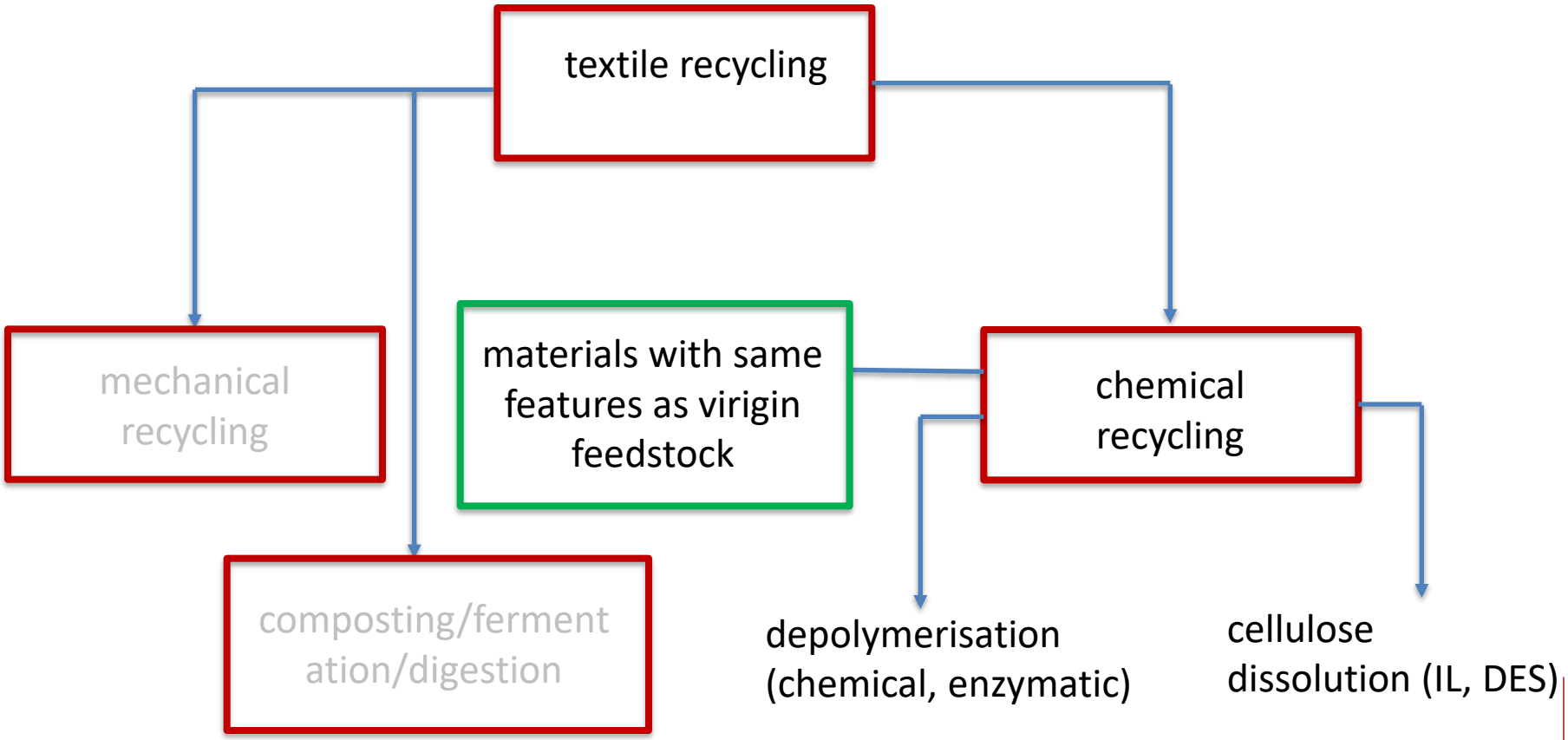
Circular options in textile materials – PART B



Circular options in textile materials

mechanical: textile fibres separation (based on NIR sorting or manually) then frayed with a variable percentage of the virgin textile

chemical: either chemical or enzymatic depolymerisation or by dissolution of cellulose with solvents (Lyocell process with NMMO)



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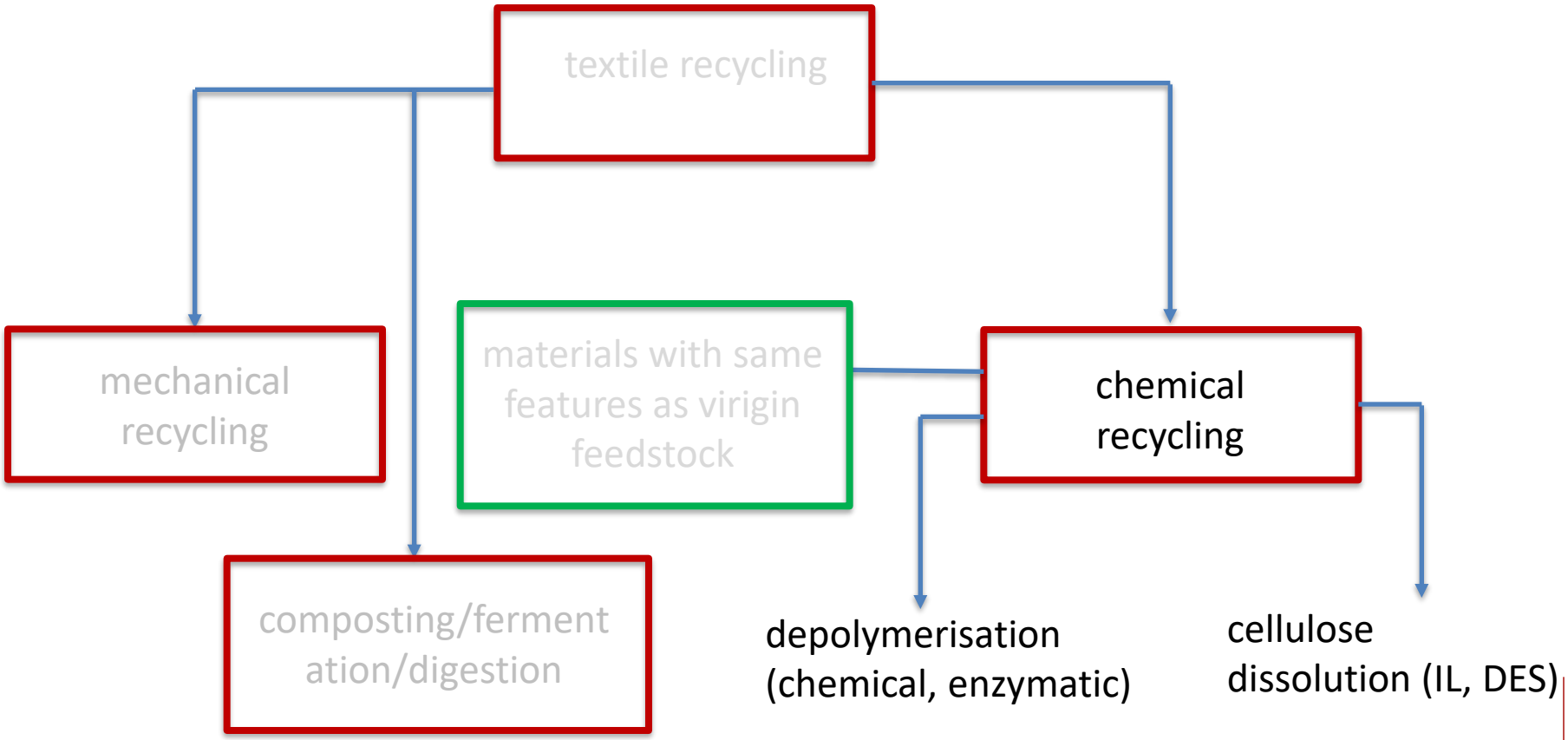
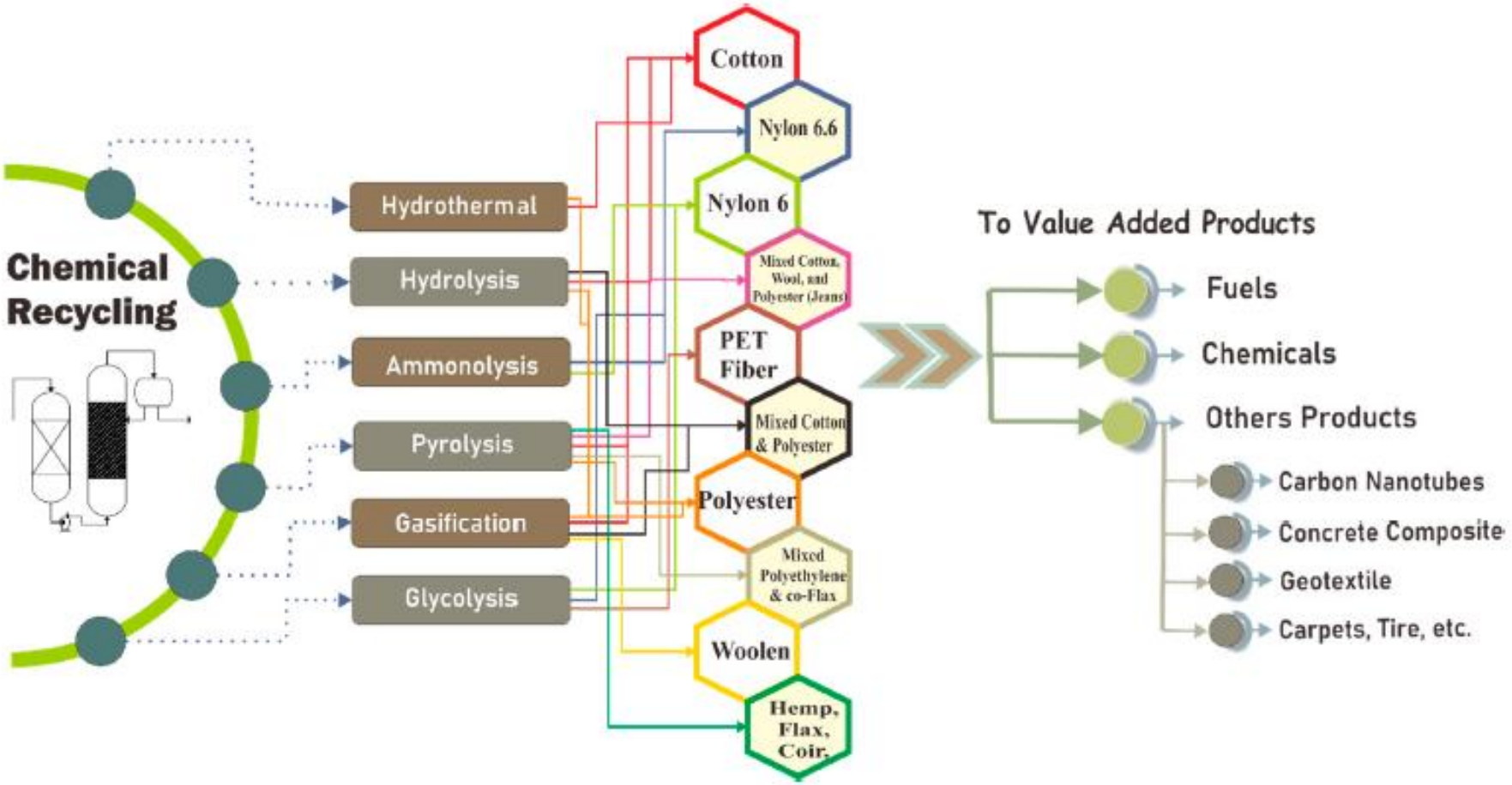


Chemical recycling of textiles



The possible pathways to recycling textiles using chemical methods
Source of the figure: Polymers **2021**, 13, 3834 7

Chemical recycling of textiles

Technique	Process Type	Yield	Main Advantages	Limitations
Hydrolysis	Acid, Thermal, Alkaline	85-97%	Well-established, effective	Requires high purity of input
Pyrolysis	Heat in inert atmosphere	~90%	High yield, no solvents	Limited to PA6
Enzymatic Depolymerization	Enzyme-based	75%	Sustainable, green option	Slow, less efficient for PA66
Ammonolysis	Ammonia reaction	~100%	High yield, closed-loop	Less studied, high temperature
Glycolysis	Glycol-based reaction	~37%	Low-cost, simple	Low yield, no industrial use
Solvent-assisted	Solvent-based methods	~85-90%	High yield, flexible solvents	Requires super/subcritical conditions

Chemical recycling of textiles

Type of Technology	Advantages	Disadvantages	Ref.
Pyrolysis	▪ Simple process ▪ Many different kinds of raw materials can be used for the pyrolysis process.	▪ High-temperature reaction process ▪ High energy consumption	[132,133]
Enzymatic Hydrolysis	▪ The novel microorganism enhances the production of biopolymers and conversion rate. It can effectively be spun into novel waste textile fibers ▪ Under mild conditions ▪ Low energy demand ▪ Utilizes environmentally friendly solvents and chemicals	▪ Only possible to recycle certain materials using enzymatic hydrolysis such as rayon, cotton, hemp, etc. ▪ Needs large amounts of water	[120]
Hydrothermal	▪ Low ash ▪ High heating values ▪ Relatively low temperatures than gasification and pyrolysis processes ▪ Reduced oxygen content	▪ Long reaction time ▪ Lower purity and heterogeneity	[134–136]
Gasification	▪ Potentially mixed textile waste	▪ High energy consumption ▪ High temperature is needed	[137]
Glycolysis	▪ Low energy consumption	▪ Low selectivity ▪ Without a catalyst, slow processing	[138]
Ammonolysis	▪ Various types of textile waste can be applied	▪ Generates a mixture of primary, secondary amines ▪ Applied toxic solvent (ammonia) ▪ High pressure and temperature	[139]

The drawbacks, advantages, and disadvantages of chemically recycling textiles.
Source of the figure: Polymers **2021**, 13, 3834 7

Recycling of textiles

Company	Material	Method
Ambercycle	Textile	Enzymatic treatment
BlockTexx	Cotton and polyester (PET)	Fiber separation technology
FENC	PET and textile	Hydrolysis
Infinited Fiber	Cellulose and polyester (PET)	Alkaline extraction
Ioncell	Cotton and polyester (PET)	Ionic liquid solvent polymer dissolution
Lenzing	Pre-consumer cotton and post-consumer garments	Closed loops and chemical recovery
Tyton BioSciences	Cotton pulp, polyester (PET), poly-cotton blends	Subcritical water treatment
Worn Again Technologies	Cotton and polyester (PET)	Dissolution polymer Solvent separation

Various chemical processes applied in textile recycling at the industrial scale
Source of the figure: Polymers **2021**, 13, 3834 7

Recycling using enzymatic hydrolysis

Biological/Enzyme-Based Processes for Textile Recycling

- **Enzymatic Depolymerization**: A type of chemical recycling where enzymes act as biological catalysts, breaking down textiles into their monomeric building blocks.

- **Advantages**:
  - **Low Energy**: Operates at ambient temperatures, using safe chemicals and solvents.
  - **Selective Depolymerization**: Enzymes selectively target and depolymerize specific polymers in blended fabrics.
  - **Recyclable Enzymes**: Enzymes can be reused, making the process more sustainable.

- **Disadvantages**:
  - **Higher Costs**: Requires chemicals and special equipment for enzyme use.
  - **Slower Reaction Times**: Processes may take hours or even days compared to chemical recycling.

- **Ideal for**: Natural fibers (like cotton and wool) and synthetic fibers.

