

Polyethylene furanoate (PEF) – a biobased alternative to PET

Kerstin Jedvert

Chalmers Industriteknik

Möjliga värdekedjor för biobaserad plast

Finansierat av Energimyndigheten inom Bio+-programmet

Version 1.3

2025-01

Klassificering

Stängd – innehåller upphovsrättsskyddade bilder



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Executive summary

The development of biobased polyethylene furanoate (PEF) as an alternative to conventional polyethylene terephthalate (PET) has reached a significant milestone, with PEF now nearing commercialization. This report highlights the advancements in PEF development, its properties and applications, and the challenges and opportunities associated with its adoption as a sustainable plastic alternative.

PEF has undergone extensive research and development over many years, leading to technological advancements, e.g., previous issues with discoloration have been successfully addressed. PEF also exhibits superior barrier properties compared to conventional PET, offering enhanced resistance to gases like oxygen and carbon dioxide. This means that less material can achieve the same or better performance, contributing to improved resource efficiency. The reduced material requirement not only conserves resources but also lowers the overall weight of PEF products and has a positive impact on the life cycle assessment (LCA) of these products.

The end-of-life scenario is crucial for the overall sustainability of plastics. Recycling is the most desired option for managing plastic waste, and initially, PEF can be mechanically recycled alongside PET. This compatibility allows for the creation of products, such as bottles and packaging, that combine the two polymers to optimize properties and shelf-life. In the long term, developing a pure PEF recycling stream could potentially enhance recycling efficiency further, and both mechanical recycling and chemical recycling processes for PEF could be viable options.

Despite its environmental advantages, PEF faces economic challenges. For the foreseeable future, PEF will remain more expensive to produce than fossil-based PET. This price disparity poses a significant barrier to market growth, as cost-sensitive industries may be reluctant to adopt PEF without financial incentives or regulatory support.

Currently, industrial production of PEF relies on primary biobased feedstock, such as fructose derived from sugar and corn. However, there is positive momentum towards the development of biorefineries capable of utilizing secondary feedstocks, such as lignocellulosics and waste materials. This shift will further enhance the sustainability profile of PEF by reducing reliance on food-based resources and promoting the use of renewable and waste-derived materials.

In summary, biobased PEF represents a promising and more sustainable alternative to conventional PET, offering superior barrier properties and better LCA performance. While economic challenges remain, strategic efforts in recycling and the use of diverse biobased feedstocks can support the widespread adoption of PEF. By continuing to innovate and invest in sustainable technologies, PEF can play a crucial role in the transition towards a more circular and resource-efficient economy.

Svensk sammanfattning

Utvecklingen av biobaserad polyetylenfuranoat (PEF) som ett alternativ till konventionell polyetylentereftalat (PET) har nått en betydande milstolpe, där PEF nu närmar sig kommersialisering. Den här rapporten belyser framstegen inom utvecklingen av PEF, egenskaper och tillämpningar, och de utmaningar och möjligheter som är förknippade med att PEF nu tas fram som ett hållbart plastalternativ.

PEF har genomgått omfattande forskning och utveckling under många år, vilket lett till betydande tekniska framsteg, t.ex. har tidigare problem med missfärgning åtgärdats. PEF uppvisar också överlägsna barriäregenskaper jämfört med konventionell PET, vilket ger förbättrat motstånd mot syre och koldioxid. Detta innebär att en mindre mängd material kan uppnå samma eller bättre prestanda, vilket bidrar till förbättrad resurseffektivitet. Det minskade materielbehovet kan också sänka den totala vikten av PEF-produkter, vilket har en positiv inverkan på livscykelbedömningen (LCA) för dessa produkter.

Hur plast tas om hand vid slutet av produktlivslängden är avgörande för den övergripande hållbarhetsbedömningen. Återvinning är det mest önskvärda alternativet för att hantera plastavfall, och initialt kan PEF återvinnas mekaniskt tillsammans med PET. Denna kompatibilitet gör det möjligt att ta fram produkter, såsom flaskor och förpackningar, som kombinerar de två polymererna. På lång sikt skulle utvecklingen av en ren PEF-återvinningsström potentiellt kunna förbättra återvinningseffektiviteten ytterligare, och både mekanisk återvinning och kemiska återvinningsprocesser för PEF kan vara tänkbara alternativ.

Trots sina miljöfördelar står PEF inför ekonomiska utmaningar. Under överskådlig framtid kommer PEF att förbli dyrare att producera än fossilbaserad PET. Denna prisskillnad utgör ett betydande hinder för marknadsstillväxt, eftersom kostnads känsliga industrier kan vara ovilliga att använda PEF utan ekonomiska incitament eller andra styrmedel.

För närvarande bygger industriell produktion av PEF på primär biobaserad råvara, såsom fruktos från socker och majs. Det finns dock ett positivt satsningar på utveckling av bioraffinaderier som kan utnyttja sekundära råvaror, såsom lignocellulosa eller avfallsmaterial. Denna förändring kommer att ytterligare förbättra hållbarhetsprofilen för PEF.

