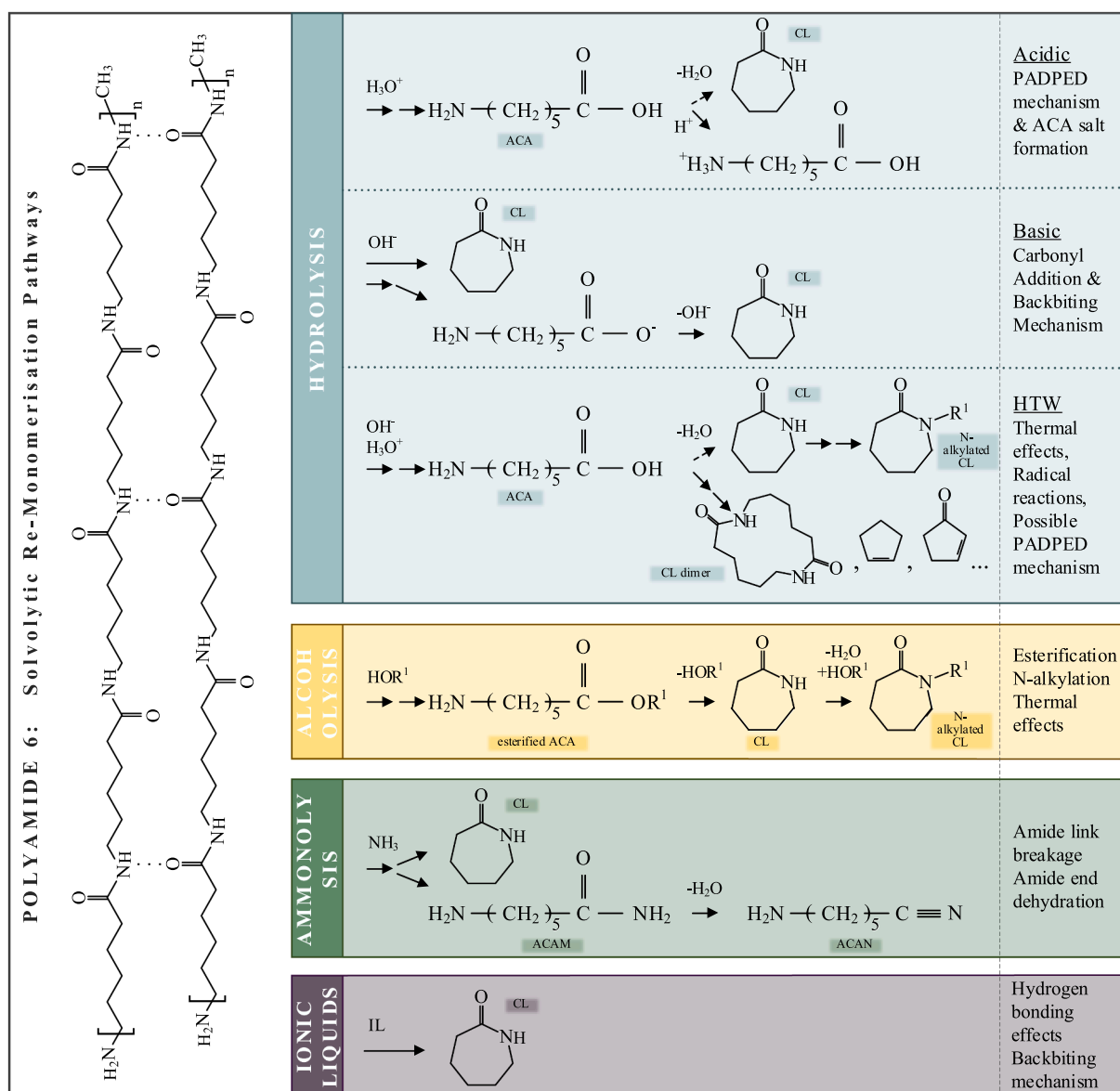


Fig. 2. Schematic overview of the reaction steps and involved side products of depolymerization of PA6 for each pathway.

Research studies about acidic, alkaline, and neutral hydrolysis of PA6 are summarized in Table 1, and their mechanisms are discussed in more detail in the following.

Hydrolysis in an acidic environment can be considered as the conventional process covered by several patents [31,36,51–53]. A negative charge on the oxygen atom occurs through the resonance effect of the amides, as mentioned above, which is why acidic hydrolysis of amides starts with the protonation of oxygen instead of nitrogen. This activation step is necessary prior to the nucleophilic attack of water. Hence, this so-called PADPED mechanism can be summarized as follows: 1. protonation at the oxygen, 2. addition of water as co-solvent ( $\text{RCOH}_2^+$ ), 3. deprotonation of the attached water group ( $\text{RCOH}_2\text{OH}$ ), 4. protonation of the nitrogen atom ( $\text{R}_2\text{NH}_2^+$ ), 5. elimination of that nitrogen ( $\text{RCOH}_2\text{OH}$  and  $\text{RNH}_2$ ), and 6. deprotonation of the one oxygen ( $\text{RCOOH}$  and  $\text{RNH}_2$ ) [54]. Interestingly, a secondary ammonium salt (ACA salt) is produced because ACA is protonated and therefore stabilized by the acid catalyst (see Fig. 2) [55]. As a consequence, any formed ACA salt cannot further cyclize to CL and is obtained as the main product by most of the studies about acidic hydrolysis [30,38,39]. Still, CL monomer is required for the industrial hydrolytic ring-opening polymerization process [7]. In the conventional process using  $\text{H}_3\text{PO}_4$ , this problem of ACA salt formation and acid catalyst consumption was partly diminished through the use of steam, which instantaneously carries CL out of the reaction equilibrium into the gas phase (see section 4.1.1) [56].

By being the first to have investigated microwave radiation for PA6 depolymerization, Klun and Krzan (2000) found that microwaves considerably decreased the degradation time. However, CL or ACA yields were not reported [30]. Yuan et al. (2014) investigated PA6 depolymerization using hydrochloric acid (HCl) and reported as the earliest group the formation of ACA hydrochloride that prohibits the formation of CL monomer, as described above. After crystallization, they obtained an isolated ACA yield of 85% [34]. Chen et al. (2010) were the first group to investigate the reaction kinetics of acid-catalyzed hydrolysis using phosphotungstic heteropoly acid (HPA). They described the PA6 degradation by pseudo-first-order kinetics in PA6 and found that the activation energy could be lowered by adding HPA [33]. This reaction order aligns with all other studies about the solvolytic degradation kinetics of PA6 [36,37,57].

Hydrolysis of polyamides can also be achieved using steam or HTW [58]. Corresponding processes have been patented by Jenczewski et al.

(1997) and Sifniades et al. (1997) [59,60]. Aquafil has successfully commercialized a process using supercritical water to recover Nylon from fishing nets for their ECONYL® yarn used for textiles [61,62].

Through the critical point of water at 374 °C and 22.1 MPa, HTW is categorized into sub- and supercritical water [43,63]. Water near the critical region can act like a polar organic solvent and dissolve PA6 having a lower dielectric constant, less hydrogen bonding ability, and a threefold higher ion product compared to ambient liquid water [64]. PA6 melting and crystallization temperatures are decreased through the sorption of water into non-crystalline parts and hydrogen bonding between water molecules and amide groups [65]. The amide hydrolysis through HTW might be a combination of several reaction mechanisms. As Wang et al. (2015) investigated, ionic hydrolysis reactions of PA6 are supported through a high concentration of hydronium and hydroxyl ions acting as both alkali and acid catalysts at subcritical conditions [43,63,64]. The acidic depolymerization mechanism described above is most likely [47,66]. Above temperatures of 300 °C, solvolytic polyamide hydrolysis is also accompanied by thermal decomposition reactions [48,66]. Elevating the temperature further beyond the critical point, the ion product drastically drops, and free radical mechanisms dominate [63]. Chaabani et al. (2017) even report on re-polymerization reactions [45]. For those reasons, the formation of many by-products is reported, as shown in Table 1 [33,43,45]. This explains the numerous downstream purification steps shown in patents [60].