Recycling using enzymatic hydrolysis

- Hydrolysis is a chemical breakdown process that occurs due to a reaction with water.
- Generally, the hydrolysis process requires a pretreatment process using acids, alkaline, and ionic liquid.
- Pretreatment is crucial in hydrolysis because it can affect the yield percentage.
- Before the recycling of PET fibers from textile waste takes place, the pretreatment process is required.
- Pretreatment methods reduce the complexity of the structures of the textile materials by eliminating unwanted contaminants and improving hydrophilicity.
- Fermentation is an enzymatic degradation procedure for recovering textile waste such as cotton, polyester, nylon, and silk. It can be used for bioethanol production

The drawbacks, advantages, and disadvantages of chemically recycling textiles.
Source : Polymers **2021**, 13, 3834 7

Recycling using enzymatic hydrolysis

Textile Materials	Type of Pretreatment	Condition of Pretreatment		Enzyme	Condition of Hydrolysis		Glucose Yield, %	Ref.
		T (°C)	T (h)		T (°C)	T (h)		
Cotton, 90% Wool, 5% Polyester, 5%	Protease (Enzymatic)	50	48	*Cellic CTec3® and Savinase 12T®*	50	70	95.0	[175]
Used Jeans	Phosphoric acid (Acid)	50	7	*Cellulase Trichoderma reesei and Aspergillus niger*	50	96	79.2	[176]
Cotton red T-shirt, 100% cotton black T-shirt, 100%	N-methyl-morpholine-N-oxide& Phosphoric Acid (Acid)	50	1	*Cellulase AP3, Aspergillus niger*	50	72	87.0–95.0	[177]
Cotton red T-shirt, 100% cotton black T-shirt, 100%	NaOH/Urea (Base)	50	1	*Cellulase AP3, Aspergillus niger*	50	72	48.0–55.0	[177]
Cotton T-shirts, 100%	1-allyl-3-methylimidazolium chloride (Ionic liquid)	110	1.5	*G. xylinus (Acetobacter aceti subsp. xylinus or A. xylinus)*	50	24	81.6	[168]
Towels, cellulose content 87.8%	Untreated Pretreatment	NA	NA	*Cellulase*	200	0.03	74.2	[169]
Waste blue jeans (polyester/cotton), 40%/60%	Sodium carbonate (Base)	150	2	*Celluclast 1.5 L and β-glucosidase*	45	72	81.71	[170]
Cotton, 100%	Sodium carbonate (Base)	150	2	*Celluclast 1.5 L and β-glucosidase*	45	72	88.0	[170]
Textile from End-of-life euro banknotes	NaOH/Urea (Base)	−20	6	*Cellulase*	50	382	96.0	[178]

Conditions for converting textile fiber to glucose via enzymatic hydrolysis
Source of the figure: Polymers **2021**, 13, 3834 7

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The drawbacks, advantages, and disadvantages of chemically recycling textiles.
Source of the figure: Polymers **2021**, 13, 3834 7

Recycling using enzymatic hydrolysis

Textile I	Type of Pretreatment	Hydrolysis		Enzyme for Hydrolysis	Fermentation Process		Microorganism	Type of Fermentation	EthanolYield, %	Ref.
		T (°C)	T (h)		T (°C)	T (h)				
Polyester/cotton (50%/50%)	N-methyl morpholine-N-oxide (Cellulose solvent)	NA	48	*Cellulase and β-glucosidase*	30	24	*Saccharomyces cerevisiae*	SHF	91.91	[197]
Polyester/cotton (40%/60%)	NaOH/Urea (Alkali)	45	72	*30 FPU C ellulase and 60 IU β-glucosidase*	36	72	*Saccharomyces cerevisiae*	SSF	70.00	[163]
Cotton, 100%	$Na_2S_2O_4$ and Na_2CO_3 (Alkali)	50	48	*Cellulase AP3*	37	48	*Zymomonas mobilis*	SSF	90.00	[198]
Viscose/polyester (60%/40%)	N-methylmorpholine-N-oxide (Cellulose solvent)	NA	48	*Cellulase and β-glucosidase*	30	24	*Saccharomyces cerevisiae*	SHF	94.99	[197]
Cotton, 100%	Na_2CO_3 (Alkali)	45	72	*Cellulase and β-glucosidase*	32	24	*Saccharomyces cerevisiae CCUG 53310*	NA	69.40	[170]
Cotton ginning trash, 100%	Sulfuric acid (Acid)	50	96	*Cellic CTec 2 cellulase*	30	NA	*Saccharomyces cerevisiae*	SSF	70.00	[199]

SHF: separated hydrolysis dermentation, SSF: simultaneous saccharification and fermentation, NA: not available.

Ethanol production after enzymatic hydrolysis and microorganism fermentation of textile wastes.

Source of the figure: Polymers **2021**, 13, 3834 7

Hydrothermal and solvothermal synthesis (REMINDER)

Definition of solvothermal reaction

Solvothermal synthesis is defined as a chemical reaction that takes place in a solvent at a temperature higher than the boiling temperature of the solvent in a sealed vessel.

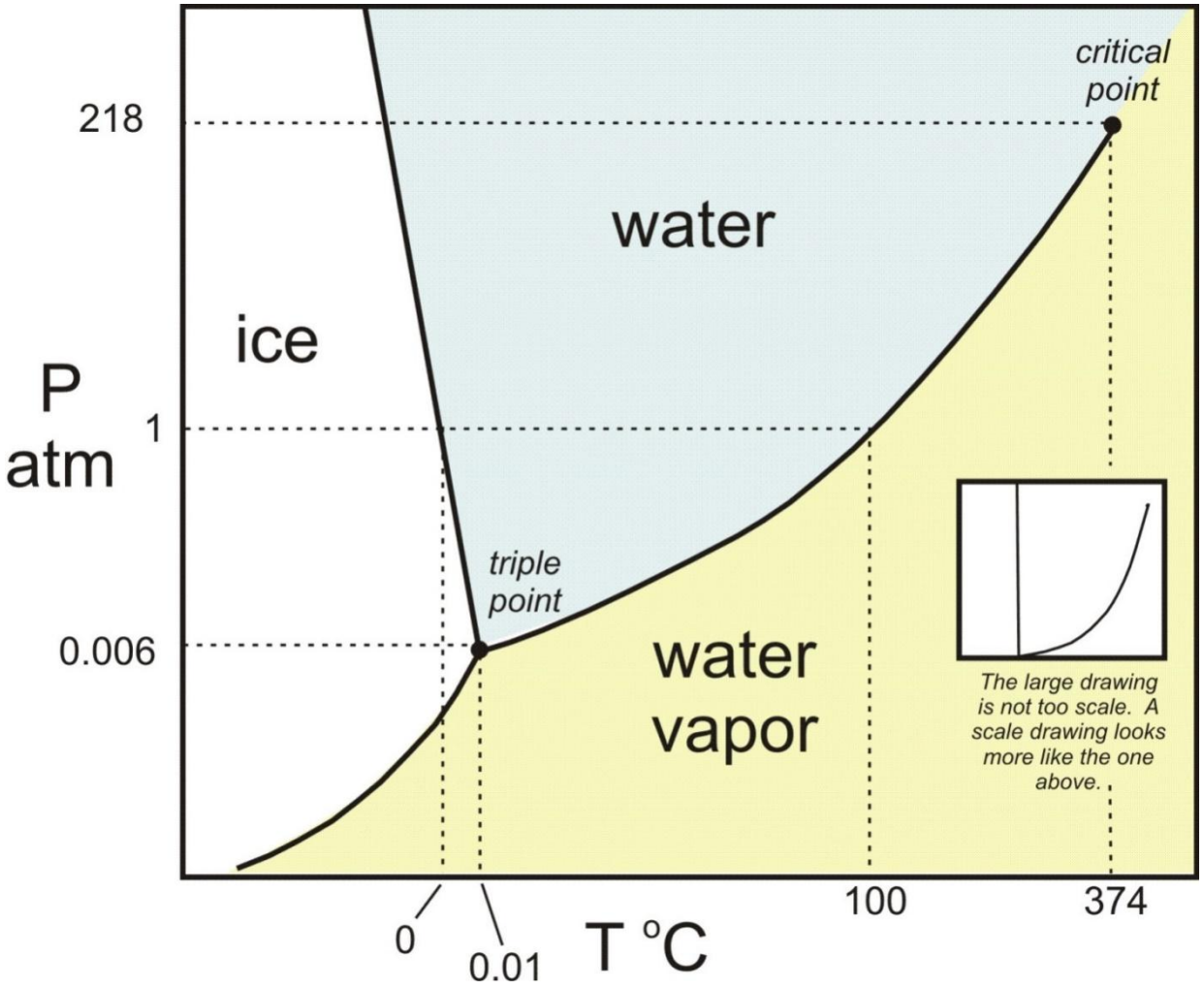
Definition of hydrothermal reaction

Heterogeneous chemical reaction in aqueous media above room temperature (normally above 100 °C) and at a pressure greater than 1 atm

- Supercritical (above SC point)
- Subcritical (below SC point)

Mari-Ann Einarsrud and Tor Grande, Chem. Soc. Rev., 2014, 43, 2187-2199
A. Rabenau, Angew. Chem., Int. Ed. Engl., 1985, 24, 1026–1040

Supercritical water (reminder)

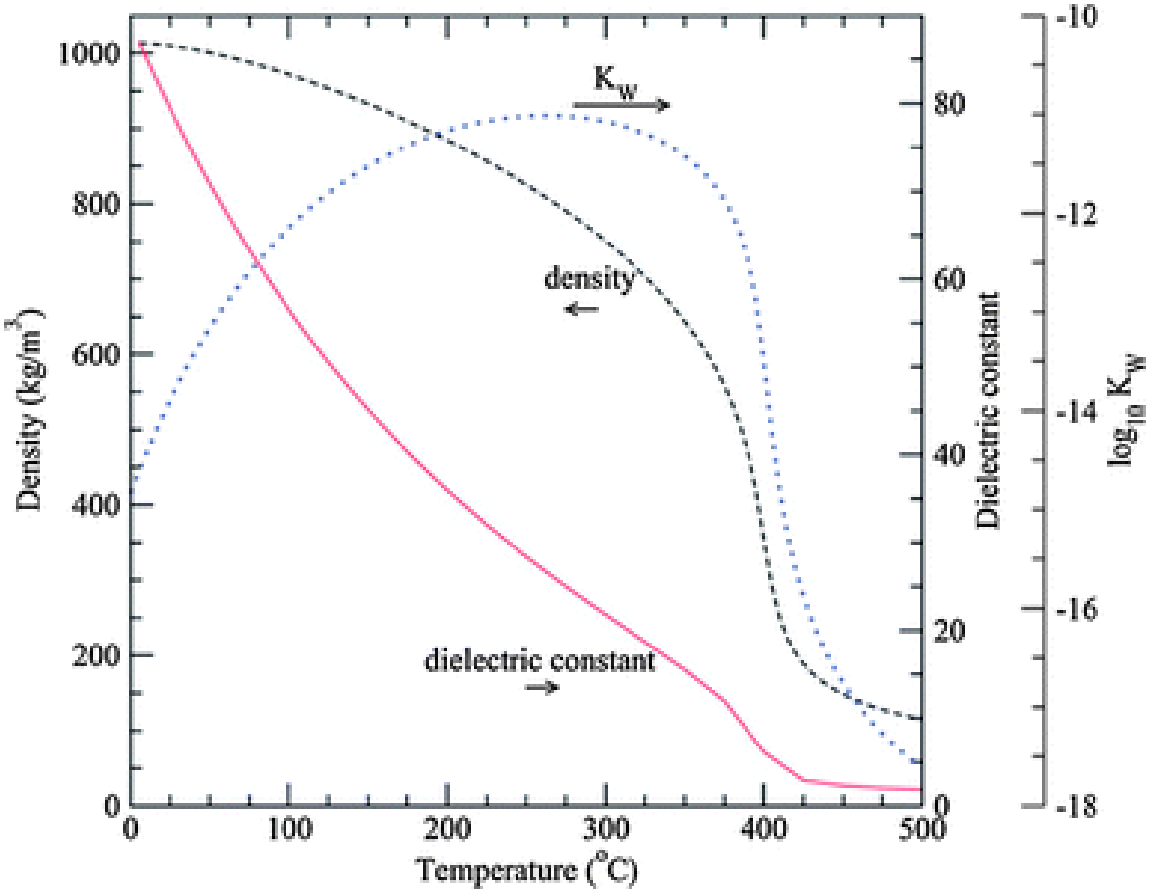


Critical point

The temperature and pressure at which the liquid and vapour intensive properties (density, heat capacity, etc.) become equal. It is the highest temperature (critical temperature) and pressure (critical pressure) at which both a gaseous and a liquid phase of a given compound can coexist.

IUPAC Goldbook:
http://goldbook.iupac.org/C01396.html

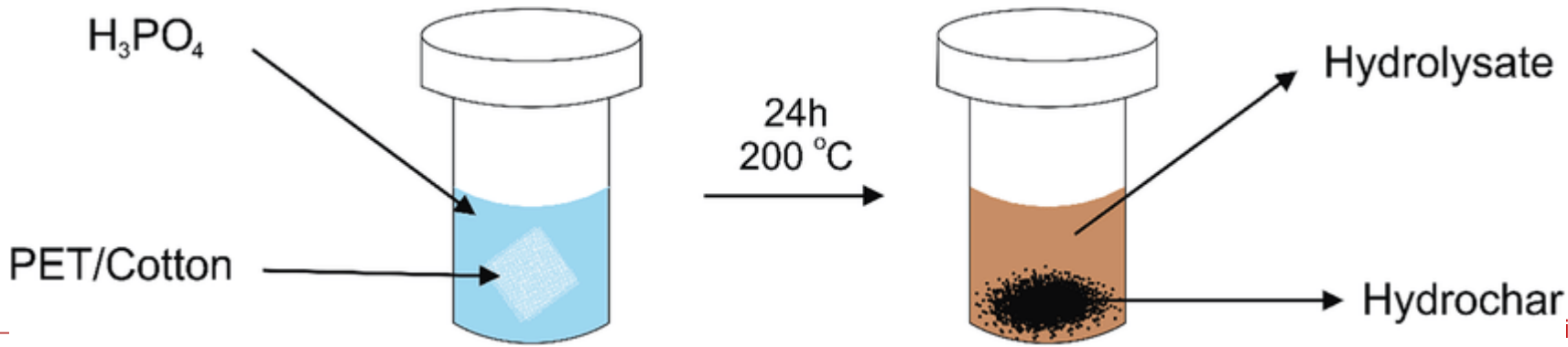
Hydrothermal conditions



Density, dielectric constant and ionic product, K_w, of pure water at 30 MPa as a function of temperature.

Recycling using hydrothermal treatment

- hydrothermal method is a decomposition process based on high temperatures and pressures, with water as the main constituent of the reaction.
- the hydrothermal method is one of the most promising alternative methods for degrading carbon-polymer waste and organic components into three product phases: liquid, solid, and gas phases.
- it is conducted in an autoclave reactor in which organic acids can catalyse the process
- the hydrothermal process does not require pretreatment
- drawbacks of the hydrothermal process are the high temperatures, high pressure, and long reaction time that are required for the material manufacturing process



Recycling using hydrothermal treatment

Feedstock	Reactor	Catalyst	Time, h	Temperature, °C	Major Product	Yield, %	Ref.
A blue cotton/polyester,	Batch	Hydrochloric acid	3	150	Cellulose powder	49.3	[205]
Waste cotton fabrics	Batch	Hydrochloric acid	1.6	150	Microcrystalline cellulose	85.5	[206]
Cotton/synthetic fibers,	Autoclave	NA	90	280	Volatile compound (CH_4, C_2H_4)	98.0	[207]
Waste cottons	Hydrothermal reactor	β-cyclodextrin	3	250	Activated carbon	NA	[208]
Cotton textile waste	Tubular	Ferric chloride	1	700	Nanopowder	32.6	[209]
Waste cotton woven	Tubular	Ferric chloride	1.5	700	Activated carbon	NA	[210]
Light blue and white uniform with polyester/cotton,	Hydrothermal reactor	Citric acid	1	225	5′-hydroxymethylfurfural	12.5	[211]
Cotton	Semi-batch	Formic acid	1	250	Glucose	83.8	[212]

Source of the figure: Polymers **2021**, 13, 3834 7

Recycling using pyrolysis

- pyrolysis is a promising technology that can be used to degrade the carbon-polymers of solid waste in order for them to become three pyrolysis products in the solid, liquid, and gas states
- pyrolysis can be utilized in diverse textile materials that have not been sorted prior or in multi-material textile products that otherwise would have only been treated in waste-to-energy facilities
- under oxygen-free conditions, pyrolysis reallocates C/H/O elements from organic molecule waste into three-phase **pyrolysates**.
- Syngas (H_2 and CO) produced by thermochemical processes can be utilized as a direct fuel or as a raw material to produce other hydrocarbons and alcohols
- the pyrolysis process does not require pretreatment, and it is a potential method for treating polluted waste.
- these factors make pyrolysis a more efficient process than chemical methods (including bio-chemicals), which require many chemicals and frequently produce a lot of trash that must be re-landfilled and takes longer to operate on a large scale.

Recycling using pyrolysis

Yields of solid, liquid, and gas products produced via textile waste pyrolysis

Raw Materials	Reactors	Catalyst	Reaction Time, Min	Temperature, °C	Yield (%)			Major Products	Ref.
					Solid	Liquid	Gas		
Egyptian banknote ELCBs Cotton, 100%	Batch	NA	30	700	15.65	29.28	55.07	2-Propanone, toluene, 3-furaldehyde, 2-furalmethanol, benzaldehyde, phenol, acetophenone	[147]
Hemp, 100%	Batch	NA	120	750	24	48.5	27.50	Activated carbon	[155]
Flax, 100%	Fixed bed	$ZnCl_2$	220	450	44.80	NA	NA	Activated carbon	[156]

Source of the figure: Polymers **2021**, 13, 3834 7

Recycling using pyrolysis

Pyrolysis in Textile Recycling

Degrades carbon-polymers of solid waste into solid, liquid, and gas products under oxygen-free conditions.

Advantages:

No Pretreatment: Can be used on unsorted textiles, multi-material products and polluted waste that otherwise would have only been treated in waste-to-energy facilities

Efficient:

Transforms organic materials into smaller molecules. Syngas (H_2 and CO), which can be used as fuel or to produce other hydrocarbons and alcohols.

Efficiency:

Pyrolysis is more efficient than chemical methods, as it requires fewer chemicals and generates less waste, with faster operation on a large scale.