Sammanfattningsvis är biobaserad PEF ett lovande och mer hållbart alternativ till konventionell PET, som erbjuder överlägsna barriäregenskaper och bättre LCA-prestanda. Även om ekonomiska utmaningar kvarstår, kan strategiska satsningar för återvinning och användningen av olika biobaserade råvaror stödja biobaserade plaster som PEF. Genom att fortsätta investera i hållbar teknik kan PEF spela en avgörande roll i omställningen till en mer cirkulär och resurseffektiv ekonomi.

Acronyms

PEF	polyethylene furanoate
PET	polyethylene terephthalate
MEG	(mono)ethylene glycol
EG	ethylene glycol
TPA	terephthalic acid
FDCA	2,5-furandicarboxylic acid
FDME	furandicarboxylic methyl ester
HMF	5-(hydroxymethyl) furfural
CMF	5-(chloromethyl) furfural
PTF	polytrimethylene furandicarboxylate

1. Introduction

The EU policy framework on biobased, biodegradable, and compostable plastics, clearly states that there is a need to improve the overall environmental sustainability of plastics (European Commission, 2022). Most of the plastic waste is still being either incinerated with energy recovery, landfilled, littered, or exported. At the same time, indication and predictions are that the production of plastics is going to double in the next 20 years (World Economic Forum, Ellen MacArthur Foundation and McKinsey & Company, 2016).

1.1 Biobased plastics

Bioplastics is a term used somewhat carelessly to describe both biobased, biodegradable, and compostable plastics. These plastics in total represent ca. 0.5% of the total plastic production capacity, with a volume over 2M tonnes per year (European Bioplastics, 2023). The forecasts for annual growth lands at 17% for biobased polymers between 2023 and 2028, where the demand from Asia and the USA is driving growth, while Europe is currently lagging (Skoczinski *et al.*, 2024). Although the overall growth for biobased polymers is faster than in previous years, it is still representing only a minor share of the total production of plastics.

Biobased polymers have the potential to bring advantages over conventional plastics by having a lower carbon footprint, showing novel functionalities and properties, and being compatible with existing recycling streams. However, there can also be negative aspects, e.g., agricultural impacts, ambiguous end-of-life scenarios and (not least) higher costs (Rosenboom, Langer and Traverso, 2022). For biobased plastics to succeed, they need to be able to compete with well-established materials that have been developed for more than a century, and where effective and sophisticated production and conversion routes exist, including growing infrastructure for recycling. It takes a long time for new materials to yield considerable revenue, and this applies also for biobased polymers. Thus, most companies producing or using plastics today are more interested in finding biobased alternatives to the established polymers (i.e., drop-in), which can be applied directly in existing conversion and disposal infrastructure (Kunamaneni, 2023).

Furthermore, it is important to note that many biobased plastics do not consist of 100% biobased content and there is currently no mandatory minimum biobased content nor agreed certification scheme or label for a plastic product to be labelled as biobased (European Commission, 2022). The crosscutting standards developed by the European Technical Committee for Standardisation for biobased products offer guidance on aspects such as measuring methods of biobased content, business-to-business, and business-to-consumer communication. These voluntary standards are widely used by the market and their application is recommended by the EU Commission (EC) to ensure a consistent approach. For measuring biobased content, the EC recommend radiocarbon-based (C14) methods.

In summary, biobased plastics must be designed for circularity, be produced safely and from sustainably sourced feedstock (prioritising the use of secondary biomass) as well as be compliant with relevant standards. For biodegradable and compostable plastics, some challenges, e.g., risks of ending up in environments where they will not biodegrade, are raised in the policy framework. Thus, in Sweden, the position from governmental agencies is that circularity and recyclability, keeping the materials and products in the economy for as long as possible, is the best way forward. This approach is also backed in some research papers, e.g., Chandran *et al.* (2020) states that compostable and biodegradable plastics are probably too expensive to manufacture and, in most cases, very slow to break down into their chemical components (Chandran, Tamilkolundu and Murugesan, 2020).

1.2 Introduction to poly(ethylene 2,5-furandicarboxylate) (PEF)

Among the most common plastics globally is polyethylene terephthalate (PET), amounting to about 24 million tonnes in 2021 (Chowdhury *et al.*, 2018)(Plastics Europe, 2022). It is a thermoplastic that has been produced from fossil feedstock since the 1940's and is used for e.g., bottles, packaging, and textiles (Evode *et al.*, 2021) One key factor contributing to PET's extensive utilization is its capability to generate various grades across a wide spectrum of molecular weights within a single multiproduct polymerization facility (Jankauskaitė, Macijauskas and Lygaitis, 2008). Another advantage of PET is its recyclability, and the separation of PET bottles from municipal waste represents one of the most successful examples of polymer recycling to date.

Considerable effort has been put into making PET from biobased resources (Pang *et al.*, 2016). Currently, there is biobased PET on the market which is partly (~30%) made from biomass, in which case one of the monomers, i.e. (mono)ethylene glycol, has been produced from biomass (Wong *et al.*, 2023). The other monomer, terephthalic acid, is more difficult to produce from biobased feedstock due to challenges of obtaining high purity and high yields and thus high production costs (Zhang *et al.*, 2021), see Figure 1.