As mentioned, neutral amide hydrolysis proceeds over ACA to CL (see Fig. 2). The literature describes the PA6 depolymerization to ACA as the rate-limiting step, whilst the cyclodehydration of ACA to CL proceeds very fast, with the equilibrium being on the CL side [42–45]. Darzi et al. (2022) and Hu et al. (2022) report that HTW quickly gives a 100% degradation of PA6 and high CL yields of over 90% [46,47]. However, Iwaya et al. (2006), who describe a decreasing CL yield over time and temperature, indicate a decomposition of CL over time [43]. Braun et al. (1999) also note that pressure significantly impacts CL yield until a specific point [41].

Among the hydrolysis pathways, the least studies have been conducted under alkaline hydrolysis. As shown by Table 1, alkaline hydrolysis has the advantage of being more selective towards CL than acidic and neutral hydrolysis. Hence, many companies investigated and applied base-catalyzed hydrolysis [56,67,68]. In most processes, a base catalyst such as potassium carbonate, sodium hydroxide, or sodium

**Table 1**

Research studies conducted about hydrolytic re-monomerization of PA6. The conditions, solvents, main products, maximum CL or ACA\* yield (Y), and availability of kinetics (K) of the respective papers are shown.

Literature	Conditions	Solvent / Catalyst	Main Products	K	Y [%]
<i>Acidic Hydrolysis</i>					
Klun and Krzan (2000) [30]	Microwave, 0–300 °C, 0–23 min	$\text{H}_3\text{PO}_4$	ACA, CL, cyclic dimer	–	–
Klun and Krzan (2002) [31]	Microwave, 8 min	Mineral salts	short oligomers	–	–
Shukla et al. (2005) [32]	Room temperature, 0–20 h	formic / sulfuric / HCl	ACA	–	94*
Chen et al. (2010) [33]	280–300 °C, 85 min	HPA	CL, ACA	x	78
Yuan et al. (2014) [34]	109 °C, 24 h	HCl	ACA	–	85*
Wang et al. (2016) [35]	160–250 °C, 1 h	lanthanum chloride	oligomers	–	–
Wang et al. (2017) [36]	300–345 °C, 0–110 min	Zeolite H $\beta$ -25, $\gamma$ -Al $2\text{O}_3$	CL	x	–
Wang et al. (2017) [37]	300–345 °C, 0–120 min	Zeolite H $\beta$	Oligomers, CL	x	63
Zagar et al. (2020) [38]	Microwave, 0–30 min, 170–190 °C	HCl	ACA salt	–	100*
Bäckström et al. (2021) [39]	200 °C, 1–6 h	$\text{H}_3\text{PO}_4$ , $\text{H}_2\text{SO}_4$ , HCl	ACA salt	–	–
<i>Neutral Hydrolysis</i>					
Reimschuessel and Nagasubramanian (1972) [40]	235–275 °C, 800–1500 kPa, 0–3 h	Water	CL	–	–
Braun et al. (1999) [41]	300–340 °C, 800–1500 kPa, 0–6 h	Steam	CL, cyclic dimer, ammonia	–	95
Goto et al. (2001) [42]	300–400 °C, 5–60 min	HTW	CL, ACA	–	60
Iwaya et al. (2006) [43]	300–400 °C, 20–35 MPa, 5–60 min	HTW	CL, ACA	x	85
Wang et al. (2014) [44]	270–370 °C, 3–16 MPa, 15–75 min	HTW	CL, ACA, CL dimer, trimer	–	89
Chaabani et al. (2017) [45]	280–600 °C, 25 MPa, 1–120 min	HTW	By products, CL	x	–
Darzi et al. (2022) [46]	250–400 °C, 30–90 min	HTW	CL, CL dimer, cyclopentene	–	75
Hu et al. (2022) [47]	280–310 °C, 20–80 min	HTW	CL, CL&ACA dimer, oligomers	–	91.6
<i>Alkaline Hydrolysis</i>					
Mukherjee et al. (1978) [48]	225–270 °C, 0.4–2 kPa, 0–9 h	Sodium hydroxide	CL	–	90.5
Nemade et al. (2010) [49]	235–250 °C, 3–4 MPa, 45–300 min	Sodium hydroxide	oligomers	x	–
Nemade et al. (2011) [50]	150–240 °C, 2.7–4.8 MPa, 60 min	Sodium hydroxide	oligomers	x	–

amino caproate is used in absence of steam [21,67] and the reactor operates under vacuum such that CL is directly distilled off [69]. Further information about the process can be found in section 4.1.2.

The mechanism for alkaline hydrolysis of PA6 also remains uncertain in the literature. However, according to general alkaline amide hydrolysis, the hydroxide-ion acts as a nucleophile towards the carbonyl group (carbonyl addition mechanism). As mentioned before, the secondary amine, as a strong base, is unlikely to break away. Still, this could occasionally occur at high temperatures in the presence of strong bases [26,70]. This would result in a primary amine (end of the polymer chain), which might attack the adjacent carbonyl atom in an intramolecular chain-end back-biting mechanism. This mechanism of an alkaline system is also supported by a very recent work by Wursthorn et al. (2022), who reported that a highly basic ligand of the lanthanide catalyst complex deprotonates the secondary amide [71]. As an alternative mechanism, the nitrogen atom of the amide bond within the polymer chain may attack an adjacent carbonyl group; however, this attack is less likely due to the lower nucleophilicity of the amide nitrogen compared to the primary amine end [72,73].

## 2.2. Alcoholysis and glycolysis

Alcoholysis describes depolymerization with alcohol at a sub- or supercritical state [15]. Glycolysis has been conducted under milder conditions with a diol, such as ethylene glycol (EG) [74,75]. This depolymerization process has also been patented [76], and all research studies about those pathways can be found in Table 2.

Kamimura et al. (2008) found that PA6 can be decomposed entirely with alcohols under harsh conditions within an hour. However, similarly, as for the HTW process, high temperatures are required. Reducing the temperature from 370 to 300 °C led to a threefold decline in CL yield to 30%, measured after evaporating the alcohol. The research group investigated several primary, secondary, and tertiary alcohols. By-products could be observed when using primary alcohols [79]. The reason for that was investigated a few years later within a mechanistic investigation where the Gibbs free energies for primary and secondary alcohols within all possible reaction mechanisms were estimated. They found that an aforementioned back-biting attack of the primary amine is not likely. Instead, PA6 esterification yields aminocaproic ester as an intermediate product that cyclizes to CL under the scission of the alcohol. Because of the steric effect, secondary alcohols do not react with CL, while primary alcohols lead to the N-alkylation of CL [81]. Minding this, Kamimura et al. (2011) investigated reaction routes and kinetics from polyamides to products of higher value to improve this depolymerization's economic performance [19,82,83]. Glycolysis seems to

undergo the same reaction mechanism, as Homme and Goethals (1998) also reported linear oligomers esterified with EG as well as EG-derived CL [78]. However, no yields were obtained in any of the studies using glycolysis, making it unsuitable for an efficient re-monomerization pathway [7].

## 2.3. Ammonolysis

Ammonolysis describes the reaction pathways where ammonia is used for the bond cleavage of polyamides. This process was invented by DuPont, who started to use this pathway to recycle Nylon carpets at temperatures around 330 °C and pressures of 140 bar with an excess of ammonia to mainly obtain hexamethylenediamine [84–86]. Several attempts have been made to achieve high product yields also under less harsh conditions [87,88]. DSM uses ammonolysis on fishing nets to produce the recycled polyamide Akulon® RePurposed [87,89].

To the best of our knowledge, ammonolysis has been addressed for the re-monomerization of PA6 only by Kafas (1998) [53]. According to him, each amide link breakage results in CL on the one hand and aminocaproamide (ACAM) on the other hand. ACAM has an amide and an amine as an end group and is dehydrated to aminocapronitrile (ACAN) by amide end dehydration. Kafas (1998) also developed a Nylon ammonolysis model using the functional group reaction approach. The model describes the evolution of the monomer as a function of the extent of polymerization. They proved that under some assumptions, those evolutions could be presented by the Flory-Schulz distribution [53].