Recycling using gasification

- textile recycling by means of gasification processes is conducted under temperatures up to 400–1000 °C.
- the reactions occur under low-oxygen or oxygen-free conditions
- compared to pyrolysis, gasification is more complicated since chemical reactions occur on the substance
- the gasification approach generates gases with high carbon and hydrogen concentrations, similar to the pyrolysis process.
- nevertheless, the gaseous fraction in gasification is dramatically higher than that in pyrolysis

Source of the figure: Polymers **2021**, 13, 3834 7

Gassification vs pyrolysis

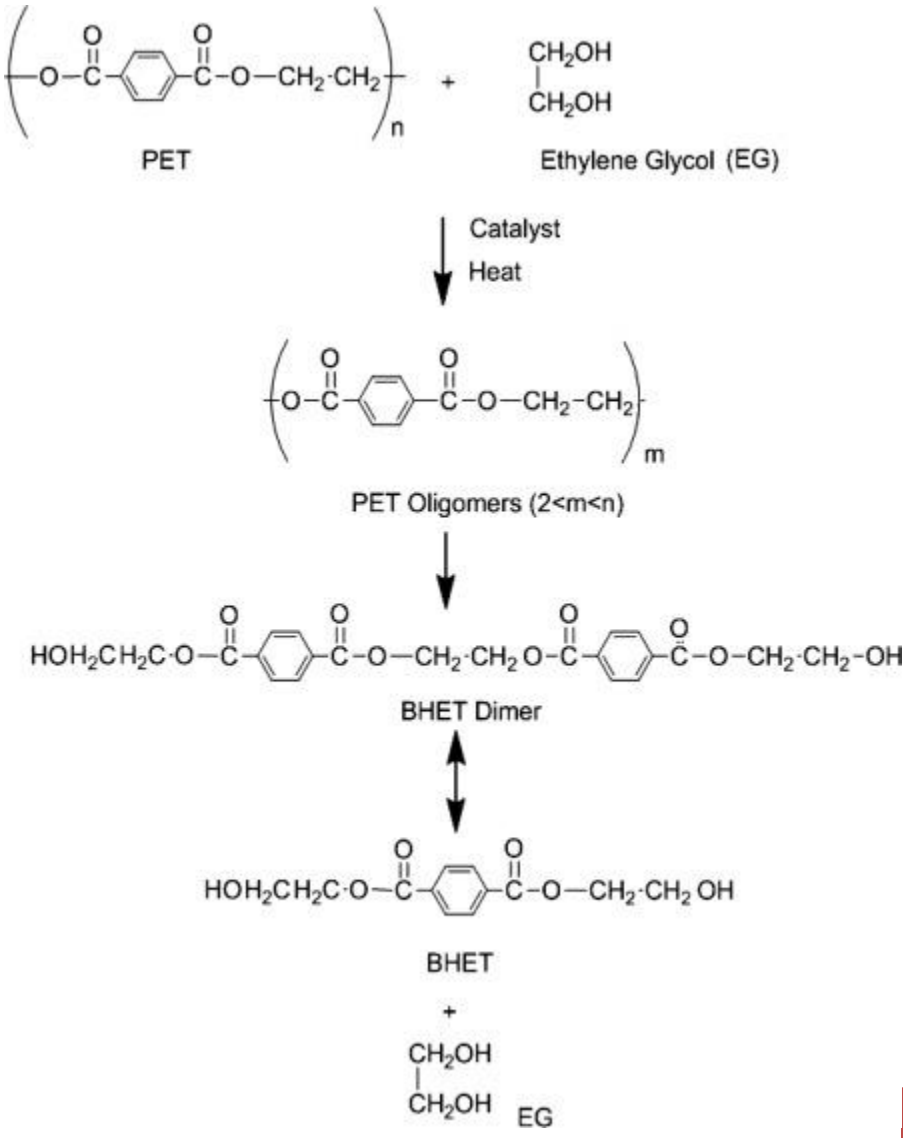
	Pyrolysis	Gasification
Oxygen	None	Limited (partial oxidation)
Temperature	~400-800 °C	~700-1,400 °C
Main product	Liquid/solid (oil, char)	Gas (syngas: CO + H_2)
Heat	External (endothermic)	Partly self-supplied
Typical use	Biochar, bio-oil, chemical recycling of plastics	Power, heat, H_2, synthesis of fuels/chemicals (Fischer-Tropsch, methanol)

Recycling using glycolyisis

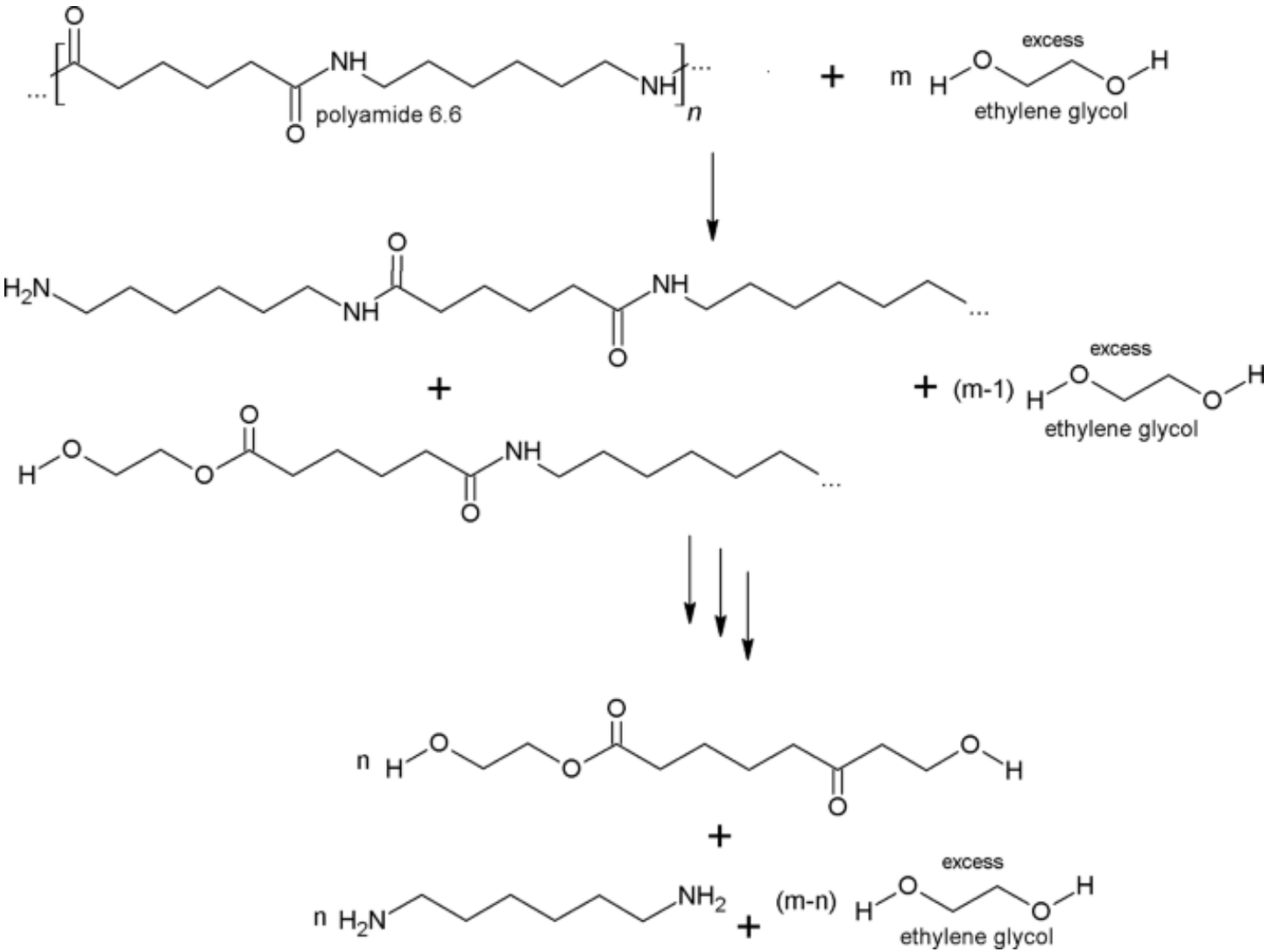
- Glycolysis is a degradation process that can be used to convert the large molecules of a textile to small molecules.
- This process is widely used to recycle textile materials such as PET, polyamide fibers and polyurethane.

Source of the figure: Plastics Design Library 2019, Pages 61-84

BHET: (bis(2-hydroxyethyl) terephthalate)

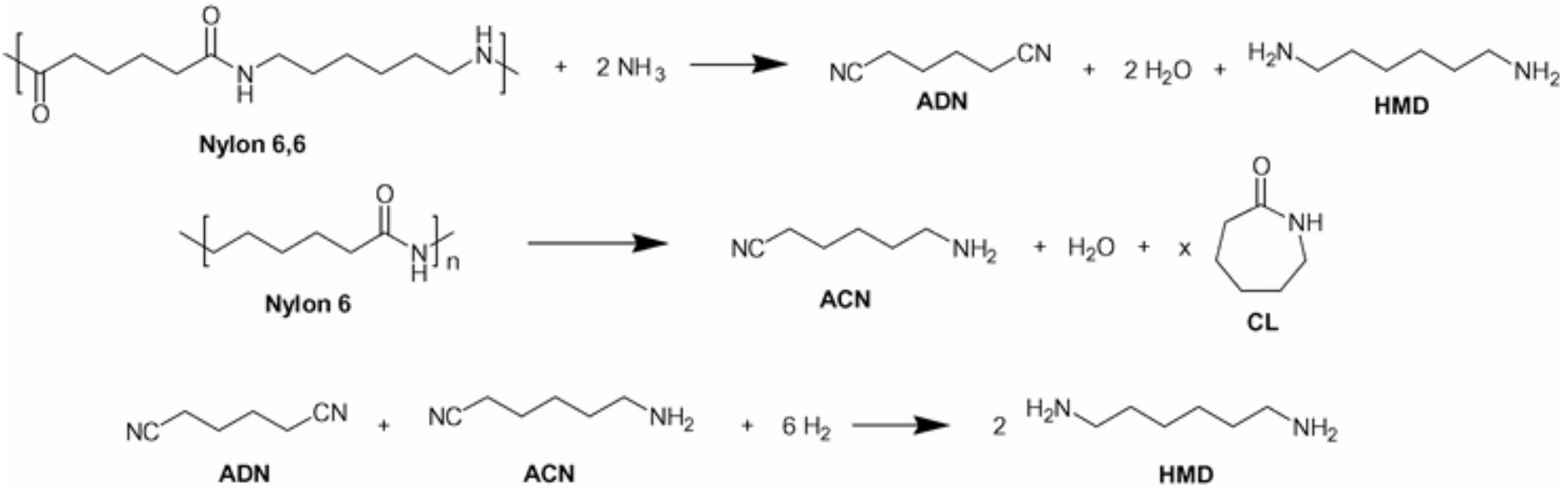


Recycling using glycolyisis



Source of the figure: Applied Catalysis A: General, 318, 20 February 2007, Pages 190-198

Recycling using ammonolysis



The idealized ammonolysis and hydrogenation chemistries of nylon-6,6 and nylon-6 recycle Hexamethylenediamine (HMD) and adiponitrile (ADN) are formed from nylon-6,6, while 6 aminocapronitrile (ACN) and caprolactam (CPL) are formed from nylon-6

Ammonolysis describes the reaction pathways where ammonia is used for the bond cleavage of polyamides. The ammonolysis process is the primary depolymerization method of nylon 6,6 carpet waste. The temperature and pressure of this process were 300–350 °C and 68 atm

Source of the figure: Applied Catalysis A: General, 318, 20 February 2007, Pages 190-198

Chemical recycling of textiles: cotton and PET

Polyester and cotton are the most used synthetic and natural fibers in the world

To chemically recycle cotton and PET, the two materials should be separated. This can be performed other by depolymerisation or dissolution of one component by keeping the other unaltered.

Chemical recycling of textiles: cotton and PET: blended

Blended fabrics contain natural fibres (cotton, wool) and synthetic fibres (PET, polyamides). As of 2023, the market value for polycotton was USD 442 million. By 2033, the market for **polycotton**** fabric is projected to grow at a compound annual growth rate (CAGR) of 3% and reach a valuation of USD 594 million.

Popular cotton-polyester blend ratios used in the textile industry are:

- 50% polyester, 50% cotton: Commonly used to make T-shirts, sweatshirts, and bed linens.
- 60% polyester, 40% cotton: Used in sportswear, work uniforms, or casual fashion.
- 65% polyester, 35% cotton: Suitable for casual wear, workwear, or uniforms.
- 35% polyester, 65% cotton: Suitable for various applications from casual wear to home textiles.
- 20% polyester, 80% cotton: Used in sleepwear, casual wear, or summer clothing.

Challenges in Blended Textile Recycling

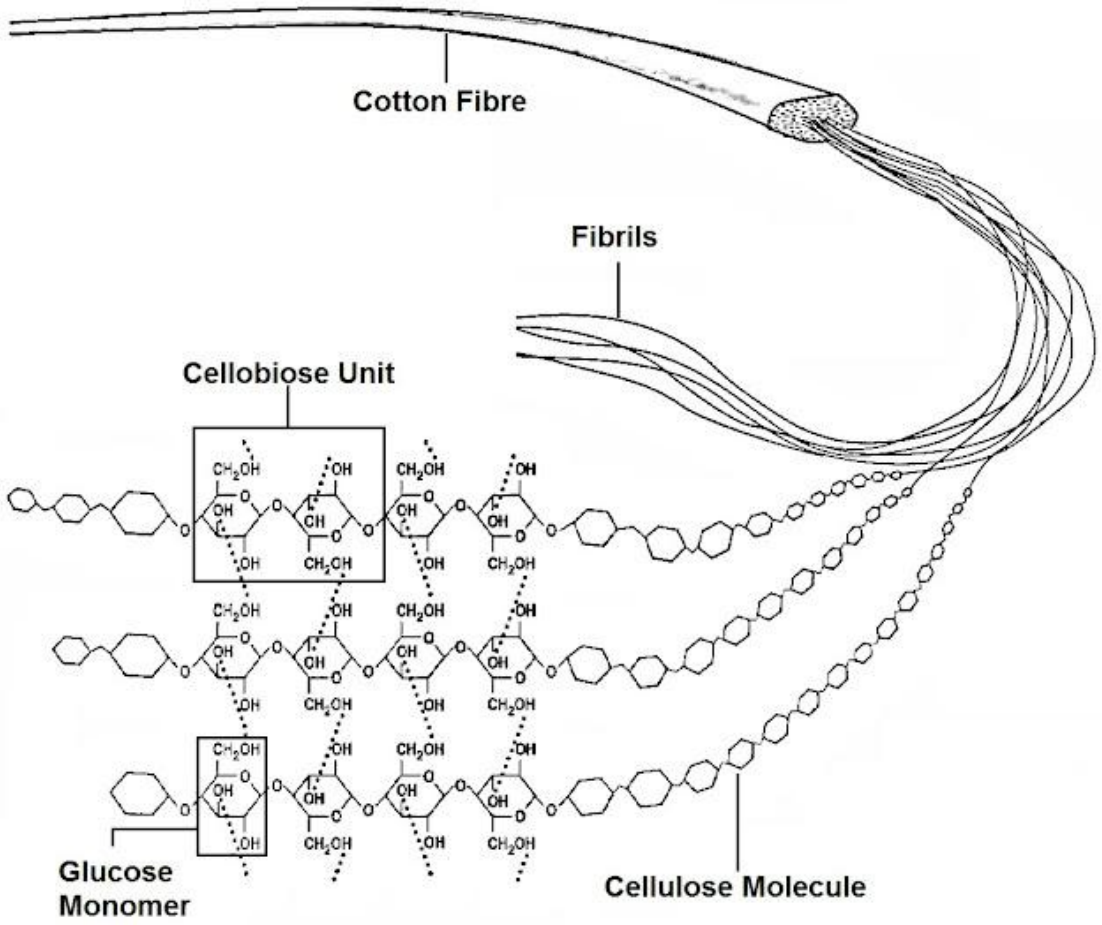
- Commercial recycling is limited due to expensive pre-treatment and the complex separation of natural and synthetic fibres.

**Polycotton is a lightweight widely available fabric, you can get it with prints on but you can also get plain polycotton too. Polycotton is a cheaper alternative to cotton fabrics as it is a blend of both cotton and polyester, natural and synthetic fabrics. Often polycotton fabrics consist of 65% polyester and 35% cotton, but the blend can vary. It combines the breathability of cotton with the durability of polyester.