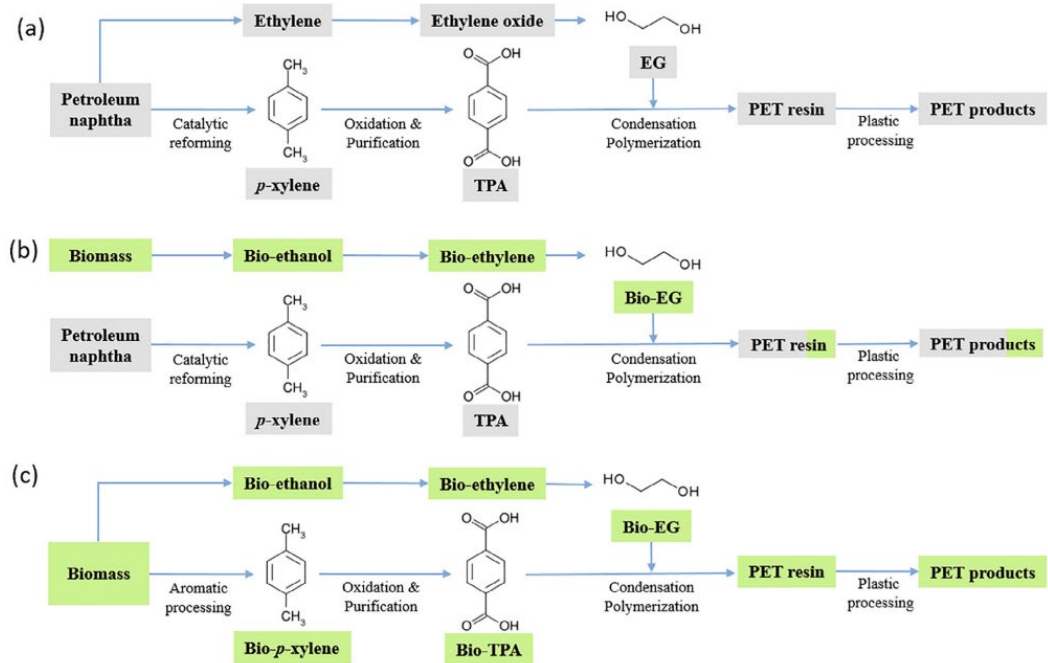


Figure 1. Production of PET from fossil- and biobased building blocks (a) fossil-based PET, (b) bio-PET (30w% biobased), (c) bio-PET (100w% biobased) (Hwang *et al.*, 2020).

Polyethylene furanoate (PEF) has earned attention as a 100% biobased alternative to PET, offering high-performance properties with reduced environmental footprint. PEF has obtained wide recognition mainly due to its resemblance to commercial PET and its suitability for many general applications, especially in the packaging of carbonated drinks (Gandini *et al.*, 2009)(Loos *et al.*, 2020), see Figure 2.

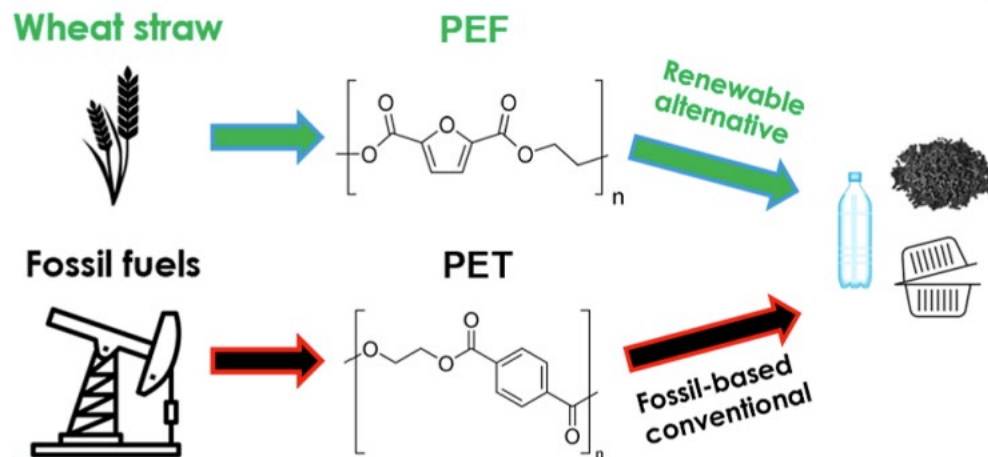


Figure 2. Production of PEF and PET (Kim *et al.*, 2022).

After 2004 when US Department of Energy named 2,5-furandicarboxylic acid (FDCA) as one of the top twelve biobased building blocks (Werpy and Petersen, 2004), there has been exponential growth in patents surrounding furanic building blocks (i.e., FDCA, furandicarboxylic methyl ester (FDME), 5-(hydroxymethyl) furfural (HMF) and 5-(chloromethyl) furfural (CMF)), see Figure 3.