## 2.4. Using ionic liquids

In recent years, ILs as non-volatile chemicals applicable to high temperatures have gained attention for depolymerizing polyamides [9]. However, the dissolution and depolymerization mechanisms are still not fully understood [90]. Similarly to cellulose, we assume that hydrogen bonding between the polyamide chains is weakened by the synergetic action of the IL's cation and anion, therefore being the critical factor in the dissolution mechanism [91]. This assumption would align with Kim and Harget (1979), who investigated inorganic salts for the suppression of the crystallization of PA6 [92].

The dissolution process and the high ionicity of ILs could support an addition elimination cleavage by nucleophilic attack of the amine end group of the polymer [9,28]. Hence, this chain-end back-biting mechanism explains why pure CL can be obtained without prior formation of ACA, similar to alkaline hydrolysis. According to Chen et al. (2012), a mixture of water and 1-butyl-3-methylimidazoliumchlorid ([bmim][Cl]) has a high H<sup>+</sup> concentration, which is why an acidic hydrolysis

**Table 2**

Research studies conducted about the re-monomerization of PA6 using alcohols. The conditions, solvents, main products, maximum CL yield (Y) and availability of kinetics (K) of the respective papers are shown.

Literature	Conditions	Solvent / Catalyst	Main Products	K	Y
Huczowski et al. (1978) [77]	N <sub>2</sub> atmosphere, 197 °C, 0–300 h	EG with other catalysts	Oligomers	–	–
Homme and Goethals (1998) [78]	250 °C, 0–110 min	EG with H <sub>3</sub> PO <sub>4</sub>	EG derivatives of CL and oligomers	–	–
Kamimura et al. (2008) [79]	370 °C, 90 min	18 alcohols	CL	–	93%
Kamimura et al. (2011) [80]	330 °C, 28 MPa, 6 h	Supercritical methanol (MeOH)	Methyl 6-hydroxycapronate, methyl 5-hexenoate, CL	x	29%
Kaweetirawatt et al. (2012) [81]	– (Simulation)	Isopropanol, MeOH	CL, N-methylated CL	–	–

**Table 3**

Research studies conducted about the re-monomerization of PA6 using ILs. The conditions, solvents, main products, maximum CL yield (Y) and availability of kinetics (K) of the respective papers are shown.

Literature	Conditions	Solvent / Catalyst	P	K	Y
Kamimura and Yamamoto (2007) [94]	300 °C, 4–5 h	[PP13][TFSI], [P13][TFSI], [TMPA][TFSI], [bmim][TFSI]	CL	–	86%
Kamimura and Yamamoto (2008) [28]	270–350 °C, 6 h, reduced pressure	[PP13][TFSI], [P13][TFSI], [TMPA][TFSI], [bmim][TFSI], [aem][TFSI]	CL	–	86%
Yamamoto and Kamimura (2009) [95]	300 °C, 6 h, reduced pressure	[PP13][TFSI] with ammonium salt containing DMAP	CL	–	80%
Chen et al. (2012) [93]	150–230 °C, 5–10 h	[bmim][Cl] and water	CL	–	31%
Kamimura et al. (2019) [96]	280–320 °C, 60 min	[emim][BF <sub>4</sub> ]	CL	–	55%



mechanism as described in [section 2.1](#) could be possible as well. However, they only found yields of 31% [93]. Research studies about the re-monomerization pathway using ILs can be found in [Table 3](#).

Kamimura and Yamamoto (2008) found that ILs with high polarity, ionicity, and  $K_w$  values gave the highest yields [28]. The authors also studied several ILs and stated that 1-methyl-1-propylpiperidinium bis(trifluoromethylsulfonyl)imide ([PP13][TFSI]) is not decomposing when being re-used in several reaction cycles at temperatures of 300 °C [28,94]. Moreover, Kamimura et al. (2019) investigated 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF4]) to recover this hydrophilic IL by extraction rather than energy-intensive flash separation. Interestingly, microwave radiation also influenced this reaction positively and reduced the required time to obtain a 55% yield to 60 min [96].

## 2.5. Process selection

Generally, one can state that experimental data is missing for some pathways. For example, no CL yields were reported for the glycolysis pathway. In ammonolysis, the experimental demonstration is lacking as well. The ionic liquid processes do report high yields and selectivity towards CL. Still, for process simulation, the vapor–liquid or liquid–liquid equilibrium data is required to simulate the described recovery of the ILs. Because of this lack of data, the process simulation cannot be done precisely enough, and those three pathways are excluded from the process simulation and techno-economic assessment.

Among the remaining studies, the most promising and essential ones need to be selected for the simulation. Hence, the conventional process using  $H_3PO_4$  is selected, representing the benchmark process patented by BASF [56]. Neutral hydrolysis using subcritical water has gained much attention and has been highlighted many times for its environmentally friendly characteristics. Wang et al. (2014) reported on both CL yields and amounts of cyclic and linear oligomers. Hence, this work is also selected for the simulation and analysis [44]. Base-catalyzed hydrolysis has the advantage of relatively pure product yields because of the potential back-biting mechanism described above. Therefore, the process of Mukherjee and Goel (1978) was selected as a CL yield of 90% was reported [48]. Lastly, Kamimura et al. (2008) have investigated the use of alcohols in a high-temperature environment and reported on the potential economic feasibility of those. Thus, this process was simulated as well [79].

## 3. Methodology

The processes were designed to closely resemble the selected literature studies of each pathway, with the aim of ensuring consistency and comparability. The simulations and analyses of the processes were conducted using a connected Aspen Plus and Python model [97]. In Aspen Plus V8.8, the process was simulated. At the same time, the Python code gave inputs such as feed rates and purity requirements to Aspen Plus, retrieved the simulation results from Aspen Plus, such as heat duties or flowrates, and performed the economic analysis based on those results [97]. For scalability and comparability reasons, all processes were designed in continuous operation mode.

### 3.1. Input conditions & process constraints

It is essential to mention that the scale-up of solvolytic chemical recycling is challenging and not much investigated [13,22,98]. There is missing data for waste compositions and kinetics of solvolytic chemical recycling of mixed plastic waste. To study it most realistically and consistently, the changes to the processes of the papers were kept at a minimum, and all processes were treated equally. However, the same CL production capacity must be chosen for comparability reasons. A typical PA6 production plant has a capacity of 80 kt per year [99]. Assuming 15% would be recovered chemically, the annual CL production capacity

amounts to 12 kt, which is set as the base for all processes. The purity of the CL stream was set to a minimum of 99.9 wt%. Depending on the yield reported by the chosen paper, different input flow rates of PA6 are required. However, for all processes, a pure PA6 stream was assumed. The temperatures of the inlet and outlet flow rates of the processes were also set equal for all pathways. The input flows enter at a temperature of 25 °C, and all exiting streams leave the process at 40 °C.

### 3.2. Simulation model & flowsheet options

The rate-based continuous stirred tank reactor (CSTR) model was chosen because of the liquid-phase reaction and relatively slow reaction kinetics [100]. Using the design specification tool with an incorporated Fortran code in Aspen Plus, the CL yield was forced to equal the one reported in the respective paper by adjusting the reactor volume accordingly. The separation and purification section ensures a minimum CL recovery of 99% for each pathway. Another design specification task compensated for any CL loss in the purification section by adjusting the PA6 input flow rate such that the yearly CL production capacity matches the chosen target of 12 kt. Simultaneously, a third design specification function ensured a fixed solvent to PA6 ratio using a Fortran Code.

In modeling the distillation columns, the inside-out RADFRAC model was utilized in conjunction with Newton's algorithm, which has been recommended for highly non-ideal systems [101]. As a constraint for the condenser pressure, the minimum pressure was set to be able to use cooling water (CW) and a liquid ring pump as cold utility and process equipment, respectively. Pressures of a distillation column sequence were determined using the connected Python and Aspen Plus model that computed the costs for various pressure configurations [97]. The most economical solution was selected.