Remind: cotton

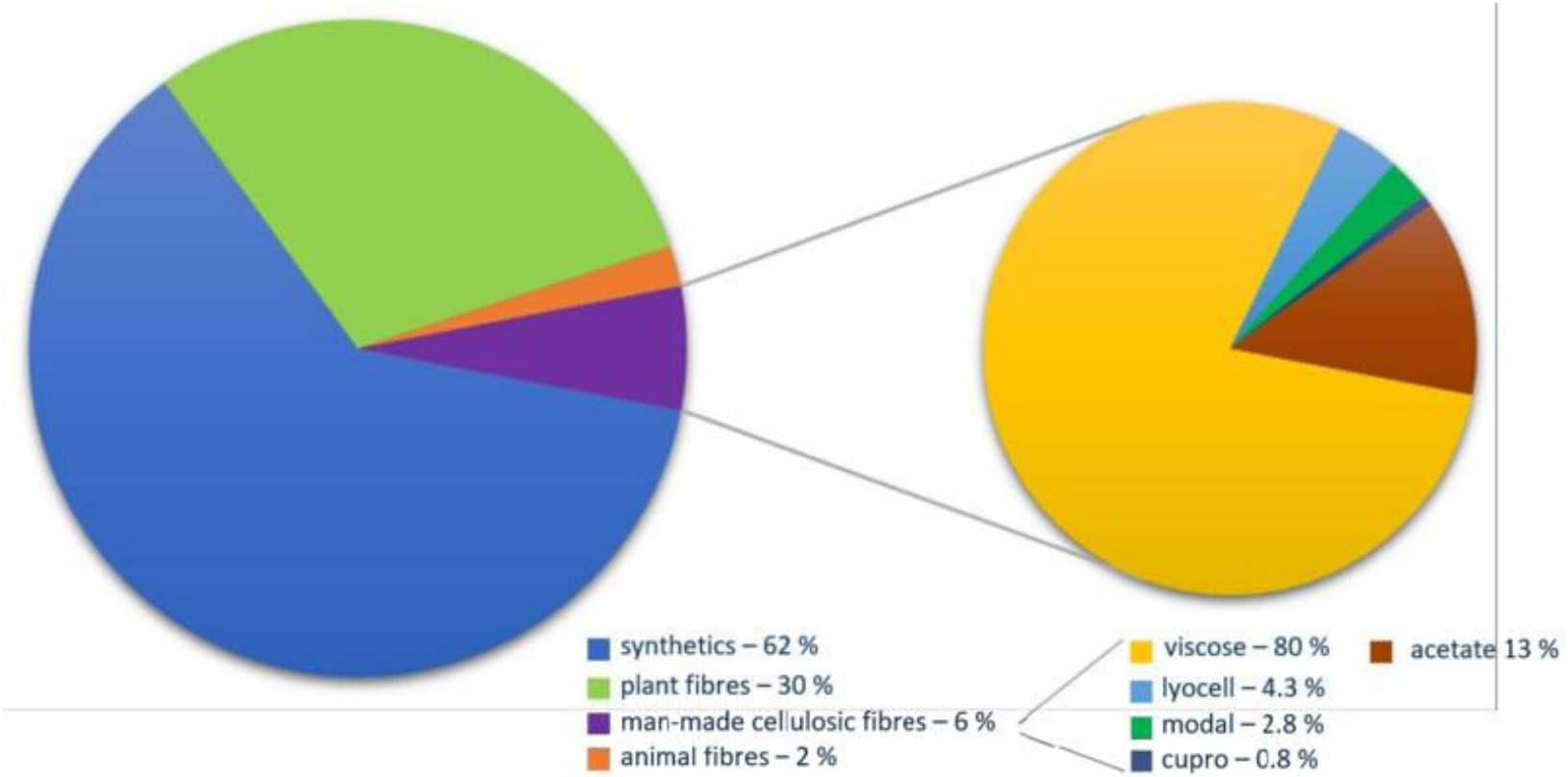
Cotton is the natural fibre of vegetable origin. Each fibre is made up of 20-30 layers of cellulose coiled on a neat series of natural springs. The cellulose is arranged in a way that gives cotton fibres high strength, durability and absorbency.

Cellulose is one of the main constituent of the cotton fibre.



Cotton and other fibers

In 2021, cellulosic fibers, including cotton, made up 22% of the global fiber market, while man-made cellulosic fibers (MMCFs) accounted for 6%.



Cotton dissolution

Cotton is made up of up to 95% cellulose.

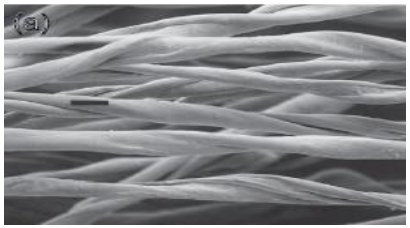


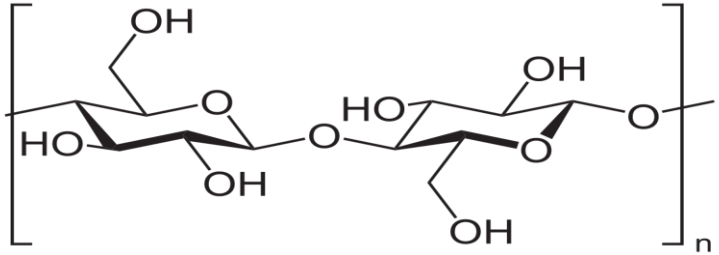
Cellulose has crystalline and amorphous regions.
The crystalline regions make cellulose insoluble in water.

To dissolve cellulose, its supramolecular structure must be disassembled, separating the chains.

- Non-derivatizing solvents disrupt the hydrogen-bond network by forming new bonds with cellulose hydroxyl groups, breaking the crystalline structure.

- Derivatizing solvents chemically modify cellulose, altering the hydrogen-bond network.

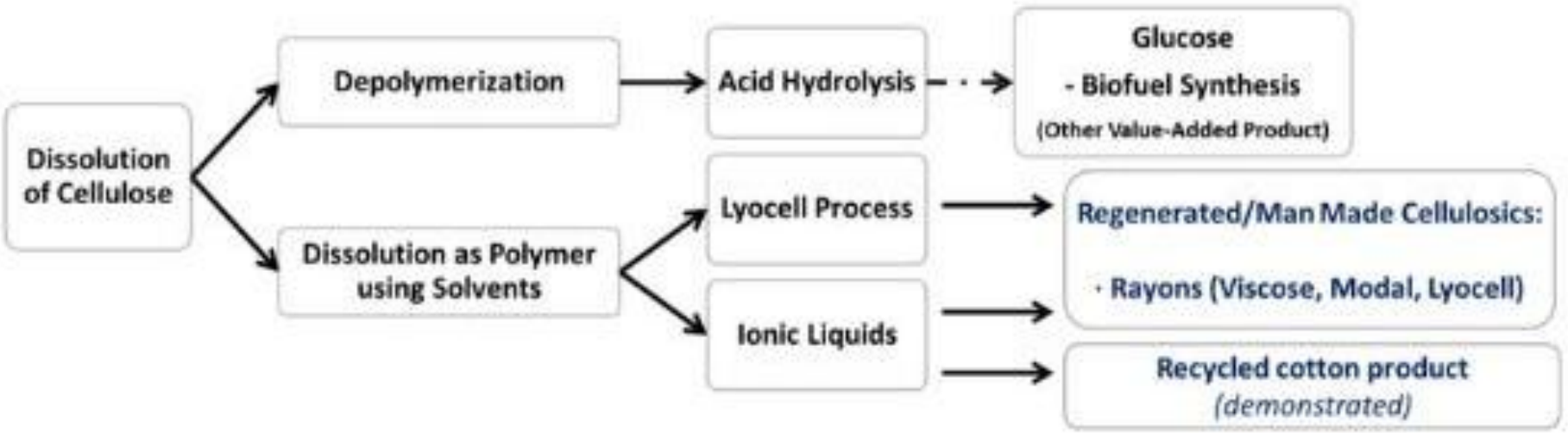




Recycling of cotton: general aspects

Cotton:

- Can be degraded by acid (Ouchi et al. 2010) or through biological processes (Bernd and Gerahard 1996).
- Can be dissolved with different solvents such as ionic liquids or by using N-metilmorfoline N-oxide (NMMO) (De Silva et al. 2014; Jeihanipour et al. 2010)



However, being a natural polymer, it cannot be further re-polymerised.

Depolymerization of Cellulose

- Cellulose consists of monomers with many functional groups, making it difficult to repolymerize through non-biochemical synthetic routes.

- **Hydrolysis** is a chemical breakdown process that occurs due to a reaction with water.

- **biological processes** (e.g., fermentation to bioethanol) produce glucose and other valuable derivatives for the chemical industry and fuel production.

➔ Generally, hydrolysis requires a pretreatment process using acids, alkaline, and ionic liquid.

Recycling of cotton (standard route)

- The primary processes used to recover the cotton were leaching with nitric acid, dissolving with dimethyl sulfoxide, and diluting with hydrochloric acid for bleaching.
- The recovery rate, carbon footprint, and economic performance of this technology were determined to be 93%, - 1534 CO_2 eq/ton, and 1466 USD/ton, respectively if textile waste is used as a renewable resource for the production of thermal energies.
- Cotton briquettes had a heating value of 16.80 MJ/kg and a cost of 0.006 EUR/kWh when used as a fuel

Various chemical processes applied in textile recycling at the industrial scale
Source of the figure: Polymers **2021**, 13, 3834 7

Reference heating values

The heat value of natural gas depends on how effective the thermal energy coming from the natural gas is. The heat content of natural gas is not related to the colour of the flame in the stove, nor to its colour or price. "A megajoule per cubic meter (MJ/m^3) is a decimal multiple of a derived unit of specific energy, heating value, energy content, or heat of combustion per unit volume." Shortly: it shows how much energy (in megajoule) is released while combusting 1 cubic meter of natural gas.

1 MJ/m^3 = 26.83 BTU/SCF (British thermal unit / cubic foot)

The heat content of natural gas might be different in various countries. For example, in Hungary, the heat value of natural gas has an average of 34.12 MJ/m^3.

Other heating values

Petrol / gasoline:	44-46 MJ/kg
Diesel fuel:	42-46 MJ/kg
Crude oil:	42-47 MJ/kg
Liquefied petroleum gas (LPG):	46-51 MJ/kg
Natural gas:	42-55 MJ/kg
Hard black coal (IEA definition):	23.9 MJ/kg

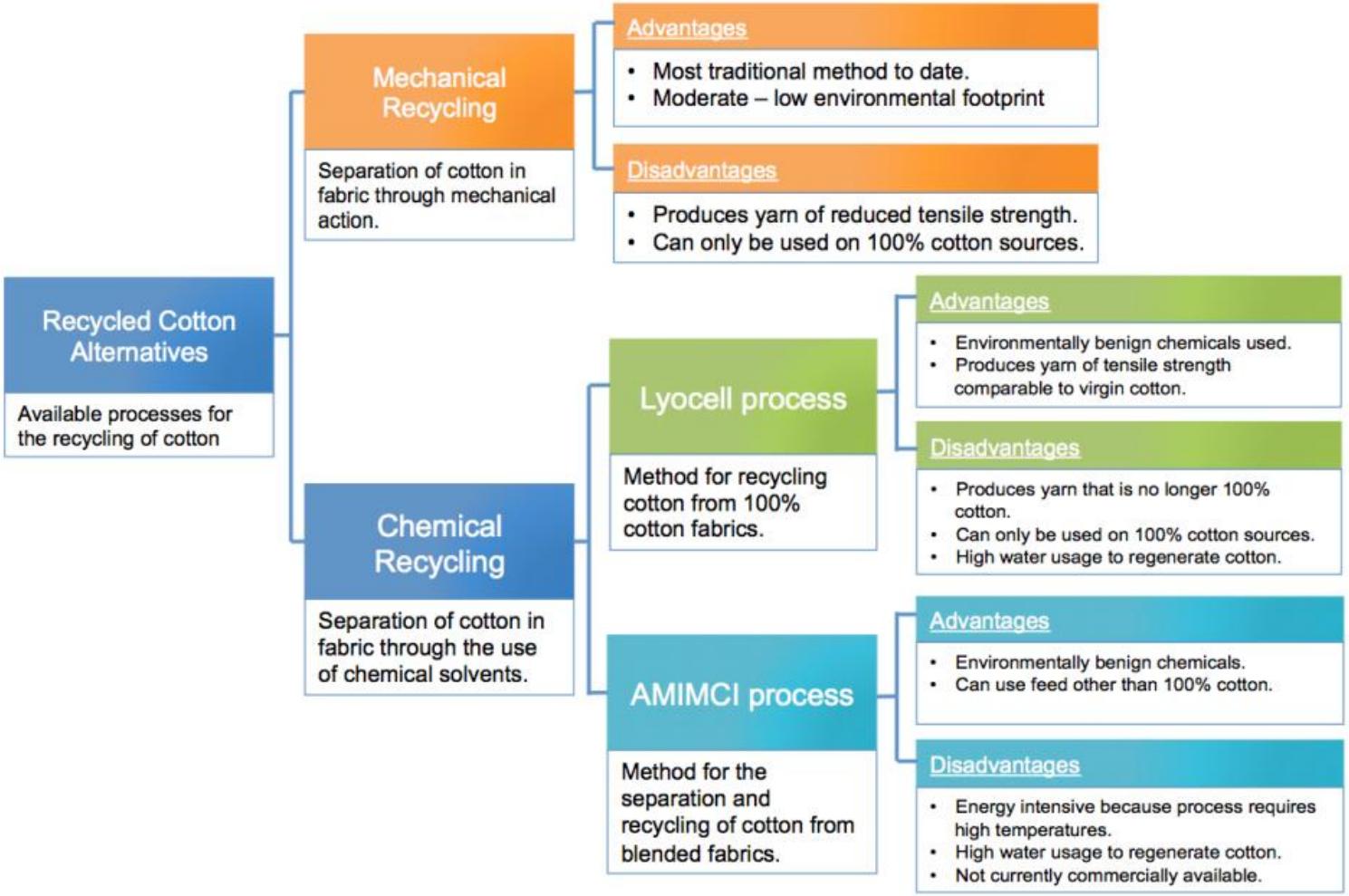
Source: https://www.world-nuclear.org/

Reference heating values

	Heat value
Hydrogen (H_2)	120-142 MJ/kg
Methane (CH_4)	50-55 MJ/kg
Methanol (CH_3OH)	22.7 MJ/kg
Dimethyl ether - DME (CH_3OCH_3)	29 MJ/kg
Petrol/gasoline	44-46 MJ/kg
Diesel fuel	42-46 MJ/kg
Crude oil	42-47 MJ/kg
Liquefied petroleum gas (LPG)	46-51 MJ/kg
Natural gas	42-55 MJ/kg
Hard black coal (IEA definition)	>23.9 MJ/kg
Hard black coal (Australia & Canada)	c. 25 MJ/kg
Sub-bituminous coal (IEA definition)	17.4-23.9 MJ/kg
Sub-bituminous coal (Australia & Canada)	c. 18 MJ/kg
Lignite/brown coal (IEA definition)	<17.4 MJ/kg
Lignite/brown coal (Australia, electricity)	c. 10 MJ/kg
Firewood (dry)	16 MJ/kg

Source: https://www.world-nuclear.org/

Recycling of cotton

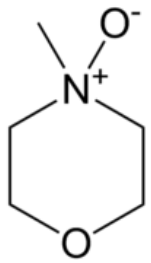


The possible recycling alternatives

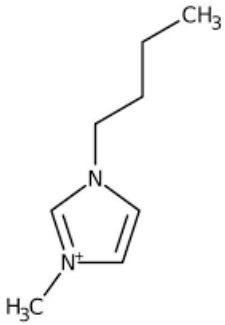
Source of the figure: MIT Sloan School of Management Strategies for Sustainable Business Final Report – Recycled Cotton for Gap Inc

Recycling of textiles: cotton

By **Lyocell** method, regenerated fibres to be mixed with products of vegetal origin. NMMO (N-metilmorfoline N-oxide) is used to obtain a solution 9% of cellulose, water (14%) and NMMO 78% starting from ground textiles. After dehydration, extrusion, yarn making and drying, cotton fibers at 60% are obtained.