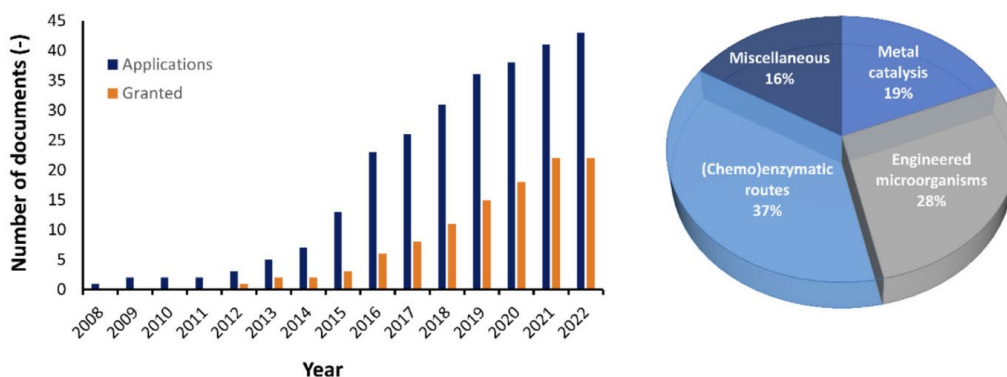


Figure 3. Patent survey related to FDCA synthesis and biotechnological methods (until Aug. 2022) (Milić, Domínguez de María and Kara, 2023).

Research on polyesters based on these monomers, like PEF and polytrimethylene furandicarboxylate (PTF), has also prospered during the last 10-15 years (Sanders *et al.*, 2024) The developments have also progressed from research level, e.g., via several large EU-financed initiatives (see list of some relevant examples below) and the journey to commercialization is taking a great leap with the finalization of the demonstration plant constructed by the Dutch company Avantium (<https://www.avantium.com/>) this year (2024). Thus, it is expected that the public, within the coming years, will be familiar with this new biobased plastic. This report aims to provide an analytical overview of the opportunities and challenges connected to the manufacture, use, and end-of-life of this polymer.

Examples of relevant EU-projects:

- **ReTapp** (2015-2018) focused on producing wood-based fructose for production of plastic bottles and all plastic packaging. <https://cordis.europa.eu/project/id/691414>.
- **TERRA** (2015-2019) aimed to develop, from TRL 3 to 5, a tandem electrocatalytic reactor (TER) coupling an oxidation reaction to a reduction reaction, for PEF (a ground-breaking synthesis route using a one-step reactor to produce MEG and 2,5-FCDA simultaneously), see Figure 4. <https://cordis.europa.eu/project/id/677471>.

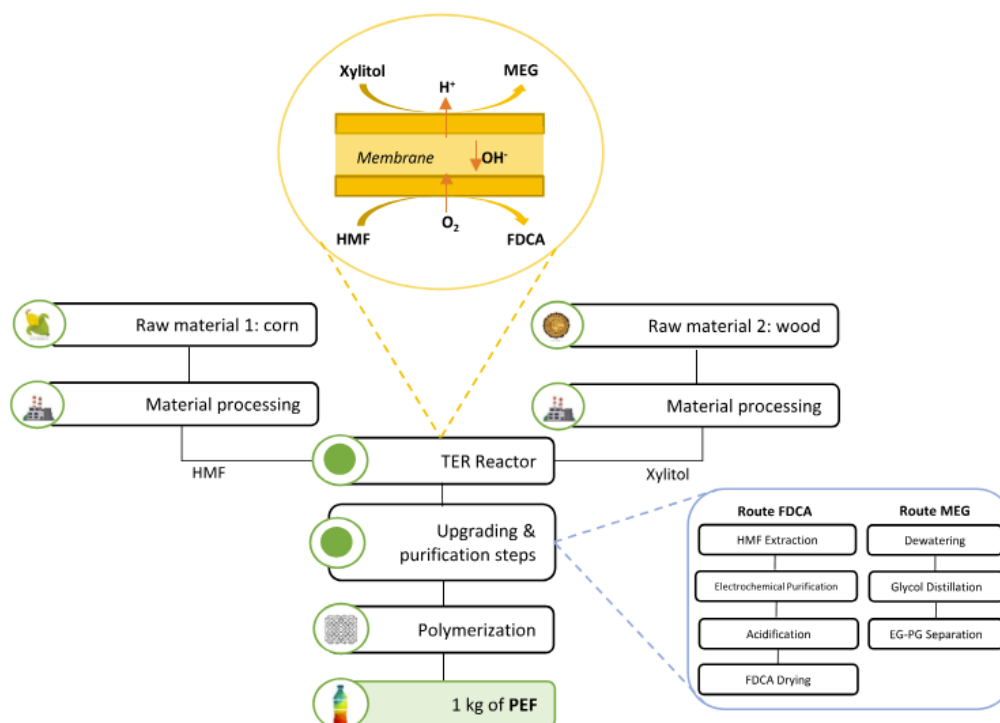


Figure 4. Simplified scheme of PEF production based on the TERRA process (Zuiderveen *et al.*, 2021).