### 3.3. Data base for component input into Aspen Plus

For the component input of PA6 to Aspen Plus, a database needed to be created. Scalar properties, such as enthalpy of fusion, and temperature-dependent properties, such as solid and liquid heat capacity, were taken from the Polymer Handbook [25]. Parameters for the temperature-dependent correlations (such as DIPPR) were regressed when necessary.  $H_3PO_4$  and PA6 were assumed to be non-volatile [102–104]. The created database can be seen in the [Supplementary document](#).

In Aspen Plus, the standard enthalpy of formation is required for the calculation of all enthalpy streams and parameters, such as the reaction enthalpy. The estimation of standard enthalpy of formation is complex and often estimated by quantum mechanical methods. For PA6, the enthalpy of formation for one amide bond can be found [105]. However, this cannot be extrapolated easily to the polymer chain [106,107]. Therefore, knowing the enthalpy of formation of CL, the enthalpy of formation of PA6 was estimated in a way that the depolymerization enthalpy equals the negative of the known polymerization enthalpy (–12.5 kJ/mol) [25]. This assumption is valid as it holds for reversible reactions.

When a component was unavailable in any of the databases, it was user-defined in Aspen Plus. Critical properties, the heat of formation and vapor pressure curves, were estimated by Aspen Plus property estimation using Joback, Benson, and Riedel method, respectively [108–110].

### 3.4. Thermodynamics and kinetics

The components' vapor–liquid equilibrium (VLE) data were retrieved from the NIST database by Aspen Plus (e.g., water and CL), and the NRTL model was used to describe the VLE behavior. Unknown vapor–liquid equilibria were estimated by the UNIFAC group contribution method (e.g., CL and ACA).

As mentioned before, a pseudo-first-order reaction with respect to PA6 was assumed in several studies [33,36,37,45,57]. This is displayed

in equation (1), where [PA6] ([PA6] = [PA6]<sub>0</sub> (1-X)) describes the concentration of PA6, and  $k'$  and X stand for the rate constant and conversion, respectively.

$$-\frac{d[\text{PA6}]}{dt} = k' \cdot [\text{PA6}] \Leftrightarrow dt = \frac{dX}{k' \cdot (1-X)} \quad (1)$$

If the kinetics were not available in the literature, the following Eq. (2) was used. In Eq. (2), the required kinetic parameter  $k'$  is derived from equation (1) using the batch data point with the final time and conversion given by the corresponding paper (Eq. (2)).

$$k' = \frac{1}{t_f} \ln \left( \frac{1}{1-X_f} \right) \quad (2)$$

### 3.5. Process and equipment design

Regarding the choice of the equipment type, heuristics for pumps, heat exchangers, vacuum equipment, columns, or vessels were used [100]. The dimensions of the equipment, such as vessel height, diameter, wall thickness, and weight, were necessary for the economic evaluation. Essential parameters for pumps included the pump head and flow rate, while the heat exchangers' costs calculation required the area and tube length. The design of the equipment was accomplished through a combination of empirical equations, such as the calculation of heat exchanger areas or column diameters, and heuristics, such as the selection of tray sizing or heat exchanger tube length [100,111]. The [Supplementary Data](#) gives those calculations and the equipment choice.

### 3.6. Utilities

CW, low-pressure steam (LP), medium-pressure steam (MP), high-pressure steam (HP), No. 2 fuel oil (OIL), and dowtherm A were chosen as utilities for heat transfer. Near-optimal approach temperatures were defined according to temperature levels, e.g. 5 °C for ambient temperature levels. The pipeline and valve pressure drop was neglected, and the heat exchanger pressure drop was set dependent on the phase of the stream [100]. The precise values and details of the utilities, as well as their costs, are displayed in the [Supplementary](#) document.

### 3.7. Economics

U.S. dollar were chosen as the currency. The capital investment expenditures (CAPEX) were computed using the Lang factor method which has an accuracy of 35% [100,112]. The Lang factor  $F_L$  is multiplied by the sum of the free onboard equipment purchase costs  $C_{pi}$  and accounts for all other direct and indirect investment costs as well as the working capital (Eq. (3)). The  $C_{pi}$  were calculated using regressed correlations as a function of equipment size factors. The equations for the determination of  $C_{pi}$ , assumptions of the Lang factor method, and the used equipment materials are given in the [Supplementary](#) document (see section A). Afterward, those costs were updated to the current year by applying the chemical engineering plant cost index I [100].

$$\text{CAPEX} = 1.05 \cdot F_L \cdot \sum_i I_{i/I_{bi}} \cdot C_{pi} \quad (3)$$

The total production costs or operational expenditures (OPEX) comprise variable costs, operational costs, fixed costs, and general and administrative (G&A) costs. The variable costs, such as raw material, utility, and waste treatment costs, were calculated using current industrial market prices (more information in the [Supplementary](#) document). A plant operating factor of 0.9 was assumed. Direct wages and benefits were determined based on the typical labor requirements of the equipment type and a five-shift schedule [113]. Maintenance, plant overhead, and fixed costs, as well as the G&A costs, were calculated as a fraction of labor costs, capital investment expenses, or sales [100,113]. The complete calculation procedure of the OPEX, as well as raw

material, utility, and product prices, are given in the [Supplementary](#) document.

The TAC are typically used to assess a chemical process's economic viability and compare the costs of different processes or production scenarios. In this work, the TAC comprise the annualized CAPEX and the direct production costs (Eq. (4)). The latter is composed of variable ( $C_{\text{variable}}$ ) and operating ( $C_{\text{operating}}$ ) costs (labor, supervision, and supplies). A reasonable minimum return on investment of  $i_{\text{min}} = 0.2$  was assumed [100]. Since the applied Lang factor method has a certain accuracy and utility prices are volatile, error bars were included for the TAC. Minimum and maximum TAC were computed by incorporating 35% accuracy of the Lang factor method and 20% utility price fluctuations.

$$\text{TAC} = C_{\text{variable}} + C_{\text{operating}} + i_{\text{min}} \cdot \text{CAPEX} \quad (4)$$

For the cash flow analysis, net earnings were calculated by Eq. (5), where S means the sales. The income tax rate was calculated according to the federal income tax rate schedule for corporations in the U.S. [100]. Subsequently, the free cash flow (FCF) was calculated by Eq. (6), where D is the depreciation. One year for the plant construction was assumed.

$$\text{Net earnings} = (S - \text{OPEX}) \cdot (1 - \text{income tax rate}) \quad (5)$$

$$\text{FCF} = (\text{Net earnings} + D) - \text{CAPEX} \quad (6)$$

The NPV is a financial profitability measure typically used to evaluate the investment potential of different processes. The time value of money was considered by a discount rate of 15% ( $r$ ), and the NPV was calculated by projecting the cash flows of the processes over a time period of  $T = 14$  years (see Eq. (7)) [100].

$$\text{NPV} = \sum_{t=1}^T \frac{\text{FCF}}{(1+r)^t} - \text{CAPEX} \quad (7)$$