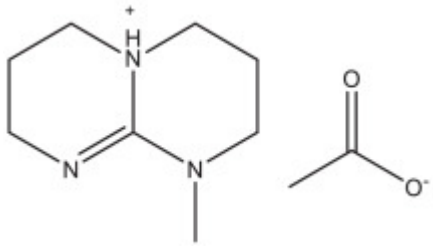


Drawbacks: high water consumption, not applicable to mixed textures



AMIMCl

In the process based on ionic liquids (= compounds completely composed of ions with melting point below 100 °C) , not flammable, not volatile, mixed textiles are ground to separate cotton from a mixture with polyester, which remains undissolved, to yield, after extrusion and spinning, fibres with feature equivalent to the virgin ones.
Drawbacks: Not yet scalable, does not work for any mixtures



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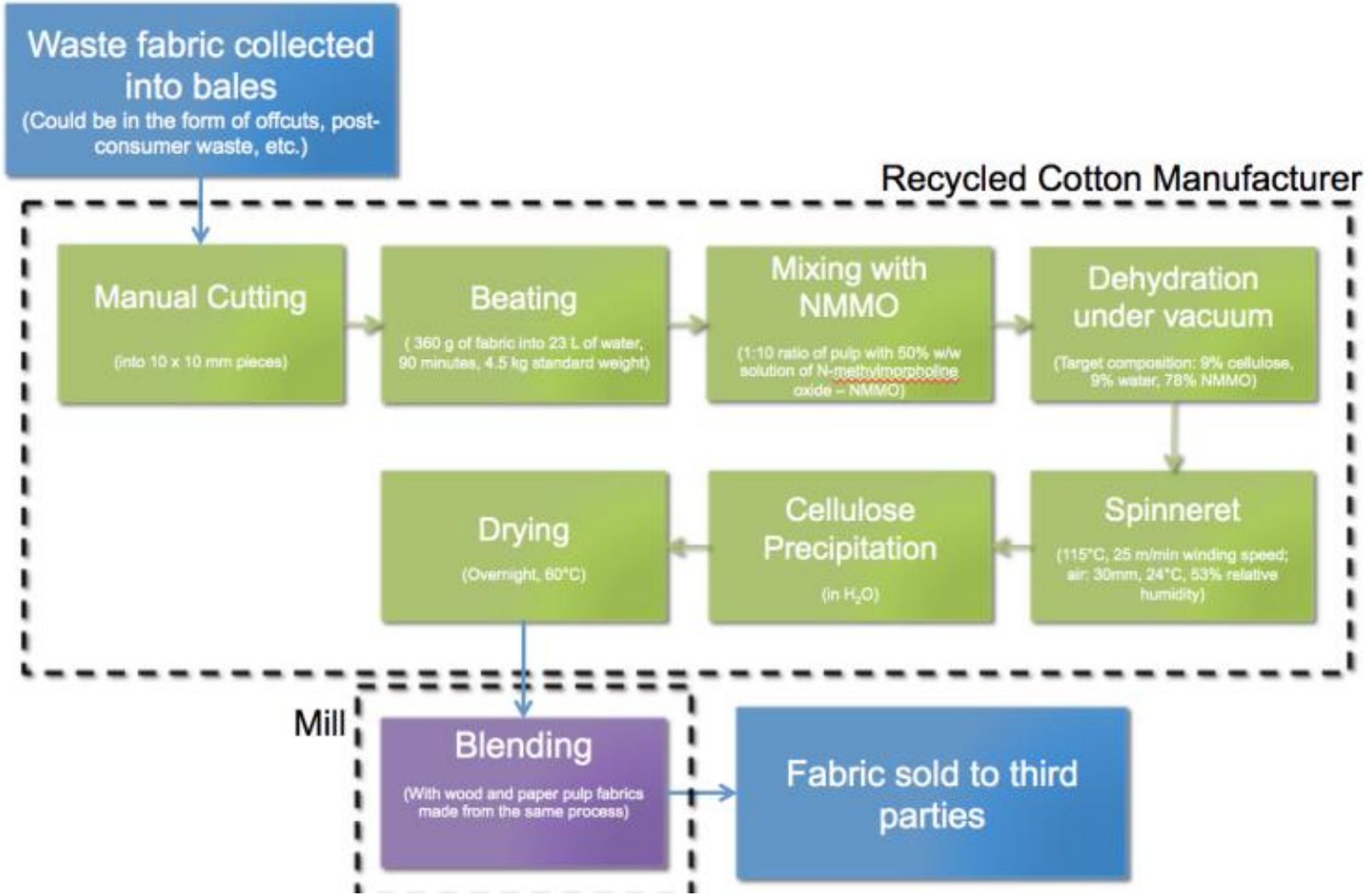
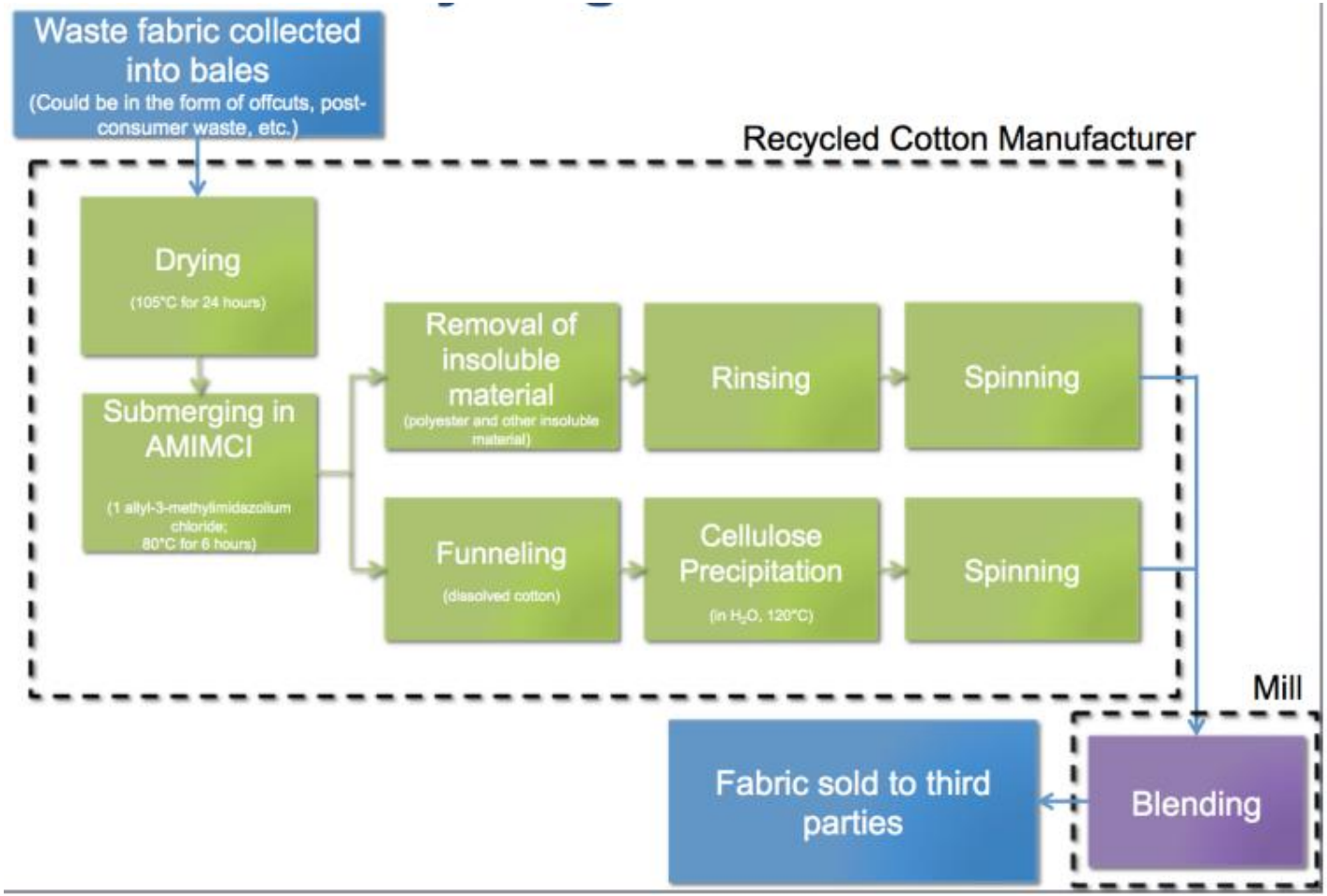
Recycling of textiles: Lyocell method



Source of the figure: MIT Sloan School of Management Strategies for Sustainable Business Final Report – Recycled Cotton for Gap Inc

Recycling of textiles: AMIMCI method



Source of the figure: MIT Sloan School of Management Strategies for Sustainable Business Final Report – Recycled Cotton for Gap Inc

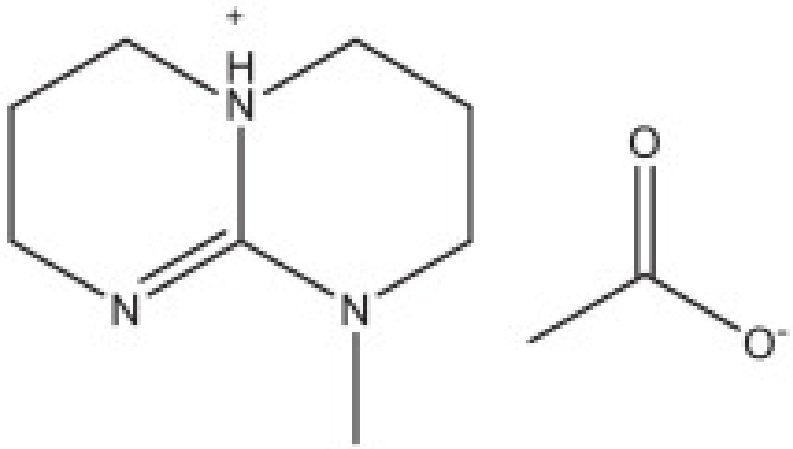
Recycling of textiles: AMIMCl method

- The AMIMCl method uses 1 allyl-3-methylimidazolium chloride (AMIMCl) to separate cotton fibers from cotton-polyester blend fabrics.
- The polyester/cotton fabrics are dried at 105°C for 24 hours to remove all moisture within the fabric. Fabrics were submerged in AMIMCl at 80°C for 6 hours.
- AMIMCl selectively dissolves cotton and not polyester, so after 6 hours the undissolved component (polyester) is removed, rinsed, and weighed.
- The cotton fibers are recovered by funneling. Then an ionic liquid, usually plain water, is used to precipitate the dissolved cotton fiber.
- The cotton dissolution is reported to occur fastest at 120°C.
- This process is also considered to be environmentally benign. The solvents employed are nontoxic to the environment in the event of a spill and cotton is regenerated using water.
- No difference was found between tensile properties between virgin cotton and the regenerated cotton.
- This process is considered advantageous because it can intake any material combination in the textile feed. However, it has similar concerns as the Lyocell process: it uses a high volume of water and the energy intensiveness of the process to achieve high temperatures requires further exploration.

Source of the text: MIT Sloan School of Management Strategies for Sustainable Business Final Report – Recycled Cotton for Gap Inc

Recycling of textiles: AMIMCl method

In the process based on **ionic liquids**, mixed textiles are ground to dissolve cotton.



[DBNH]OAc

Drawbacks: Not yet scalable, does not work for all starting compositions (suitable for 50:50 cotton / PET). Hydraulic pressure filtering was used to separate the undissolved polyester fraction from the cellulose solution.

Viscose production

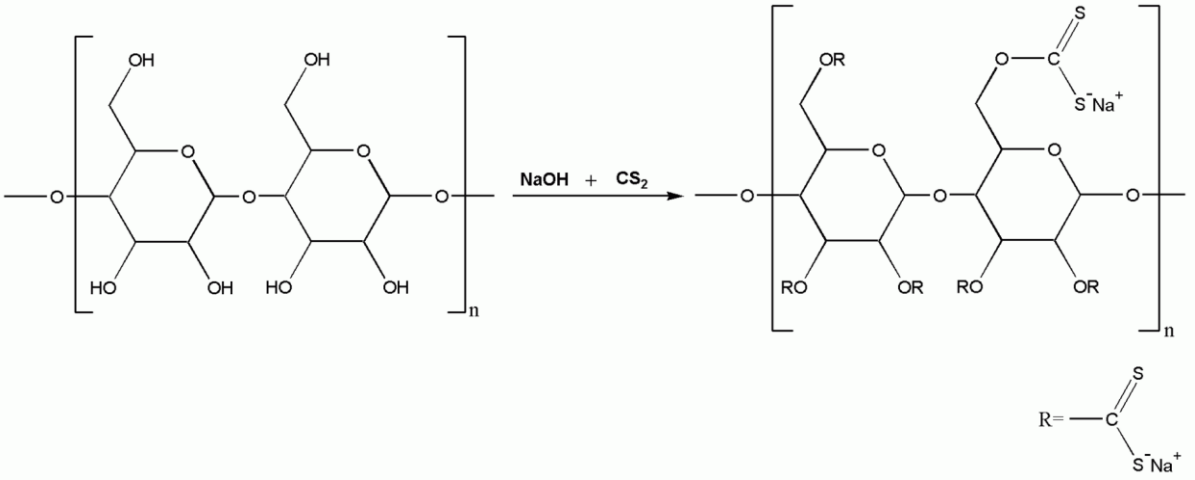
Cotton Waste in Viscose Production

•Cotton waste can be integrated into the **viscose** production chain, the first man-made fiber.

•The process involves **partially depolymerizing cotton fabric** into cellulose fiber, which is then converted into **viscose** (cellulose yarn).

Process: Cellulose is dissolved in **17.5% NaOH** and reacted with **carbon disulfide (CS2)** to form **cellulose xanthate**.

The xanthate is transformed into fibers, and the functional group is removed with **sulfuric acid**.



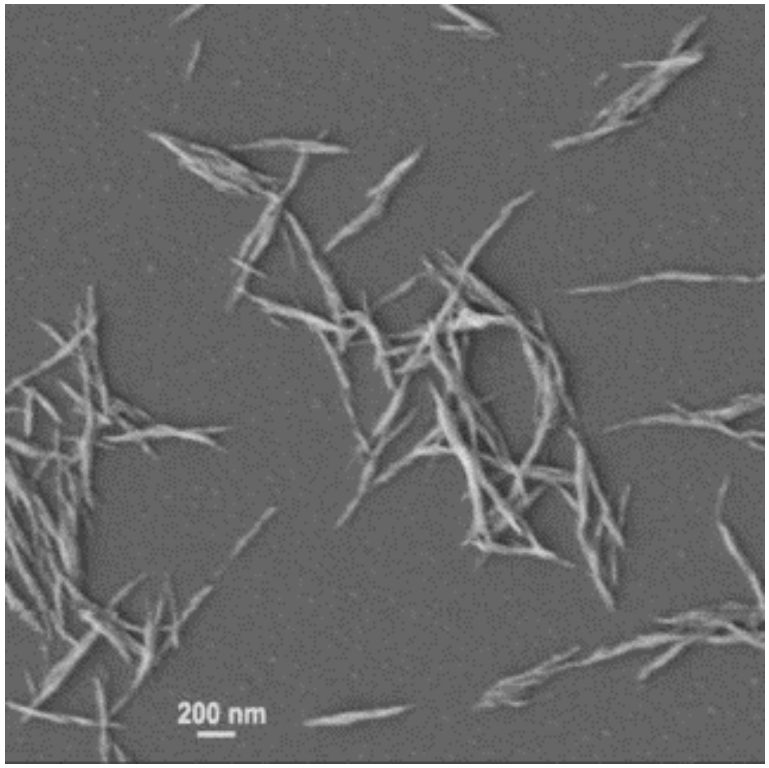


Partial hydrolysis of cotton

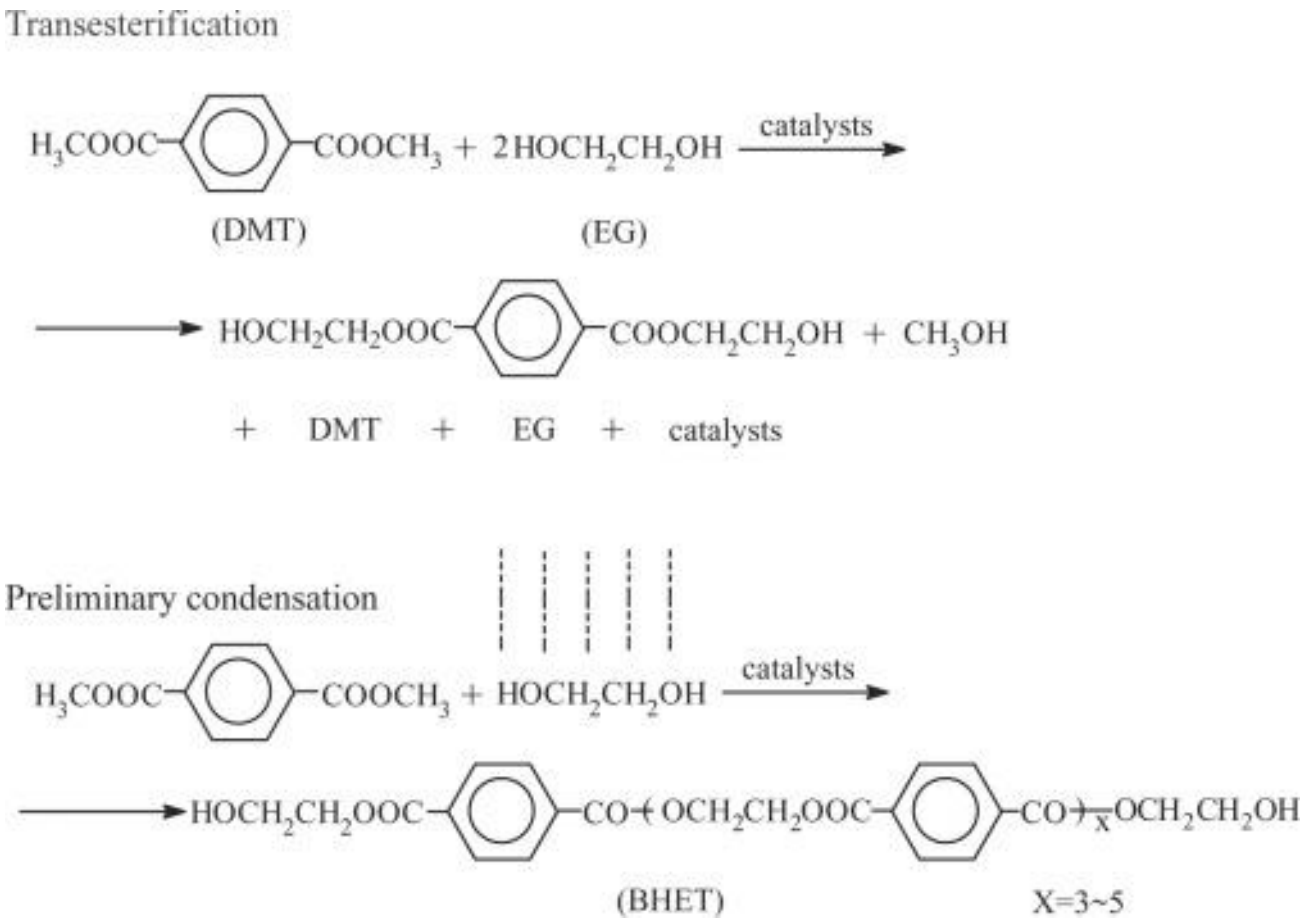
Partial hydrolysis can yield derivatives with valuable applications, such as nanocrystalline cellulose (CNC) or ***nanocellulose***, which can be extracted from waste cotton through acid hydrolysis (using H_2SO_4) in the presence of ammonium persulfate.