- **EnzOx2** (2016-2019) aimed at new biochemical technologies based on the use of oxidative enzymes, e.g., efficient conversion of HMF to FDCA, <https://www.enzox2.eu/>.
- **PERFORM** (2019-2023, incl. both Avantium and AVA Biochem) focused on establishment of platform infrastructure for highly selective electrochemical conversions, incl. showing that biobased building blocks can be obtained efficiently and sustainably in a single-step electrochemical process rather than multiple steps. <https://performproject.eu/>.
- **PEference** (2017-2025): <https://peference.eu/> which focuses on the construction of the flagship plant to produce purified FDCA and demonstration and validation of end products thereof.
- **ReBIOlution** (2023-2026) focuses on food packaging and mulch films and aims to establish well-defined properties to enhance sustainability, utilizing non-toxic substances, reducing non-renewable resource consumption, and ensuring recyclability and biodegradability at the same time, both in home composting as well as in soil, freshwater and marine environments. <https://rebiolution-project.eu/>.

2. Manufacturing of PEF

PEF is produced from the two monomers: (mono)ethylene glycol (MEG) and 2,5-furandicarboxylic acid (FDCA, Figure 5 and 6). Both monomers are possible to produce from biomass, meaning that PEF can be 100% biobased. Bio-MEG is commercially available and is the same monomer used also for bio-PET.

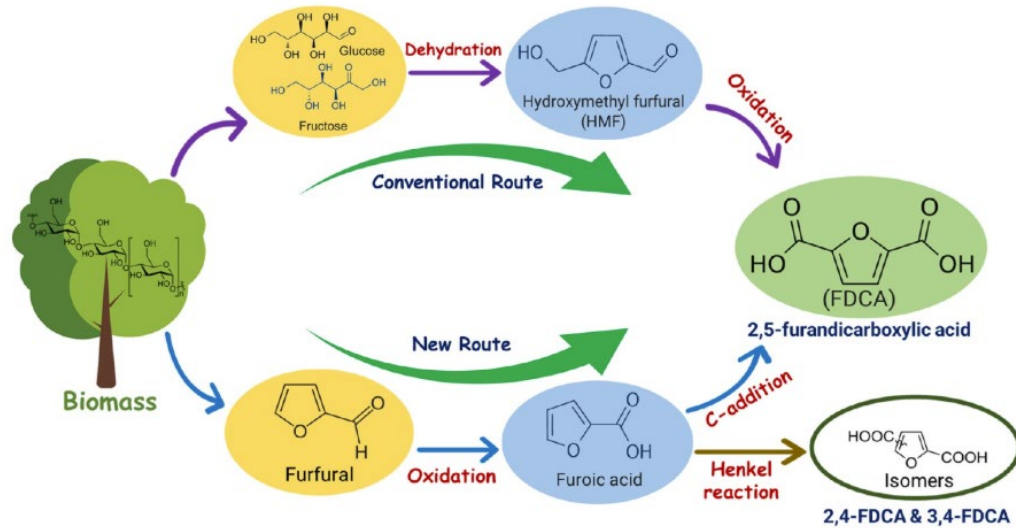


Figure 5. Synthesis of FDCA and its by-products from biomass (Sahu, Thorbole and Gupta, 2024).

PEF synthesis is a stepwise polymerization and can be produced via two routes: polycondensation of MEG with FDCA or transesterification using dimethyl-2,5-furandicarboxylate (DMF) (Guigo, Forestier and Sbirrazzuoli, 2019)(Fei *et al.*, 2020). The first PEF synthesis was patented already in 1946 (Drewitt and Lincoln, 1947), who used melt polymerization. The transesterification pathway has been studied by e.g., (Khrouf *et al.*, 1998) and is more efficient.