## 4. Results & discussion

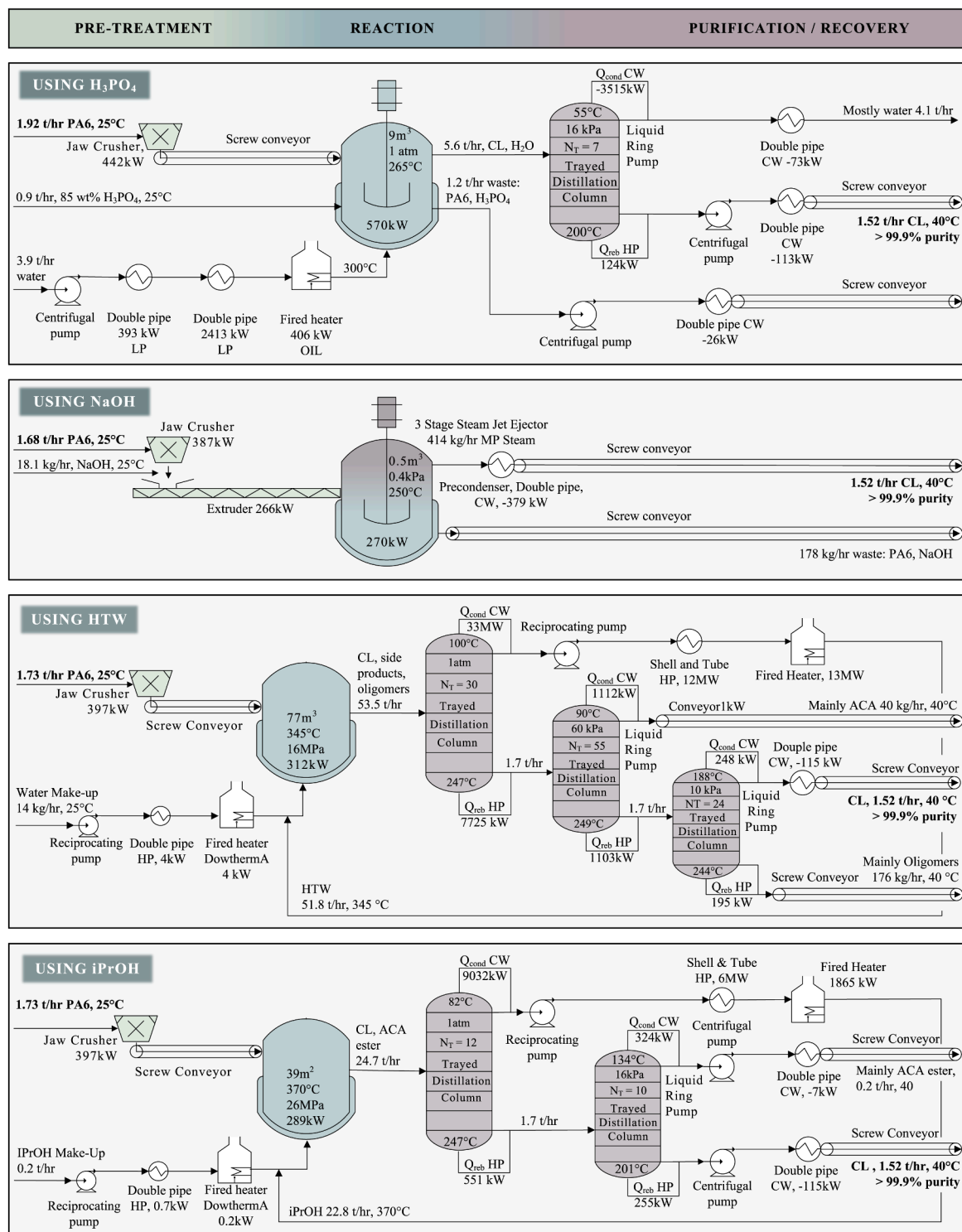
### 4.1. Descriptions of the simulated processes

Each process consists of the pre-treatment, reaction, and purification section as indicated by the different colorization. Process flow schemes and simulation results of all four processes can be seen in [Fig. 3](#). In the following, those processes are discussed individually in detail.

#### 4.1.1. Process using $\text{H}_3\text{PO}_4$

The chemical recycling of PA6 using  $\text{H}_3\text{PO}_4$  was simulated according to the conventional process using PA6, steam, and  $\text{H}_3\text{PO}_4$  as input flows into the reactor with a subsequent vacuum distillation column for the CL purification [56,86,114–117]. To achieve the specified product capacity of 1.5 tonnes per hour, 1.92 tonnes of PA6 per hour are required (see [section 3.1](#)).

In the reactor, superheated steam serves multiple purposes: it provides heat for the endothermic reaction, supplies water for hydrolysis, facilitates agitation in the reaction system, and removes CL monomers to alter the reaction equilibrium [17]. As a result, two reactor effluents are obtained: a liquid stream at the bottom and a vapor stream with a 80% yield of CL at the top. The protonation of ACA by  $\text{H}_3\text{PO}_4$  and salt formation (see explanations [section 2.1](#)) prohibit ACA vaporization despite its lower boiling point compared to CL. Instead, the resulting ACA  $\text{H}_3\text{PO}_4$  salt complex, as well as unreacted PA6, dimers, trimers, oligomers, or other compounds with high boiling points, are disposed of as hazardous waste at the bottom of the reactor. In practice, the  $\text{H}_3\text{PO}_4$  is very difficult to recover due to the salt formation, other neutralization reactions with potential alkaline fillers in PA6 and thermal degradation reactions [39,69,118]. This leads to the consumption of the catalyst  $\text{H}_3\text{PO}_4$  and the need for high feed rates of this raw material, as described in our previous work [118].



**Fig. 3.** Schematic presentation of the processes for each of the four re-monomerization pathways. The pre-treatment zone (green), reaction zone (blue), and separation zone (purple) are shown. Temperatures, mass flow rates, and energy requirements can be seen as well.

For product purification purposes, CL is separated from water through a single vacuum distillation column. Our previous work showed that also the addition of further distillation columns for the separation of other impurities would have only very minor effects on the results [118]. The product stream at the bottom of the distillation column is cooled to 40 °C (see section 3.1) and dried by a heat exchanger and screw conveyor.

#### 4.1.2. Process using NaOH

The process using NaOH was simulated based on the lab-scale procedure described by Mukherjee et al. (1978) [48]. Before describing the process in detail, it is important to mention that the scale-up of this process could lead to technical difficulties in practice due to the use of a solid catalyst and extrusion [69]. More precisely, because of the viscous reaction system, mass and heat transfer limitations could occur, posing a



barrier to the distillation of CL out of the reactor and the assumed reaction kinetics.

On the other hand, as can be seen in Fig. 3, this simulated process would be the simplest and could show many advantages if practically achievable. The reaction and separation are performed simultaneously in a single unit which is achieved by operating the reactor at vacuum conditions and distilling CL. At the same time, all other components are non-volatile and leave the reactor at the bottom [48]. As reported by Braun et al. (2001), the catalyst is incorporated into PA6 through extrusion [69]. The high selectivity towards CL due to the chain-end back-biting mechanism, as described in Section 2.1, enables the achievement of the desired production capacity with a relatively small amount of PA6 compared to the acidic process. Catalytic amounts of NaOH can be used, as they are not consumed, allowing for a minimal reaction volume. The high vacuum level of the reactor necessitates a three-stage steam jet ejector system using medium-pressure steam, preceded by a pre-condenser. The NaOH cannot be recovered and is disposed of as waste, while the purified CL is transported and dried using a screw conveyor similar to the process of acidic hydrolysis.

#### 4.1.3. Process using HTW

The neutral hydrolysis process was simulated based on Wang et al. (2014) and uses an extensively hot and pressurized water stream for the depolymerization. As shown in Fig. 3, this results in a large reactor volume. It can also be seen that the subcritical water process has the most complex purification section compared to the other three processes. As explained in section 2.1, the high-temperature environment (345 °C) during hydrolysis results in the formation of side products and oligomers, which need to be separated using three distillation columns. The pressures of those distillation columns are determined as described in section 3.2. The water is separated in the first distillation column and then heated to the necessary temperature of 345 °C before being recycled to the reaction unit. According to the depolymerization mechanism, no water is consumed [47]. Still, since it is not fully recovered, a make-up stream is introduced. To simulate the network of complex thermal reactions occurring at subcritical conditions, oligomers and side products with high boiling temperatures are lumped together, represented, and simplified as ACA dimer. This pseudo-compounds' quantity is set to match the combined concentration of all linear and cyclic oligomers, as determined by Wang et al. (2014) and separated in the final vacuum distillation unit [44]. In the same way, also lower boiling side products are lumped and represented by ACA, which is separated in the second vacuum distillation column. ACA, ACA dimer, and CL are dried and transported using conveyors.