CNC exhibits excellent mechanical properties, low density, hydrophilicity, and degradability.

It is suitable as a reinforcing filler for packaging, bio-composites, antibacterial films, and flexible electronic devices.



Remind: polyester



Polymerisation of polyester from Dimethyl Terephtalate (DMT) and ethylenglycol (EG)

Source of the picture: Polyesters and Polyamides, Woodhead Publishing Series in Textiles 2008, Pages 62-96, https://doi.org/10.1533/9781845694609.1.62

Remind: polyester

PET is valued for its chemical inertness, lightness, high melting point, tenacity, and low cost. Its durability, versatility, low moisture absorption, and gas permeability make it a preferred material in various applications.

Table 1. Physical and chemical properties of PET [27].

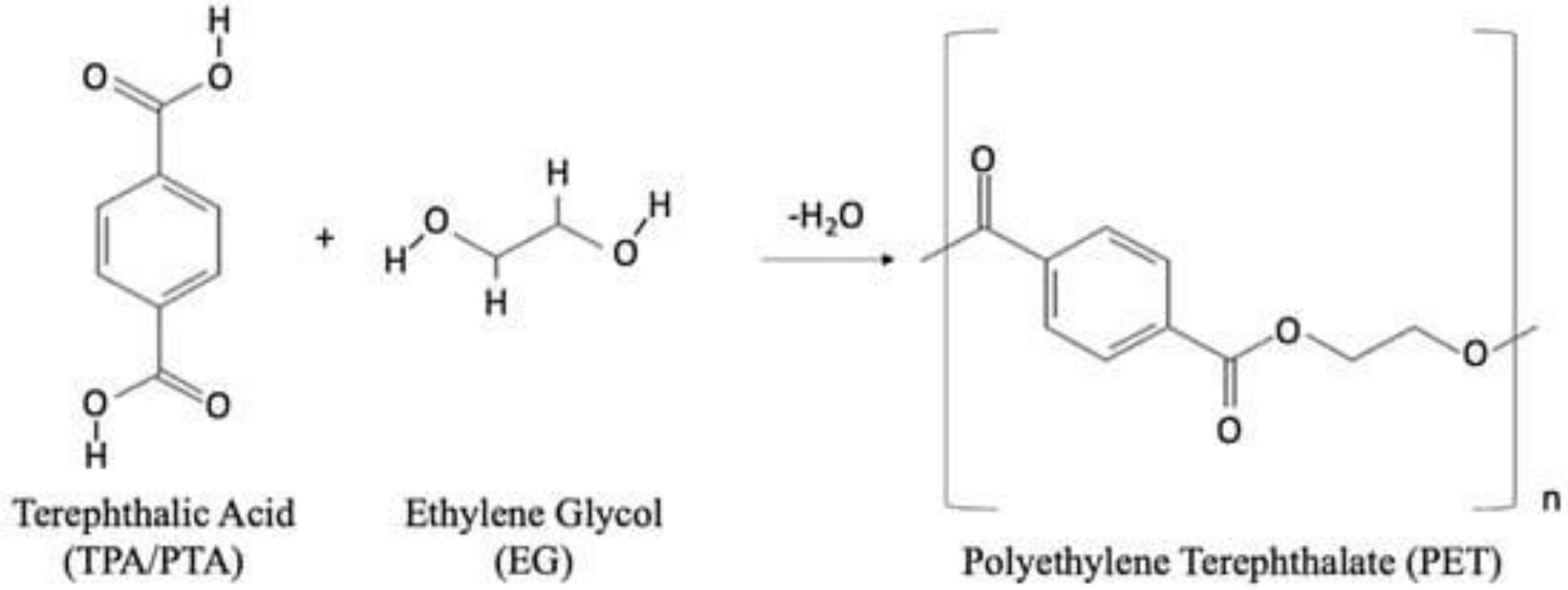
Property	Test Method	Value (Unit)
Molecular weight (of repeating unit)	-	192 (g mol^{-1})
Mark–Houwink parameters	-	$k = 3.72 \times 10^{-2}$ (mL g^{-1}) a = 0.73
Weight-average MW	-	30,000–80,000 (g mol^{-1})
Density	-	1.41 (g cm^{-3})
Glass transition temperature	(DSC) [1]	69–115 (°C)
Melting temperature	(DSC) [1]	265 (°C)
Heat of fusion	(DSC) [1]	166 (J/g)
Breaking strength	Tensile	50 (MPa)
Tensile strength (Young's modulus)	-	1700 (MPa)
Yield strain	Tensile	4 (%)
Impact strength	ASTM D256-86	90 (J m^{-1})
Water absorption (after 24 h)	-	0.5 (%)

[1] Differential scanning calorimetry (DSC).

Remind: polyester

Polyethylene terephthalate (PET) is synthesized using terephthalic acid (TPA) or dimethyl terephthalate (DMT) with ethylene glycol (EG).

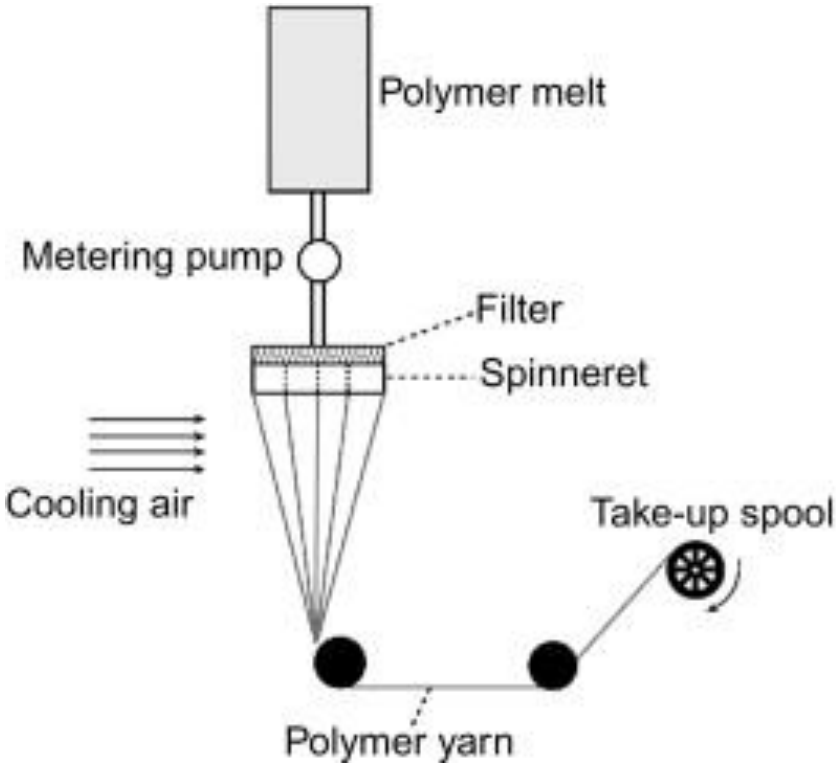
Direct esterification, using TPA and EG (1:1.5–3 molar ratio) at 240–260°C, typically requires no catalyst.



Terephthalic Acid (TPA/PTA) + Ethylene Glycol (EG) → Polyethylene Terephthalate (PET)

PET fibers production

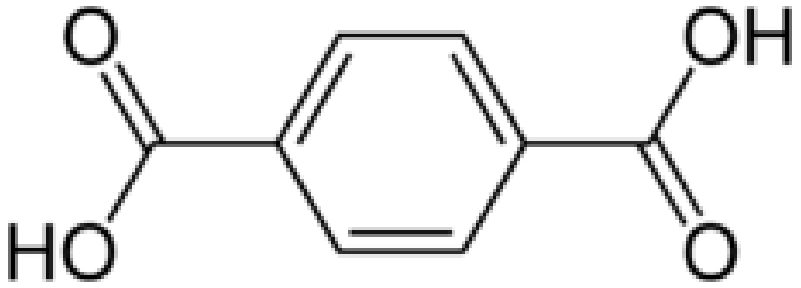
PET fibers are typically produced using melt spinning, where molten polymer is extruded through a spinneret into monofilaments of various cross-sectional shapes. These are cooled, drawn through rollers to achieve the desired thickness, and, when extruded in parallel, form a multifilament yarn (Islam, Rahman, & Mazumder, 2020).



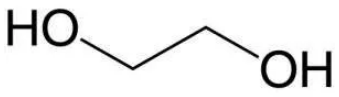
A spinneret is defined as a type of die used in fiber manufacture, typically a metal plate with multiple small holes through which a melt is extruded to produce filaments. It usually features circular orifices that create fibers with a round cross-section and can contain 50 to 110 small holes

Depolymerisation of PET

- Selective **depolymerization of textile polyester** (PET) from cellulose/PET blends renders the monomers of PET while cellulose remains in fiber form
- Recovered EG and TPA can replace the monomers achieved by fossil fuels and can be used to produce PET again, as well as resins, polyurethanes, and other materials.
- PET produced by recycled monomers display the same quality and properties as that produced by virgin precursors
- Low economic advantage due to low cost of virging feedstocks



TPA

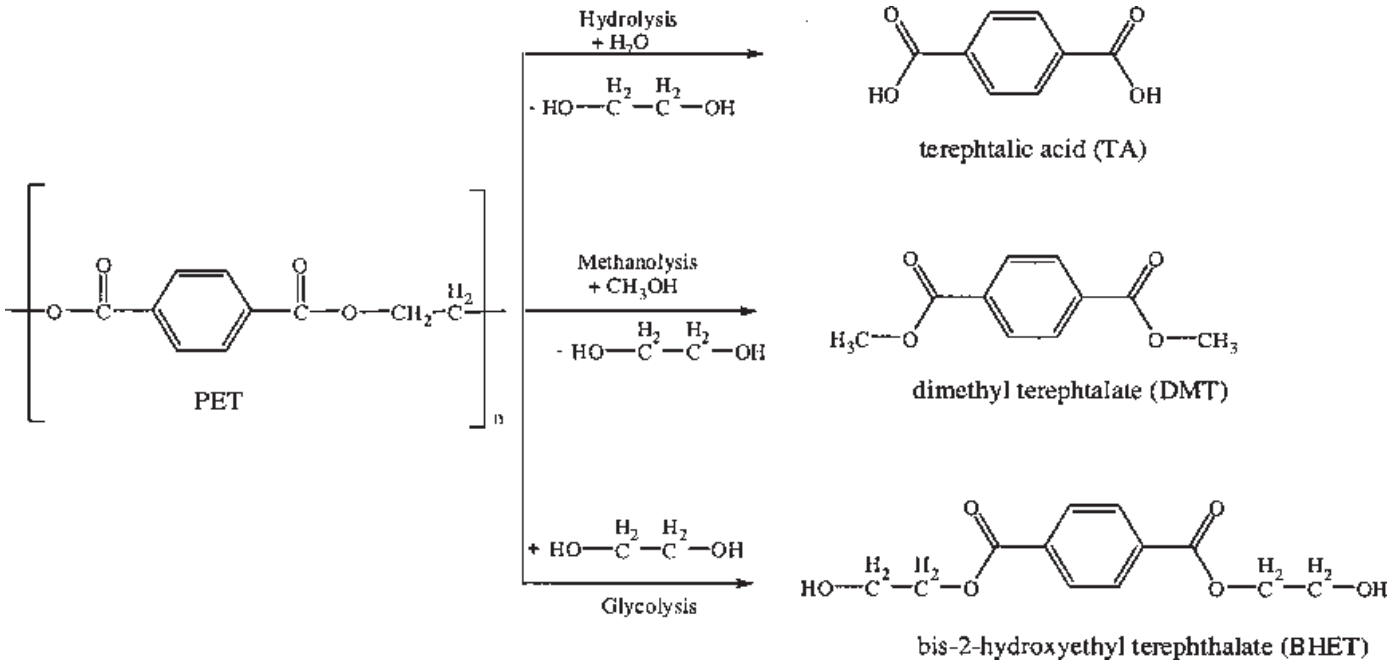


EG

PET solvolysis

Polyester ester bond generally broken by solvolysis. Different monomers obtained

Gycolysis
Methanolysis
Hydrolysis



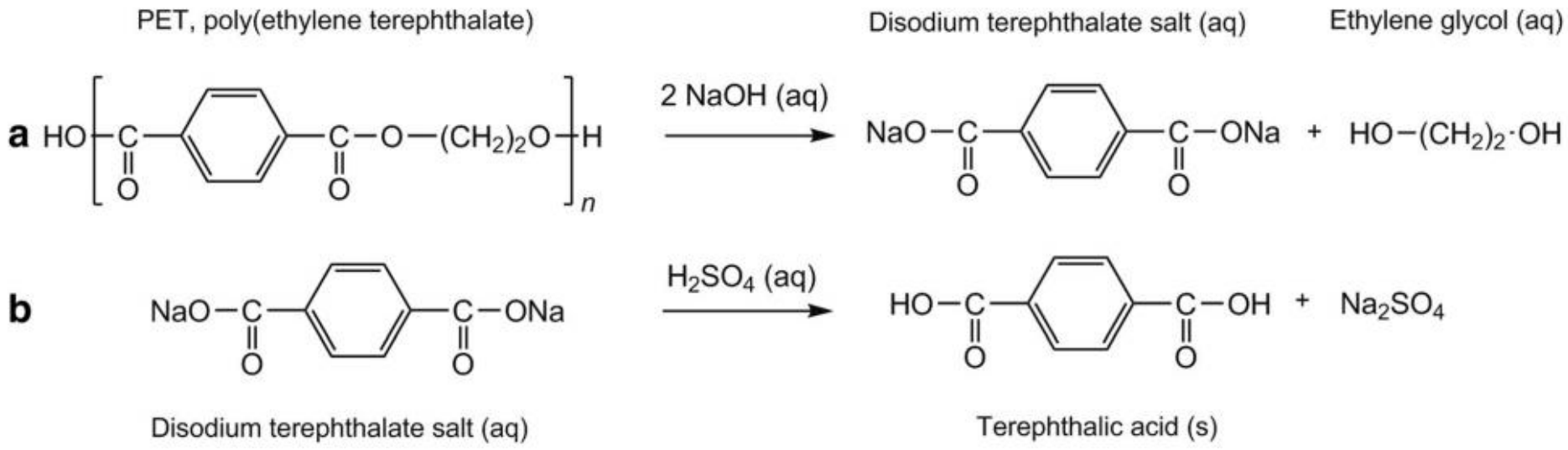
In chemical recycling, the ester bond of polyesters is commonly cleaved by solvolytic methods; the main ones being glycolysis, alcoholysis, methanolysis, and hydrolysis (acid, neutral, or alkaline). that render small-molecule building blocks of PET with slightly different chemistries.

Source of the figure: J. Bengtsson et al. Sustainability **2022**, 14, 6911

Alkaline hydrolysis of PET

Alkaline hydrolysis (NaOH 5–15% wt) is efficient in PET depolymerisation (weight ratio textile:solution 1:100) at mild temperature (70–95 ° C).
Alkaline hydrolysis of PET is the preferred hydrolysis option, as it can be applied to treat PET waste with higher impurities.