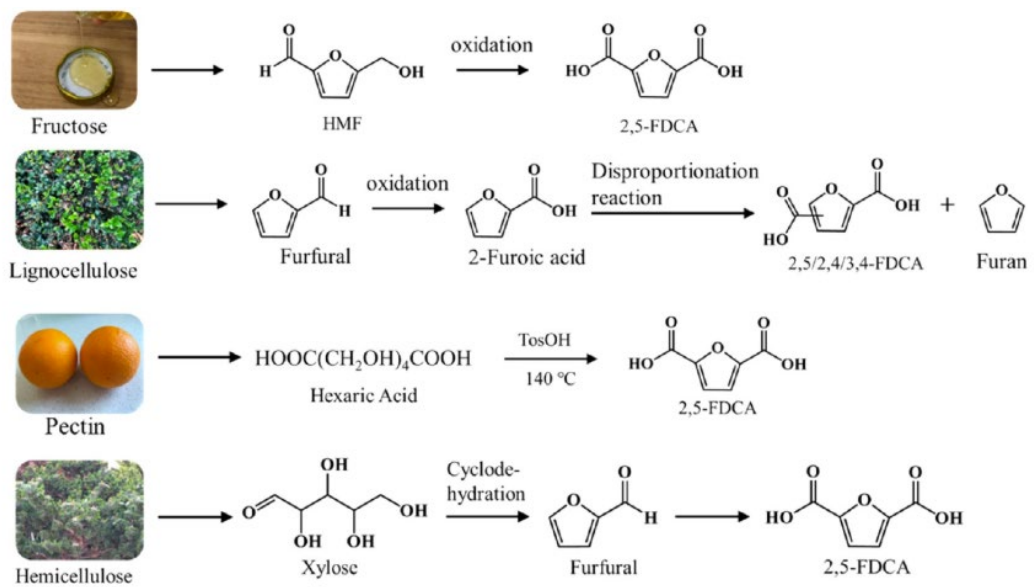


Figure 6. Schematic illustration of FDCA synthesis from different platform chemicals (Fei *et al.*, 2020).

2.1 Producing industrial sugars from biomass

Biomass, such as agricultural products and residues, contain carbohydrates that are generally hydrolysed using chemical or microbial processes to obtain sugars. The sugars can then be converted to produce, e.g., furfurals and MEG. Furfurals are obtained by acid catalysed dehydration of sugars while MEG can be produced either using chemical or microbial processes. Depending on the type of resource, there are

different types and amounts of C5- or C6-sugars available, which means that the processes will differ. Primary resources, such as corn, sugarcane, potatoes and wheat, contain high amounts of starch or sucrose, which are easier to convert to monomeric hexose sugars compared to more complex mixtures, e.g., lignocellulosic residues or various types of waste streams from agriculture and forestry side-streams. Some major sugar producers are Braskem in Brazil, Südzucker group in Europe, Bajaj Hindusthan Sugar Ltd. In India, American Sugar Refining in the US and Guangxi Guitang Group in China, most of which are using sugarcane as feedstock.

A lot of research and development efforts are aimed at biorefining processes to utilize secondary resources (non-food) biomass for the sugar platform. One industrial example is the Dawn technology¹, developed by Avantium, where forestry and agricultural residues are converted into industrial sugars and lignin, currently at pilot scale (2024). One study shows the potential of producing furfural and 5-chlorofurfural (CMF) from saccharides in HCl without any prior purification in a biorefinery, resulting in molar yields of 80-90%. They also studied the optimum conditions and concluded that the combined factors of the stirring rate and the polarity of the organic solvent had the highest impact on the yield, followed by the temperature with the reaction time (Bueno Moron, van Klink and Gruter, 2023). The topic of biorefinery and sugar production from different types of biomasses is covered in a lot of papers and reviews, for example (Guragain and Vadlani, 2021), (Zhu and Pan, 2022), and (Ashokkumar *et al.*, 2022).

2.2 5-(hydroxymethyl)furfural (HMF)

A lot of research has been done on production on 5-(hydroxymethyl)furfural (HMF) which, in its pure form, is a low-melting crystalline solid that is essentially freely miscible with water (van Putten *et al.*, 2013)(Chheda, Román-Leshkov and Dumesic, 2007)(Chacón-Huete *et al.*, 2022). HMF is preferably formed from fructose, which typically results in higher yields compared to glucose, with molar yields around 60-80%. Molar yields of HMF from cheaper whole biomass feedstocks are lower and generally around 50% or less. Synthesis of HMF reported in scientific literature has been done in water, however with some disadvantages such as catalyst deactivation and poor yield due to, e.g., formation of humins and insoluble structures of cellulose (Menegazzo, Ghedini and Signoretto, 2018). Synthesis has also been performed using solvents like DMSO and ionic liquids (IL), where cost and recovery of solvent could provide challenges for up-scaling. So far biphasic systems using low boiling solvents have provided superior product yields and recovery (Sayed *et al.*, 2020). Several catalysts have been studied, e.g., acid catalysts (H₂SO₄ and HCl) or heterogeneous catalysts (e.g., zeolites, metal oxides, mesoporous silica and carbon-based materials, ion-exchange resins), however challenges related to cost and environmental friendliness of many of the catalysts still need to be overcome. Nevertheless, continuous improvements are being made. For example, a recent

¹ <https://avantium.com/technologies/dawn/>.

study where a catalytic amount of NaCl was explored to enhance catalysis by a cation exchanger showed promising results; fructose achieved a 99% conversion rate with an 81% HMF yield within 1 h at 110°C (Thuy Vu *et al.*, 2023).