#### 4.1.4. Process using iPrOH

The alcoholysis process using iPrOH was simulated based on the study of Kamimura et al. (2008) [79]. PA6 is completely decomposed at 370 °C, resulting in a 93% yield of CL. Despite this high-temperature environment, fewer by-products can be expected compared to the HTW process. As evidence for this, the group evaporated iPrOH and determined a close match between the products boiling point and the boiling point of CL [79]. The remaining decomposed PA6 (7%) is assumed to be esterified ACA (isopropyl 6-amino-caproate). This is a reasonable assumption since the reaction mechanism shows this compound as an intermediate product, and it has a similar boiling point as CL. Therefore, two distillation columns are necessary, one for recovering iPrOH and one for purifying CL from the esterified ACA. These products are dried and transported by use of conveyors.

## 4.2. Analysis and comparison of the processes

In this section, the processes are compared regarding their energy requirements, profitability, and TAC, and lastly, concluding advantages and disadvantages of each process are listed.

### 4.2.1. Energy requirements

Fig. 4 shows the energy requirements categorized by utility type and by pre-treatment, reaction, separation, heat exchanging, and pumping zones. Tabulated utility requirements are given in the Supplementary document in the results section E.

As can be seen in Fig. 4A, the alcoholysis and HTW hydrolysis processes show the highest energy requirements due to the high reaction temperatures, CL purification from by-products, and solvent recovery. Hence, huge quantities of HP and dowerm A are needed. Still, the energy requirements for the HTW process are triple compared to the alcoholysis. The reasons for that are the bigger solvent stream and the formation of several by-products. This can also be seen in Fig. 4B, where the separation section for the HTW process is much more dominant, as those by-products and water need to be separated in an energy-intense distillation column sequence. However, it should be noted that both processes might have a great potential for heat integration (see Table 4 advantages).

The alkaline process is by far the least energy intense process due to the small flow rates, absence of water, and the integration of reaction and CL purification. Compared to that, the energy requirements for the hydrolysis using  $H_3PO_4$  are more than double due to the use of superheated steam, which is mainly heated up using LP. Hence, the heat exchanger section is superior in this conventional process (see Fig. 4B).

Another remark is that the energy required for the PA6 pre-treatment and the reaction is closely comparable for all processes. Despite contrary statements in the literature, it can be seen that the reaction zone with

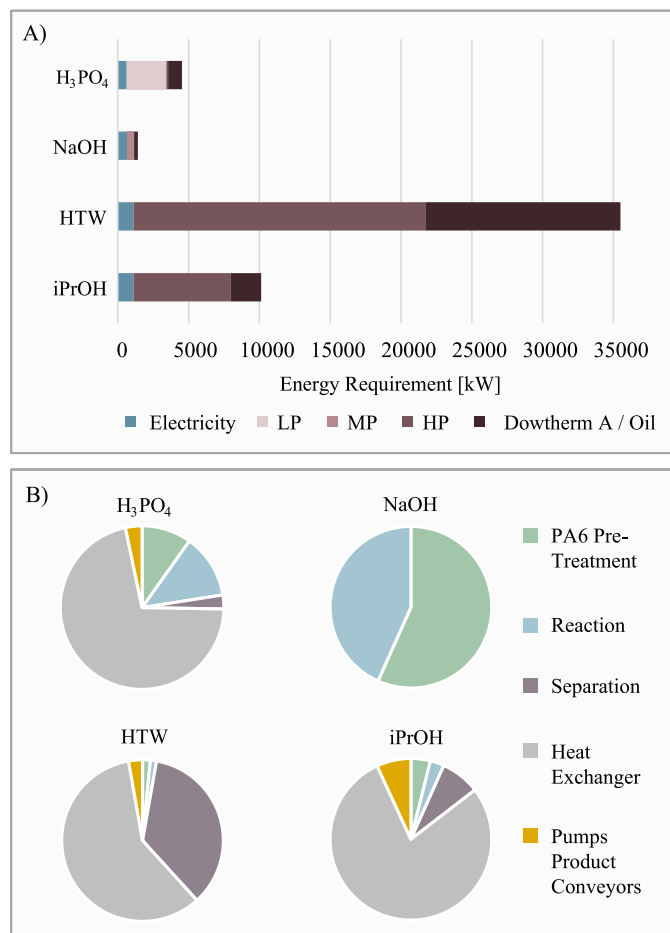


Fig. 4. A) Energy requirements of the four re-monomerization processes categorized by utility usage: electricity, LP, MP, HP, and dowerm A or oil. B) Pie chart with energy requirements categorized by pre-treatment, reaction, separation, heating, and pumping operations.

energy requirements for the endothermic PA6 depolymerization is not dominant for any of the four processes [38,47], which we also explained further in our previous work [118]. The alkaline hydrolysis involves extrusion for incorporating the catalyst into the PA6 melt and therefore has slightly higher electricity requirements for the pre-treatment compared to the other processes. In addition to the heating duty for the endothermic high-temperature reaction, the acidic and alkaline processes also have to provide for the enthalpy of vaporization for CL. However, this contributes only minimally to the overall energy requirements.

#### 4.2.2. Costs and profitability

To analyze the contribution of the energy demand on the overall costs, the TAC are evaluated. In Fig. 5, the TAC is shown, and operating, raw material, utility costs, and CAPEX are colorized. The bars indicate TAC in best- and worst-case scenarios and incorporate possible errors such as volatilities of the utility prices as well as the inaccuracy of the Lang factor method of 35%. For the acidic hydrolysis process, an additional distillation column is added for the maximum TAC to account for the removal of acidic impurities [56,118]. The minimum TAC of the neutral hydrolysis using HTW incorporates a potential recovery of the oligomeric bottom stream of the second distillation column, thereby reducing the PA6 raw material stream, assuming equal reactivity and kinetics as for PA6 depolymerization. The Supplementary document gives a tabulated cost breakdown of the OPEX and CAPEX for all processes.

Expectedly, the HTW hydrolysis process has the highest TAC due to the high utility costs for the energy requirements which make up 43% of the total OPEX. Even considering the potential inaccuracies, the TAC of the HTW remains economically the most unfavorable. Also, the CAPEX are higher compared to the other processes to account for the bigger reactor size and three distillation columns. Furthermore, high temperatures and pressures require more expensive process equipment with thicker walls which can be seen in both the HTW hydrolysis and

alcoholysis processes. On the other hand, the bars of the TAC showing incorporated inaccuracies and potential errors indicate that this process has a huge potential for optimization.

Surprisingly, despite lower energy requirements, the conventional acidic hydrolysis process shows approximately 25% higher TAC than the alcoholysis pathway. This is because of the increased raw material costs caused by the  $\text{H}_3\text{PO}_4$  consumption and lacking recovery, as explained in section 4.1.1 [118]. In our previous work, we could show that  $\text{H}_3\text{PO}_4$  raw material costs, and the waste treatment of the  $\text{H}_3\text{PO}_4$  hazardous waste stream, make up 47% of the OPEX. Hence, the  $\text{H}_3\text{PO}_4$  amount is this process's bottleneck and most sensitive parameter [118]. Because of the expensive hazardous waste treatment, the acidic hydrolysis process has approximately equal overall utility costs as the high-temperature alcoholysis process. In contrast, iPrOH can be recovered to a great extent and therefore shows benefits over the conventional acidic process with regard to the TAC.

As anticipated from the energy requirements and process flow diagrams, the TAC for the alkaline hydrolysis process are low, with raw material costs being the most significant contributor. This process is by far the most economical, even when considering the worst-case scenario with the maximum costs.

After this investigation of the energy requirements and TAC, the question arises whether some of the four processes could be profitable at the chosen scale. Therefore, the cash flow analysis, including all NPVs, was performed as depicted in Fig. 6.

The cash flows for 14 years show that all processes except the HTW hydrolysis become profitable. As expected, alkaline hydrolysis has the shortest payback period. It can be seen that the alcoholysis process takes longer to become profitable compared to the acidic hydrolysis but then surpasses the latter process because of its lower OPEX. Overall this shows that chemical recycling processes can be very promising at a production scale of 12,000 tons of CL per year.