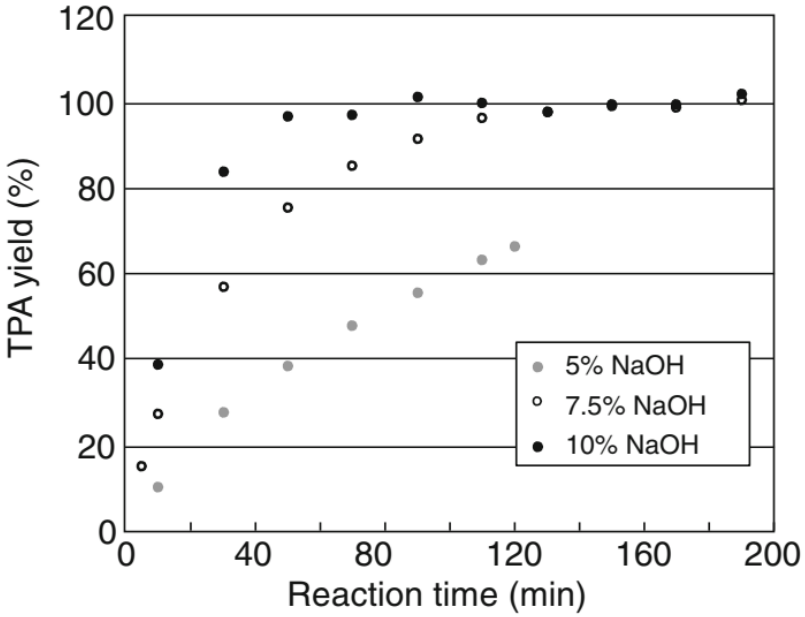
a) Ester bonds are cleaved by nucleophilic attack by the hydroxide ions of sodium salt to terephtalate, both soluble in aqueous phase
b) At the end of the reaction, the aqueous phase is cooled, filtered to remove the cellulose and acidified at pH 3 to promote the selective precipitation of TPA (isolated after drying at 105°C)

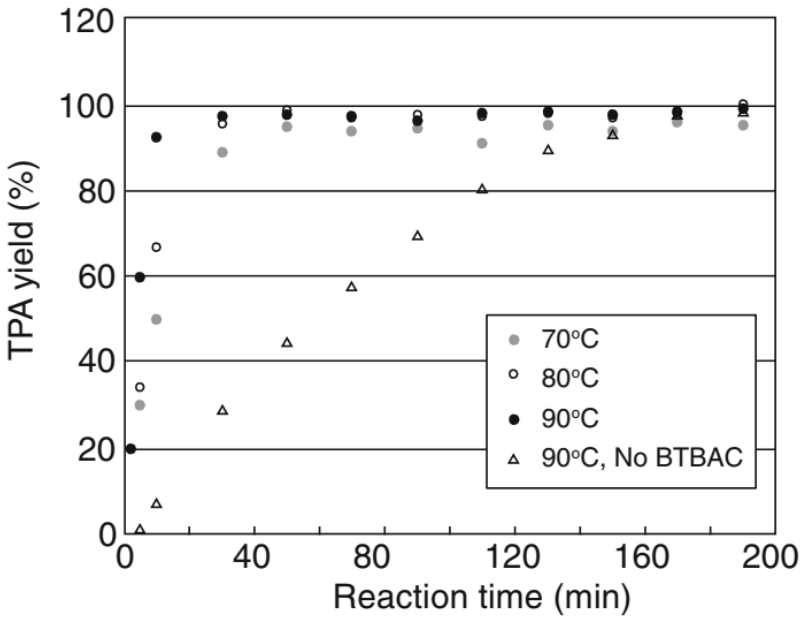


Souce of figure: Palme et al. Textiles and Clothing Sustainability (2017) 3:4

Condizioni di reazione

Reaction time reduced by: i. higher concentration of NaOH, ii. higher temperatures, iii. addition of phase transfer



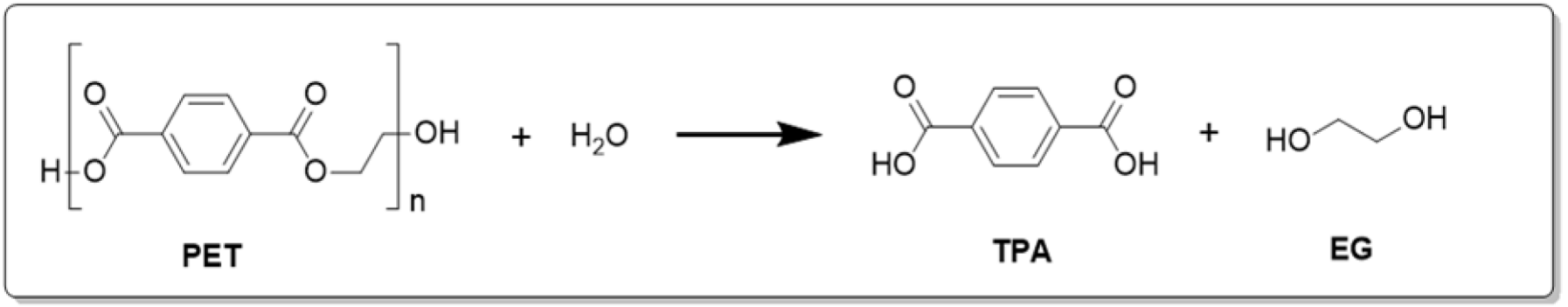


Source of the figure: Palme et al. Textiles and Clothing Sustainability (2017) 3:4

Acidic hydrolysis of PET

- PET hydrolysis in acidic conditions occurs at **25-100°C with mineral acids** (e.g., 15 M sulfuric acid, chloridric acid or nitric acid). Not yet deveopled for fibers.

- The yields of the hydrolysis reaction are typically high, approaching 100% while both glycolysis and methanolysis typically have lower yields. Furthermore, hydrolysis can be conducted under mild conditions than neutral hydrolysis



Neutral hydrolysis of PET

- Neutral hydrolysis involves **treatment with water or steam**. Unlike acid and alkaline hydrolysis, PET is degraded without forming unwanted liquid effluents containing inorganic salts.

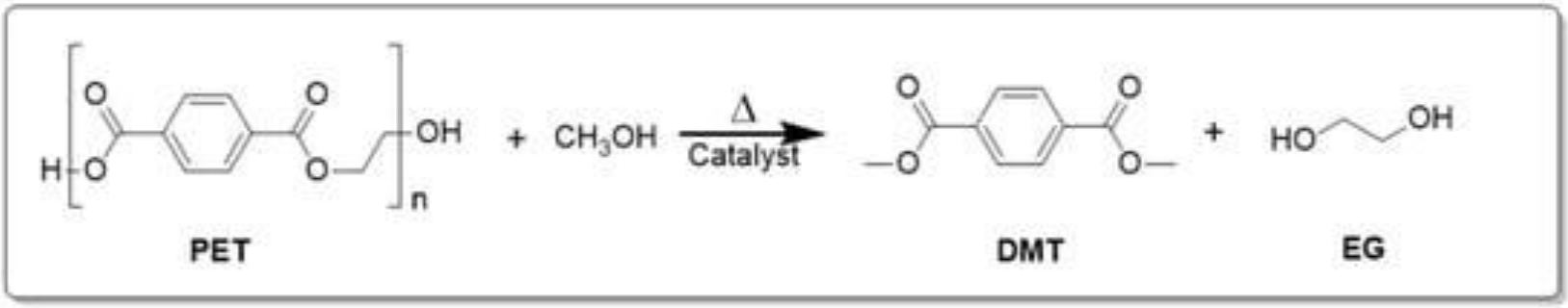
- This process is typically carried out under pressure (10-40 atm) at temperatures between **200 and 280°C**.

- Alkali metal acetates are commonly used as catalysts to promote PET hydrolysis. The reaction proceeds more slowly, requiring several hours to achieve high PET conversions.

Recycling of polyester using methanolysis

- Alcoholysis is the depolymerisation of PET in an alcohol medium under high temperature and pressure conditions. The most commercially used methodology for PET recycling. Methanol, and also ethanol, butanol, and trimethylolpropane, have been reported.

- Methanolysis entails the depolymerisation of PET to dimethyl terephthalate (DMT) using methanol. Liquid-phase methanolysis is conducted at high temperatures (180–280 °C) and pressures (20–40 atm) in order to afford DMT in high yield. The DMT is usually purified by distillation or crystallization to be reintroduced into the polymerization process. Compared to BHET, DMT is produced with higher purity



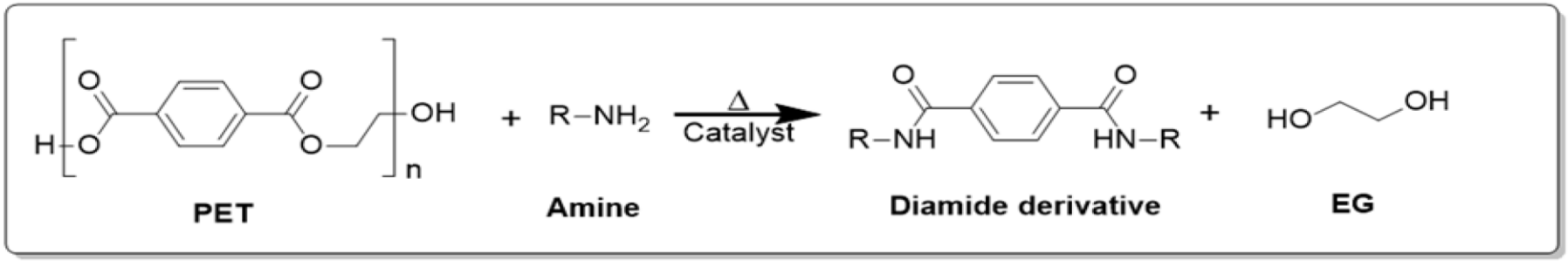
- Metal catalysts such as zinc, lead, and manganese acetates are required to enhance this rate. T*riethylamine was used for depolymerisation of polycotton enabling the isolation of cotton, which was further processed into viscose fibres.*

Recycling of polyester using aminolysis

Milder reaction conditions than alcoholysis: Due to higher nucleophilicity of amines compared to hydroxyl groups, but still makes use of toxic amines and high temperatures.

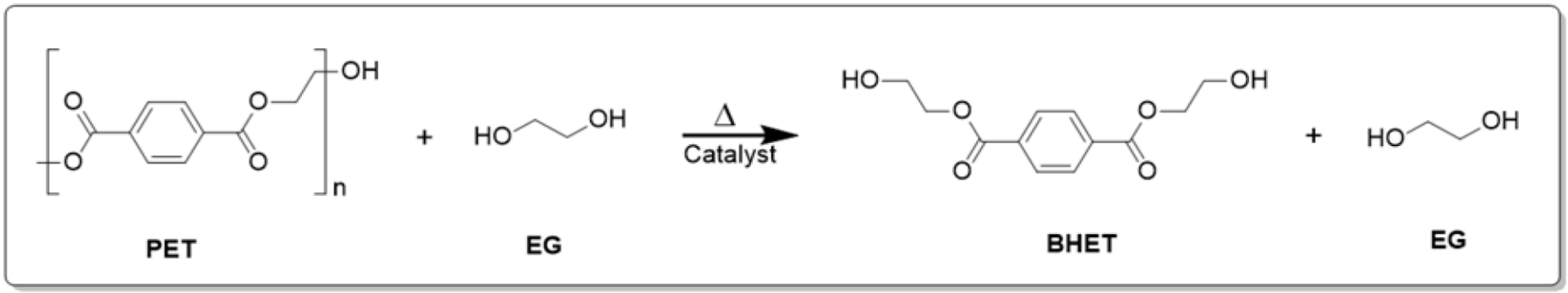
Catalysts: Homogeneous or heterogeneous catalysts**:** Acetates, sulphates, carbonates, and bicarbonates of metals like sodium, potassium, zinc, or lead.

1. Formation of terephthalamide-based monomers.
2. Currently at the laboratory scale.
3. More developed→ the aminolysis to partially modify PET fibres and Introduces functional groups (e.g., dyes, antibacterial, hydrophilic).



Recycling of polyester using glycolysis

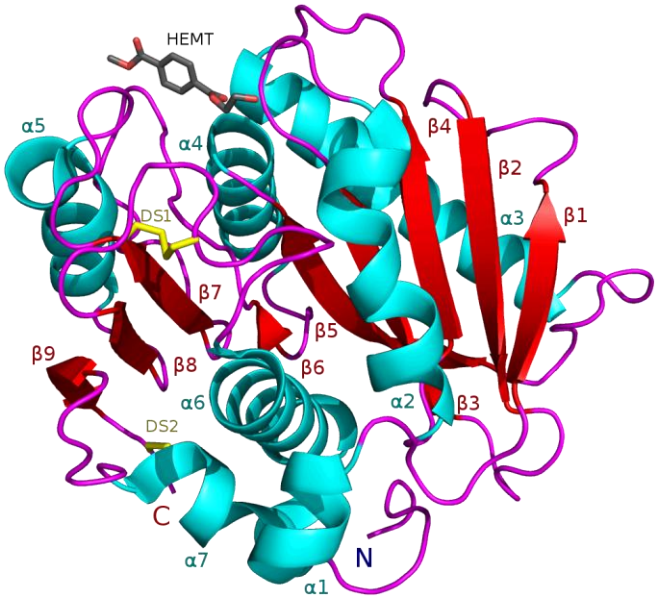
- Glycolysis is the most established approach for recycling waste PET due to the relatively mild reaction conditions (180-240°C) and the low volatility of ethylene glycol.
- Widely used to recycle textile materials to obtain the monomer BHET (Bis(2-hydroxyethyl) terephthalate). *Although BHET is an intermediate in PET synthesis, it does not offer advantages over using TA as the starting monomer.*
- The depolymerisation process involves the glycol diffusing into the polymer, causing the polymer to swell up, thus increasing the diffusion rate.



Recycling of polyester using Enzymatic degradation

- As a hydrophobic material with highly crystalline polymer morphology in its fibrous form, PET is not easily attacked by hydrolase enzymes.

- However, some thermophilic cutinases found in actinomycetes have been identified, known for their durability and speed of action. At temperatures of 65–70°C, these enzymes can achieve PET hydrolysis rates of up to 90%.



PET-ase

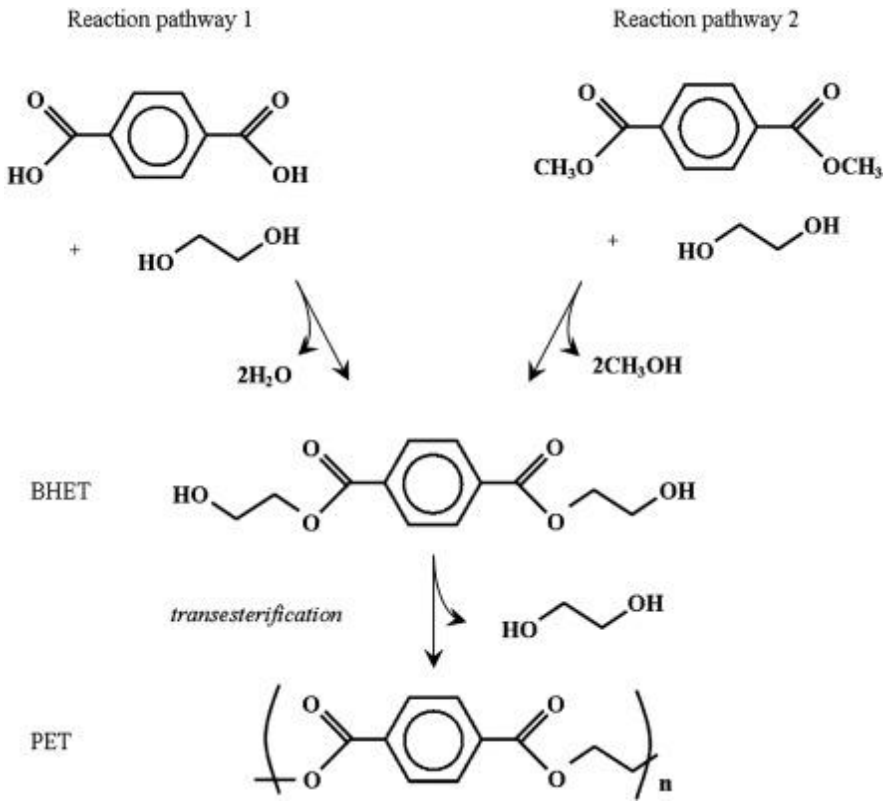
The process works best with highly chopped samples or with oligomers from pretreatments by neutral hydrolysis.

ACS Sustain. Chem. Eng. 2020, 8, 8894–8908

Back to PET: transesterification

- transesterification of DMT with EG. In transesterification, DMT reacts with EG (1:2.1–2.3 molar ratio) at 170–210°C in a nitrogen-rich environment with catalysts, producing bis-(2-hydroxyethyl) terephthalate (BHET).