Industrially, the overall physicochemical properties of HMF, which limit its recovery from the production process and prevent stable storage and transportation, are disadvantageous for scaling up efficient processes. Thus, it is beneficial or even necessary to produce HMF at the same site as production of downstream products. (Menegazzo, Ghedini and Signoretto, 2018). Large-scale HMF production will most likely also generate substantial waste streams of which some can have a value (e.g., levulinic acid) while others will be more challenging to generate value from, e.g., humins and other polymeric materials. As a result of these challenging properties, there are only few commercial suppliers of HMF, and the price is relatively high. However, there are examples of companies that see the potential in the renewable platform chemicals and interesting processes can be found in the patent literature, processes for direct conversion of fructose to FDCA via in-situ formation of HMF and HMF-analogues have for example been patented by DuPont and Archer Daniels Midland Company (Howard *et al.*, 2016). Micromidas Inc has filed a patent which describes a pilot-scale process for converting lignocellulosic biomass originating from municipal wastewater to a mixture of HMF, furfural and CMF by treatment of the biomass with dry hydrogen chloride gas (Masuno *et al.*, 2012) and Novamont S.p.A. has filed a patent describing a process for manufacturing HMF from fructose in the ionic liquid tetrabutylammonium bromide (TBAB, 3% water) (Capuzzi, Carotenuto and Ferrari, 2020). In addition, Rennovia Inc. developed a process starting from fructose or high fructose corn syrup using HCl in low concentrations and/or solid resin acids as a catalyst system in a mixture of a polar ether solvent and water (Sokolovskii *et al.*, 2017), and this process seems to form the basis of the FuraCore™ process currently being developed by Stora Enso (Murphy *et al.*, 2019; Torssell *et al.*, 2020). Another firm active in biobased building blocks is AVA Biochem, which has been producing HMF using a hydrothermal carbonisation (HTC) process for research purposes as well for sale at its 20 tonnes/y facility in Muttenz, Switzerland (Kläusli, 2014). In 2020, it entered into a joint development agreement with Michelin to build the world's first commercial-scale production facility for HMF.²

Some actors in the field have avoided HMF as intermediate in favour of more complex but also more stable, readily isolated and purified esters of HMF (for instance O-acetyl or O-methyl-analogues of HMF). Furanix Technologies B.V. published a patent for formation of methoxymethyl furfural (MMF) starting with converting fructose as a suspension in methanol to methyl fructoside using sulfuric acid as catalyst (De Sousa Dias, Gruter and Van Putten, 2012), and this process seems to form the basis of the YXY®-process currently being developed by Avantium.

² Press release, 2020, <https://www.enzox2.eu/files/related-info/press-release-ava-biochem-jan-31-2020.pdf>.

2.3 Oxidation of HMF and its analogues to 2,5-furandicarboxylic acid (FDCA)

Unlike HMF, FDCA is in its pure form relatively stable and is a high-melting crystalline solid. It is almost completely insoluble in water and poorly soluble in many organic solvents. Overall physicochemical properties of FDCA appear advantageous for isolating purified material by crystallization and in general for scaling up efficient processes for its manufacture. Storage and transportation are probably also not an issue. There are two fundamentally different strategies for making FDCA from carbohydrates:

- Oxidation of HMF and its analogues
- Dehydration cyclization of previously oxidised hexoses/sugars

In this report, we only consider the former. This process can be achieved through chemical and enzymatic catalytic conversion as well as electrochemical conversion pathways (Ait Rass, Essayem and Besson, 2013; Barwe *et al.*, 2018; Chen *et al.*, 2020; Pham *et al.*, 2020; Troiano, Orsat and Dumont, 2020; Saikia *et al.*, 2022; Kumar Vaidyanathan *et al.*, 2023; do Nascimento *et al.*, 2024). Development of reaction chemistry, catalysts, and operating conditions for FDCA production from sugars and carbohydrates were also summarized in a review by (Deshan *et al.*, 2020), see Table 1.

Table 1. Summary of different HMF oxidation processes to FDCA from (Deshan *et al.*, 2020).

Entry	Homogeneous catalysts	Heterogeneous catalysts	Biocatalysts	Electrochemical oxidation
1)	Difficult to separate	Facile separation	Possible facile separation	Facile separation
2)	Recycling deficiencies	Facile recyclability	Recycling deficiencies	Recycling deficiencies
3)	Low yields with mild conditions	Low yields with mild conditions	Mild conditions (ambient temperature and atmospheric pressure) are used	Mild conditions are required
4)	Oxidant is needed	Oxidant is needed	Oxidant may or may not be needed	External oxidant is not necessary
5)	Less environmentally friendly	When inorganic base used, process becomes less environmentally friendly	Green process	Green process

Among the chemical catalytic methods, heterogeneous catalysts were found more suitable due to easier separation and good recyclability.

In another comprehensive review on catalytic processes for conversion of HMF to FDCA, it was similarly concluded that most procedures investigated and published in the academic literature are focused on noble metal-, base metal- and transition metal-catalysed oxidation conditions, which are technically viable but not economically feasible (Hameed *et al.*, 2020). Main reasons are the high price of HMF and the dilute conditions used during oxidation to avoid catalyst deactivation issues, which are particularly serious for some noble metal catalysts. Another issue is leaching of catalyst metal to the reaction mixture in many cases. Au-based catalysts appear to show a better performance in catalyst selectivity and stability for the aerobic oxidation of HMF into FDCA in water, compared to Pt-, Pd-, Ru-, and Rh-based catalysts, owing to the better resistance to water and oxygen (Hameed *et al.*, 2020). Since FDCA has low solubility in water, applications of these catalysts often require the addition of base (NaOH or NaCO₃) to keep FDCA dissolved in solution

and prevent its precipitation onto the catalyst surface. This makes the process less eco-friendly, and the requirement of a homogeneous base is also disadvantageous because mineral salts (for example, NaCl) is produced along with FDCA.