#### 4.2.3. Advantages and disadvantages

Concluding from these results, as well as the literature findings, an overall comparison between all re-monomerization pathways can be drawn. In Table 4, the advantages and disadvantages of ammonolysis, alcoholysis, neutral, acidic, and alkaline hydrolysis, as well as the pathway using ILs, are shown.

In conclusion, the depolymerization pathways are diverse, and each has its own advantages and disadvantages. The main drawbacks of the conventional acidic process are the hazardous waste stream and the huge required  $\text{H}_3\text{PO}_4$  amount. On the other hand, this process uses comparably moderate temperatures, and only a few by-products are formed. ILs, due to their non-volatility and high-temperature tolerance, have been demonstrated in lab-scale as a high potential depolymerization medium [94]. However, the non-volatility of this solvent and the scarcity of experimental data poses a significant challenge. Neutral hydrolysis deals with high temperatures and pressures, causing not only high utility costs but also safety risks and by-products. The required purity levels of CL might be difficult to obtain [10]. On the other hand, the waste streams and their disposal have little effect on the environment due to the environmentally friendly nature of water. In alcoholysis, iPrOH can be separated and recovered by distillation with moderate energy requirements. As a result of this and relatively low waste streams, this pathway is the second most profitable pathway. However, the high temperature and pressure of the reactor might cause similar problems as for the HTW process. Lastly, alkaline hydrolysis is the most profitable process and incorporates several advantages, such as high selectivity towards CL due to its back-biting mechanism and an integrated reaction-separation unit. However, in this process, difficulties might arise in the scale-up (see section 4.1.2). The PA6 must be free from metals for the extrusion. Also, the NaOH is not recovered, and the waste stream causes environmental and economic challenges.

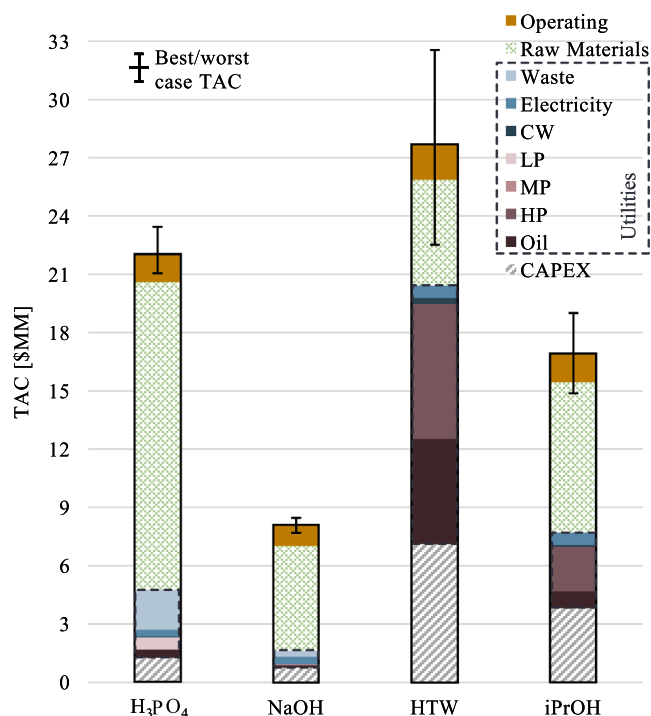
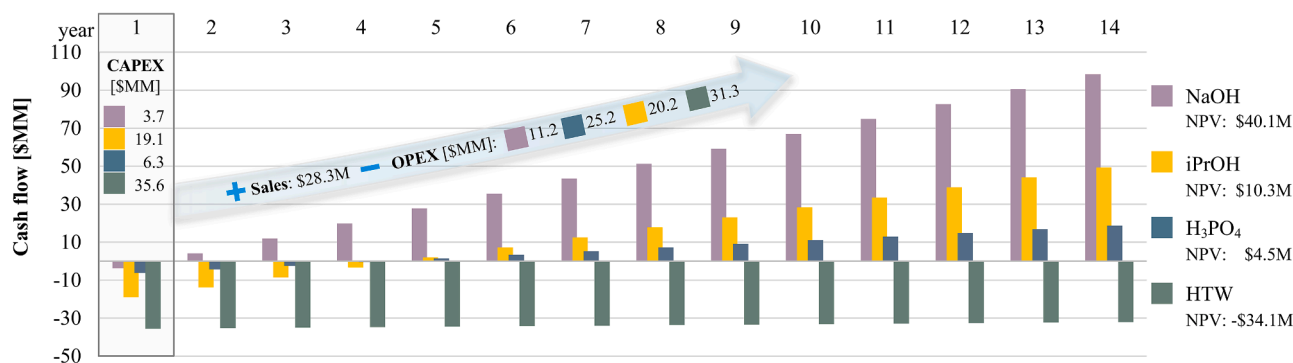


Fig. 5. TAC for each re-monomerization pathway that is divided into operating costs (orange), raw material costs (green), utility costs (grey dashed box) and CAPEX (grey lines). A minimum interest rate of 0.2 was assumed. The best and worst case bars which incorporate possible errors or model inaccuracies are also shown.



**Fig. 6.** Cash flow of the four re-monomerization processes over 14 years, assuming one year for plant construction (see CAPEX). Shown are also the OPEX and NPV of each process, assuming a discount rate of 15% for the latter.

**Table 4**

Summary of all advantages and disadvantages of the ammonolysis, alcoholysis, neutral, acidic, and alkaline hydrolysis as well as the pathway using ILs obtained from the literature and simulation of this paper.

Pathways	Advantages	Disadvantages
Acidic Hydrolysis	<ul style="list-style-type: none"> <li>- Well-established (conventional) process [31,36,51–53]</li> <li>- Acids are very effective for amide hydrolysis [70]</li> <li>- Moderate temperatures and pressures</li> </ul>	<ul style="list-style-type: none"> <li>- Difficult <math>\text{H}_3\text{PO}_4</math> recovery, as explained in section 4.1.1</li> <li>- Huge and costly hazardous waste stream</li> <li>- <math>\text{H}_3\text{PO}_4</math> is consumed (high <math>\text{H}_3\text{PO}_4</math> amount required)</li> <li>- Only moderate yields due to ACA salt formation</li> <li>- Problem for alkaline fiberglass or silicate fillers: even more <math>\text{H}_3\text{PO}_4</math> would be required [17,69]</li> <li>- Expensive equipment material or corrosion process equipment [35]</li> <li>- Possible traces of acid in the recovered CL [51]</li> </ul>
Alkaline Hydrolysis	<ul style="list-style-type: none"> <li>- Very high yield and selectivity are possible due to back-biting mechanism</li> <li>- No problem with alkaline fillers [69]</li> <li>- Combined reaction and separation unit</li> <li>- Least complex process</li> <li>- Cheapest process</li> </ul>	<ul style="list-style-type: none"> <li>- Strong base is required because of difficulties in the alkaline hydrolysis of amides [70]</li> <li>- Expensive equipment material or corrosion process equipment</li> <li>- Catalyst NaOH is not recovered - waste stream</li> <li>- Challenging scale-up [69]</li> <li>- Problems if PA6 mixed with polypropylene and latex [59] or if PA6 is not free from metals (extrusion) [69]</li> <li>- High temperatures and pressures, and safety risks [79]</li> </ul>
Neutral Hydrolysis with HTW	<ul style="list-style-type: none"> <li>- Potentially easy recycling of oligomers and even higher yields as shown in the best case bar of the TAC [69]</li> <li>- Potential for big improvements through optimization as shown on TAC bars</li> <li>- Potential for heat integration</li> <li>- Environmental friendly solvent [119,120]</li> <li>- High reaction rate achievable [43]</li> </ul>	<ul style="list-style-type: none"> <li>- Highest costs in CAPEX and OPEX</li> <li>- Side reactions, by-products, and possible re-polymerization [45]</li> <li>- Decreased CL yield after some reaction time [43]</li> <li>- High amount of water (possibly wastewater)</li> <li>- Huge reactor volume required</li> <li>- No experimental yields available</li> </ul>
Ammonolysis	<ul style="list-style-type: none"> <li>- Availability of a simulation of reaction mechanism &amp; chain length distribution [53]</li> <li>- Flexible regarding PA6 composition (fillers, adhesives, etc.) [53]</li> </ul>	<ul style="list-style-type: none"> <li>- High pressures and temperatures [53]</li> <li>- Nitrilation reactions [53]</li> <li>- Toxic solvent [121]</li> <li>- High pressures and temperatures, safety risks [79]</li> <li>- Relatively high equipment costs</li> </ul>
Alcoholysis	<ul style="list-style-type: none"> <li>- Almost no by-products when using secondary alcohols [81]</li> <li>- High yields, very effective [79]</li> <li>- Almost complete recovery of the alcohol possible</li> <li>- Potential for heat integration</li> </ul>	<ul style="list-style-type: none"> <li>- Temperature sensitivity of ILs [122]</li> <li>- High costs of ILs [123]</li> <li>- Challenges in the recovery of ILs [9,123]</li> <li>- Moderate to high reaction times or low yields [96]</li> <li>- Many properties are undetermined for ILs [124]</li> <li>- Equilibrium data missing [125]</li> </ul>
Using ILs	<ul style="list-style-type: none"> <li>- Non-volatility of ILs [94]</li> <li>- Tuneable properties of ILs [94]</li> <li>- Moderate pressures and temperatures of the process [94]</li> <li>- High selectivity (chain-end back-biting mechanism) [28]</li> </ul>	