- In the final polycondensation step, BHET is heated to 280°C under vacuum (<1 mmHg) to form PET. The entire process takes 5–10 hours

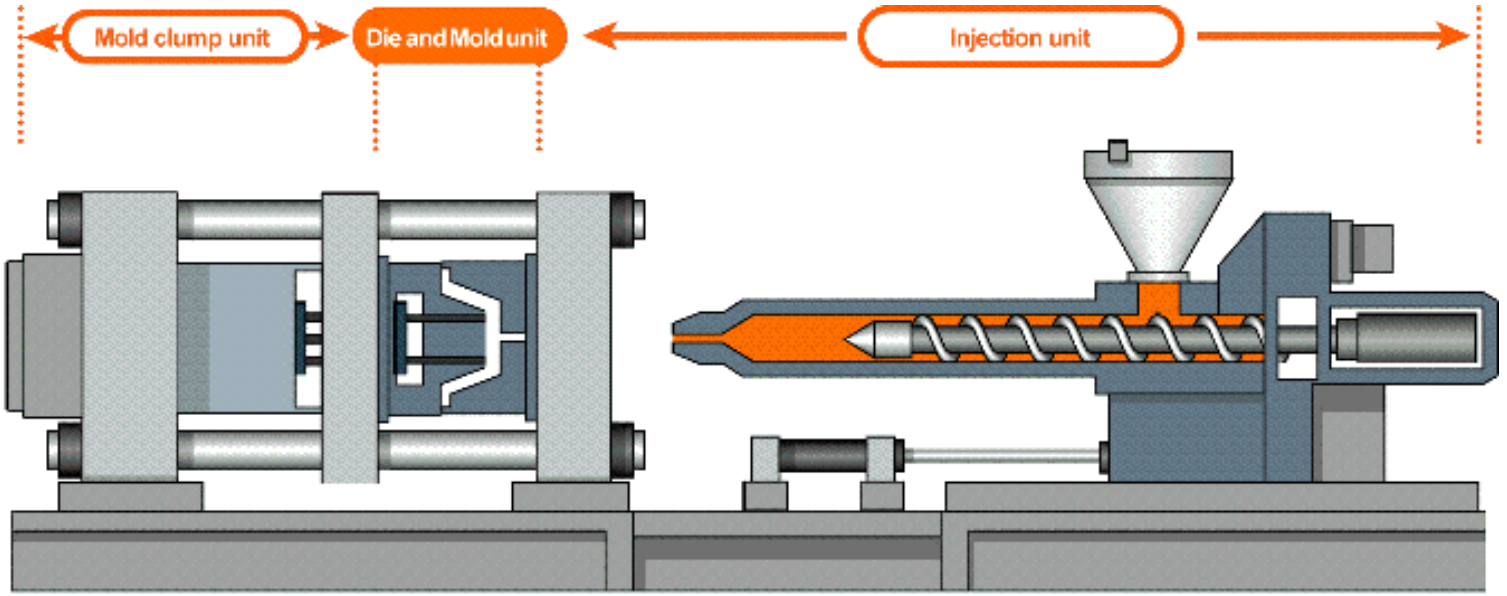


thermomechanical techniques

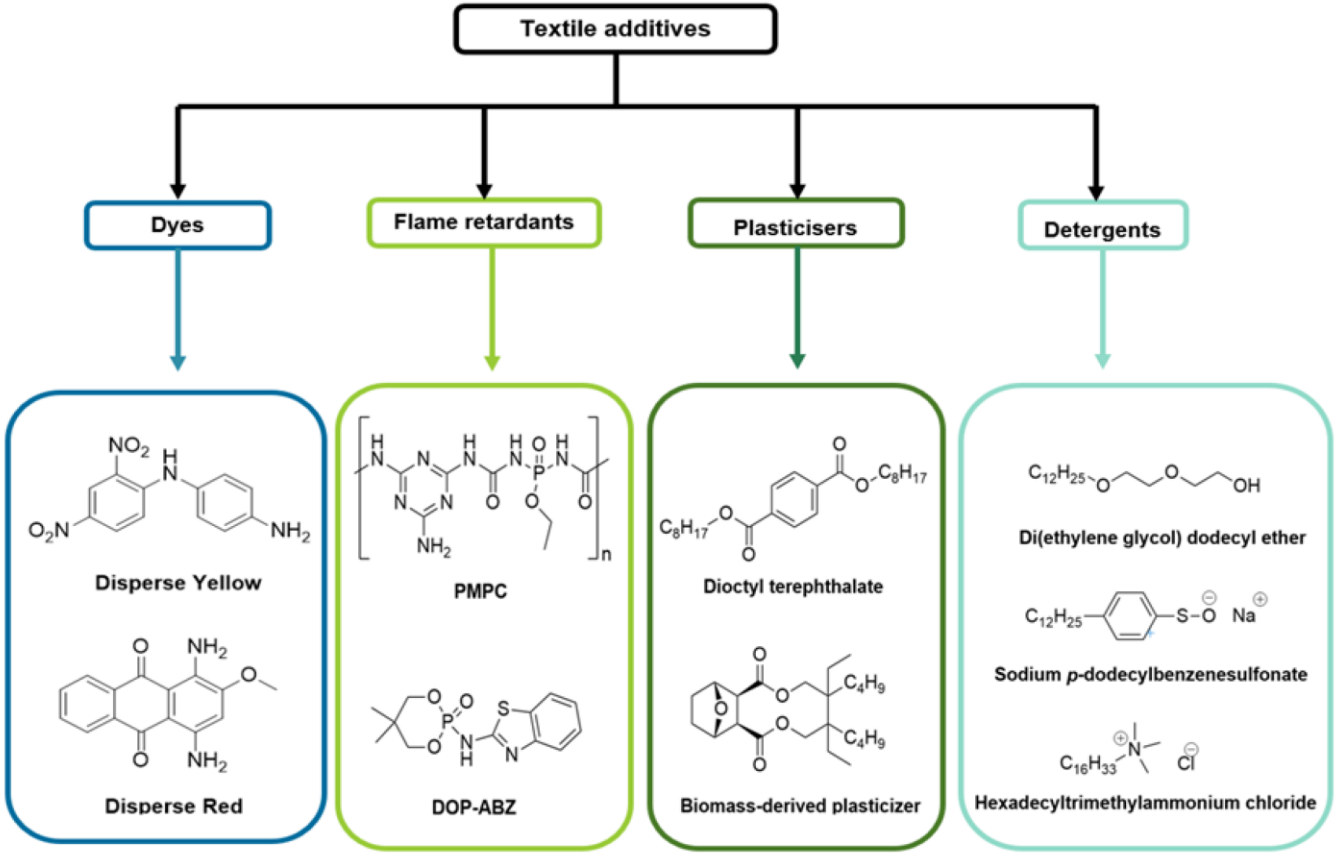
Since laundering is performed under alkaline conditions, and the ester bonds in the PET fibers are sensitive to alkali, it is probable that significant degradation occurs after many laundering cycles (International Fabricare Institute 1995).

In this case, thermomechanical techniques like extrusion or injection moulding, in which PET is melted and reshaped, typically yield materials with lowered molecular weight and inferior mechanical properties

For PET, the recycling of PET fibers and fabrics are typically downcycling processes.

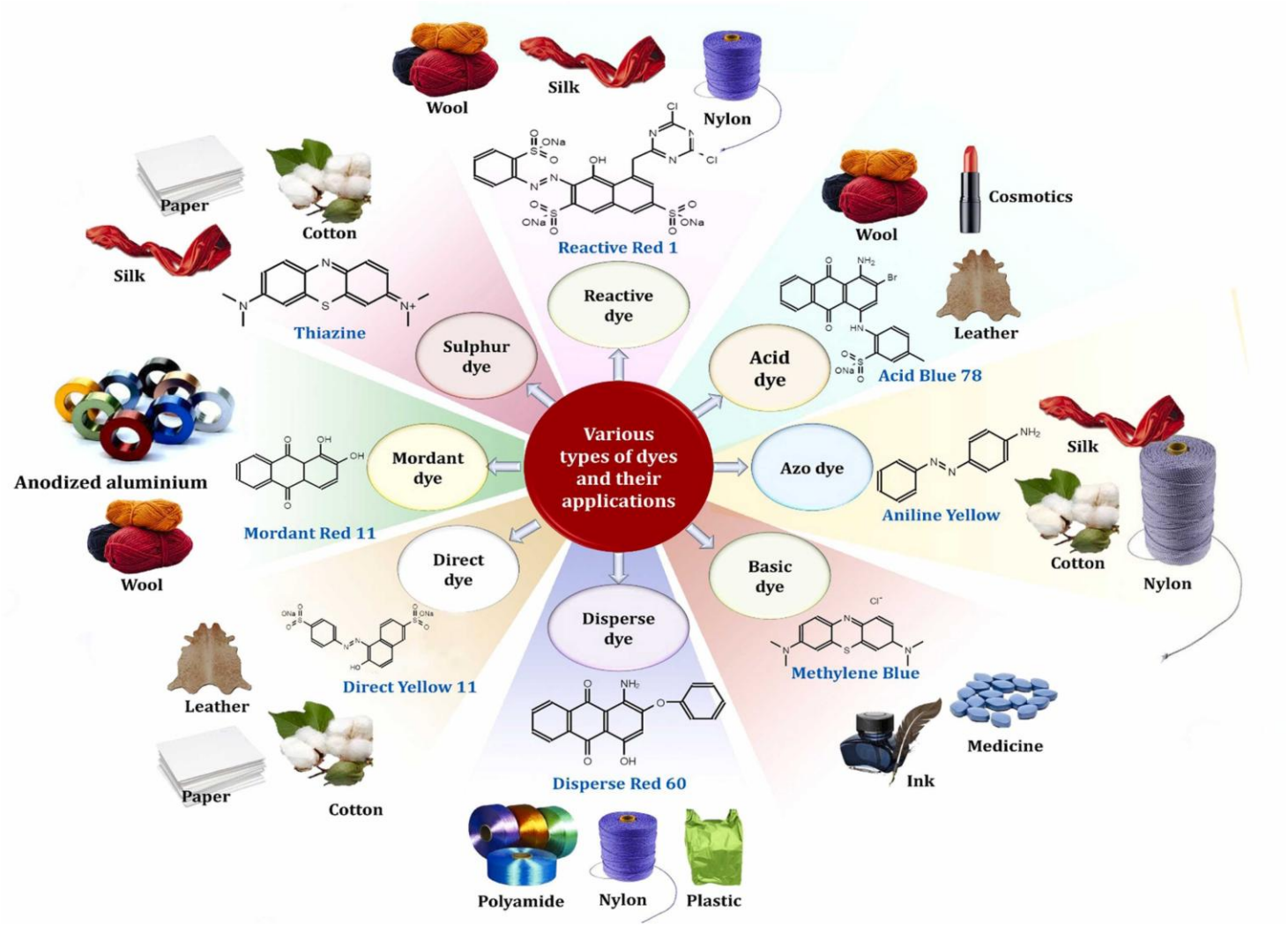


Decolorisation of textiles



Additives in natural or synthetic polyester fibers can affect recycling performance and reduce the quality of recycled products. These additives, which offer features like UV protection, water repellence, and fire resistance, are often difficult to remove during recycling due to their resistance to friction and washing.

Decolorisation of textiles



R. Al-Tohamy, et al. *Ecotoxicology and Environmental Safety*, 2022, 231, 113160,

Decolorisation of textiles

- decolorization technology is a critical problem in the high-quality chemical recycling and recovery of textile wastes.
- only 1% of textile wastes, mainly white-colored wastes, are recycled, so the final color quality of regenerated fibers is uncontrollable.
- color removal is required for the large-scale circulation of non-thermoplastic fibers
- Technologies for color removal from textile wastes are **dye destruction or extraction**, which take place during the pre-recycling process.
- dye destruction methods, such as oxidation and photodegradation, may damage polymers and change the dyeability of the regenerated textiles.
- to lower the chemical potential of the dyes in solution, harsh extraction conditions such as ultra-high temperature (>150 °C), lengthy time, and the use of excessive corrosive solutions can lead to structural damages to the polymers.
- dye extraction focuses on finding solvents with high dye solubility, but dye extraction fails to remove all of the dye from textiles.

Potential Solutions for dye removal

•**Dye-destruction**: uses oxidation and photodegradation but damages fibers, affecting future dyeability. For example, nitric acid can remove dyes from cotton/polyester blends.

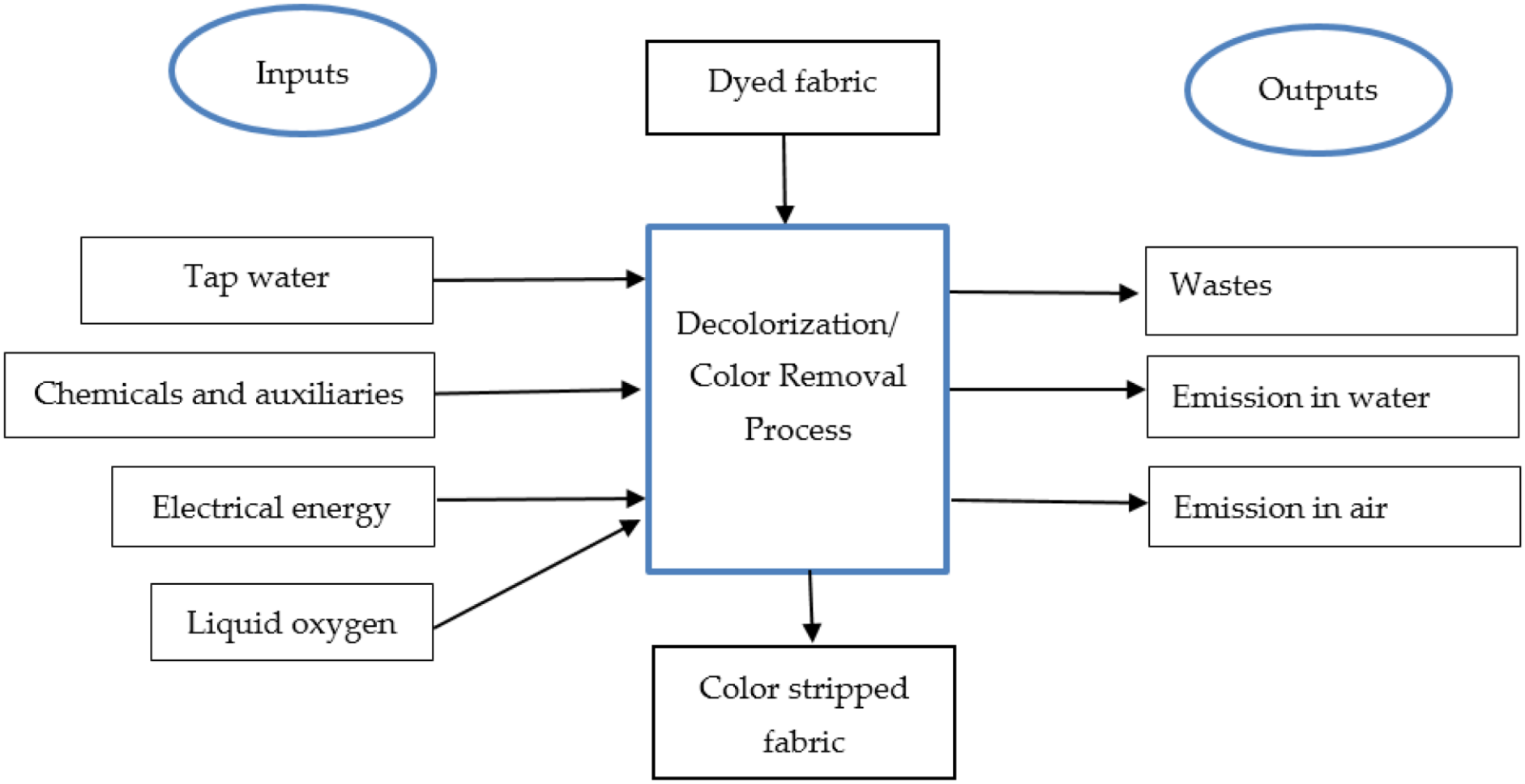
•**Dye-extraction**: requires solvents (dimethyl sulfoxide (DMSO) and ionic liquid, or steam and ethanol), high temperatures, and chemicals, risking fiber integrity. to lower the chemical potential of the dyes in solution, harsh extraction conditions such as ultra-high temperature (>150 °C), lengthy time, and the use of excessive corrosive solutions can lead to structural damages to the polymers.

•**Dye extraction** fails to remove all of the dye from textiles. Ion-exchange resins have been developed to improve the decolorization process during PET recycling.

•**Polyester dissolution**: separates dyes from liquefied polyester but is costly and complex, especially for cotton-polyester blends.

➔ The high cost of dye removal remains a key barrier to textile recycling.

Decolorisation of textiles



System boundaries of the decolorization process of the reactive dyed cotton
Source of the figure: *Sustainability* **2021**, *13*(3), 1225

Challenges in dye removal

- Textile dyes, especially in synthetics, are highly durable and resistant to degradation.

- Color removal extends textile life cycles and reduces reliance on virgin materials. Removing dyes simplifies both mechanical and chemical recycling.

- Unremoved dyes compromise fiber quality and release harmful substances, leading to environmental pollution.

- High costs and technological difficulties make dye removal a major hurdle in large-scale textile recycling.