#### 4.3. Recommendations and opportunities for chemical recycling of PA6

The previous analysis leads to recommendations and opportunities for the investigated pathways. An efficient and cost-effective method to enhance the conventional acidic process's overall economic and environmental performance might be the recovery of  $\text{H}_3\text{PO}_4$  from the ACA salt using ion exchange [34]. Also, the process using HTW could be considerably improved by recycling the ACA and oligomeric waste stream and optimizing the reaction as well as the purification conditions. For this, a detailed kinetic model would be required. The huge water stream considerably increases the costs of the HTW process, which

is why this solvent-to-PA6 ratio could be improved as well. For both alcoholysis and neutral hydrolysis, a high-temperature environment leads to heat sources and sinks, allowing heat integration to be a promising tool for saving utilities and reducing costs. It was shown that the alkaline hydrolysis process is already economically attractive, but the feasibility under large-scale operation needs to be investigated in detail.

From the results of this paper, the ideal version of the process and solvent characteristics can be derived. First, low temperatures and pressures are required to suppress by-product formation and high costs. Second, microwaves have been proven to considerably reduce the

reaction time at lab-scale, as shown by the literature [30]. Third, the integrated separation of CL straight from the reaction zone not only shifts the reaction equilibrium towards CL but also massively saves on utility and capital costs, as shown by the acidic and alkaline hydrolysis process. This direct integration of reaction and separation in a single unit can be achieved by either operating under vacuum conditions for straight CL distillation or by stripping off CL with steam or inert gas. To avoid further costs through the separation of CL from the stripping gas, the reaction under vacuum would be preferred, as seen in the process using NaOH.

This leads to the formulation of the ideal solvent. For the distillation of high-purity CL from the reaction equilibrium, the ideal solvent should be non-volatile. Furthermore, an acidic solvent should be avoided, as it entails salt formation with the obtained products, inhibits reaction to CL, and is consumed in this process, resulting in high raw material and waste treatment costs. Instead, a solvent that simultaneously catalyzes the chain-end back-biting mechanism of the amine end group to the adjacent carbonyl group is preferred for a high selectivity towards CL. Finally, a liquid solvent that can be separated from unreacted PA6 or oligomers through filtration would be ideal. In that way, scale-up challenges, potential extrusion damage, and unnecessary waste streams could be avoided, and the solvent could be recovered for environmental and economic benefits. A potential ideal solvent that fulfils all of these criteria would be an ionic liquid such as [PP13][TFSI] or [emim][BF<sub>4</sub>]. However, as described in section 2.5, insufficient experimental data is available to simulate the process and further evaluate its potential.

## 5. Conclusion

This study provided the first overview of the depolymerization pathways of PA6 to CL, along with a presentation of the reaction mechanisms and a simulative comparison of four selected processes. It is shown that each pathway's depolymerization mechanism is different, leading to different selectivities, yields, and, most importantly, divergent technical needs, energy requirements, and economic potentials. For instance, the acidic hydrolysis of PA6 involves the protonation of ACA and salt formation, which entails the need for simultaneous removal of CL to shift the reaction equilibrium and avoid ACA protonation as much as possible. Through salt formation, the solvent catalyst is consumed, and therefore, the H<sub>3</sub>PO<sub>4</sub> waste treatment and raw material costs play the biggest role in the TAC and profitability of the process. Another example is the HTW depolymerization, accompanied by thermal decomposition reactions with by-products and the requirement of a large separation section to purify CL. This leads to high energy requirements as well as equipment and utility costs. In contrast, the alkaline hydrolysis with NaOH works at moderate temperatures with a likely back-biting mechanism in which the amine end of PA6 attacks the adjacent carbonyl atom such that CL is sequentially cleaved from the chain end. This leads to straight CL production and avoidance of ACA and other by-products, and thereby low utility usage and overall costs. Furthermore, it can surprisingly be concluded that for none of the processes, the energy requirements and costs of the reaction zone (endothermic PA6 depolymerization) are dominant.

When comparing the four processes, it is shown that the energy requirements for the four pathways rise in the following order: NaOH, H<sub>3</sub>PO<sub>4</sub>, iPrOH, and HTW. However, the TAC follow a different order, with the iPrOH process being less costly than the conventional H<sub>3</sub>PO<sub>4</sub> process, which has an expensive hazardous waste stream. The TAC of the alkaline process are even less than half of any of the other depolymerization processes. Hence, this work shows that the alkaline hydrolysis and alcoholysis pathways are more promising for the chemical recycling of PA6 than the conventional acidic PA6 hydrolysis. However, the scale-up of these chemical recycling technologies needs to be addressed in further research [13,98]. Still, even when considering potential inaccuracies and errors of the used methods and best and worst-case

scenarios in the TAC (Fig. 5), the results, conclusions and rankings of the pathways remain the same.

Except for the HTW process, it is shown that all processes become profitable within five years at the chosen scale. Still, the processes profitability has room for improvement with the following recommendations: designing solvent recovery for the H<sub>3</sub>PO<sub>4</sub> process, improving reaction conditions with a minimal solvent-to-feed ratio, optimizing separation conditions for the HTW process, using heat integration for both the neutral hydrolysis as well as the alcoholysis process and investigating the scale-up of the heterogeneously catalyzed NaOH process.

This work is completed with the elaboration of the ideal imaginable process and solvent or catalyst conditions for depolymerizing PA6 to caprolactam. A solvent or catalyst supporting the chain-end back-biting mechanism would be favorable for high selectivity towards CL. To avoid by-product formation and high separation costs, high temperatures and pressures should be avoided. Instead, for shifting the reaction equilibrium and minimizing costs for CL purification, it would be beneficial to integrate the reaction and separation by distilling or stripping off CL, as shown by the alkaline and acidic hydrolysis process. As a non-investigated improvement compared to all simulated processes, a non-volatile and green solvent that can be separated and recovered from solid oligomers and unreacted PA6 would save costs and support environmental sustainability. All of the above-mentioned criteria are fulfilled for some ILs [96]. Furthermore, very recent work about a solvent-free lanthanide-organic catalyzed depolymerization of PA6 (proving chain-end back-biting mechanism) shows promising results [71,126]. However, to further elaborate on the potential of those agents in terms of a simulation and techno-economic analysis, the collection of experimental and thermodynamic data is required.

Overall, it can be concluded that the systematic classification of the depolymerization pathways, the elaboration of its effects on reaction mechanisms, energy requirements and economic potential, and the amplification of the differences between the pathways considerably improved the understanding of chemical recycling of PA6.

## Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Ann-Joelle Minor reports financial support was provided by Ministry for Science, Energy, Climate Protection and Environment of the State of Saxony-Anhalt..

## Data availability

Data will be made available on request.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2023.145333>.

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