Several examples are published where fructose is dehydrated to HMF at high yields. As an example, (Motagamwala *et al.*, 2018) reported a 70% yield of HMF using a γ -valerolactone (GVL)/H₂O solvent system and where HMF was subsequently oxidized to FDCA over a Pt/C catalyst with 93% yield. Comparisons of catalytic conversions of biomass-derived HMF to FDCA, showing the different oxidants, catalysts, potential addition of base and the resulting HMF conversions and FDCA yields were reported by (Hwang *et al.*, 2020), see Table 2.

Table 2. Different studies on catalytic oxidation of HMF to FDCA from (Hwang *et al.*, 2020).

Reaction condition	Oxidant	Catalyst	Base	HMF conversion (%)	FDCA yield (%)
T = 100 °C, t = 5 h	9 mmol TBHP	MnFe ₂ O ₄	Acetonitrile (base-free)	100	85
T = 120 °C, t = 16 h	10 bar O ₂	Ru/ZrO ₂	H ₂ O (base-free)	100	97
T = 100 °C, t = 12 h	4 bar O ₂	Pt/ZrO ₂	H ₂ O (base-free)	100	97
T = 130 °C, t = 2.5 h	5 bar O ₂	Au/CeO ₂	NaOH	100	87
T = 110 °C, t = 6 h	7 bar O ₂	Au/GC	NaOH	100	97
T = 140 °C, WHSV = 1 h ⁻¹	30 bar O ₂	Ru/Al ₂ O ₃	Na ₂ CO ₃	100	98
T = 70 °C, t = 4 h	10 bar O ₂	Au/Al ₂ O ₃	NaOH	100	99
T = 100 °C, t = 24 h	10 bar O ₂	β -MnO ₂	NaHCO ₃	> 99	86
T = 85 °C, t = 10 h	1 bar O ₂	Co ₄ Mn ₁ -L	Na ₂ CO ₃	100	95
T = 140 °C, t = 6 h	10 bar O ₂	H ₃ PMO ₁₂ O ₄₀	[BMIM]Cl (base-free)	> 99	89
T = 160 °C, t = 24 h	20 bar O ₂	Ce _{0.5} Fe _{0.15} Zr _{0.35} O ₂	[BMIM]Cl (base-free)	> 99	44
T = 160 °C, t = 4 h	20 bar O ₂	Amberlyst-15, Fe _{0.6} Zr _{0.4} O ₂	[BMIM]Cl (base-free)	100 (fructose)	46

There seem to be general agreement that it is more beneficial with base-free conversion, however, the use of ionic liquids as reaction media results in other challenges related to primarily price and toxicity.

There are also some interesting results where electrosynthesis is used to produce FDCA from HMF, e.g., using NiOOH and TEMPO electrocatalysts, which resulted in high molar yields of 90% (Latsuzbaia *et al.*, 2018). Similar results were presented by (Vo *et al.*, 2024) using TEMPO as a redox mediator, which led to a highly efficient and selective electro-oxidation of HMF into FDCA in a basic buffer solution.

In a paper from 2023, the authors explore patents related to FDCA production with emphasis on enzymatic catalytic methods. Opportunities for innovation exist, however current production metrics in biotechnological methods remain mostly at the proof-of-concept level (Milić, Domínguez de María and Kara, 2023). The paper includes some interesting references on (chemo)enzymatic cascades (BIOME Bioplastics, Novozymes, Synthetic Genomics Inc. (now Viridos)), engineered microorganisms (mostly academic papers), and metal catalysts.

The oxidation of HMF and analogues has been accomplished using protocols like those used for oxidizing p-xylene to terephthalic acid (i.e., the Amoco process, where compressed air is used as oxidant) with overall quite promising results for industrial applications, see Figure 7.

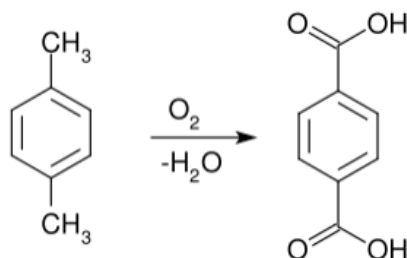


Figure 7. Schematic illustration of the Amoco process (Wikipedia).

Acetic acid appears to be able to dissolve FDCA so that beneficial concentrations can be processed to achieve a high-capacity process, and several companies have submitted patents describing different versions of the Amoco-process to make terephthalic acid (TPA) from para-xylene applied to HMF (or its analogues) as starting material.

In addition to FDCA, there are also interesting results reported for esters of FDCA due to their better solubility and easier purification and polymerisation compared to FDCA. One example was presented by (van Strien *et al.*, 2024), who synthesized FDCA methyl esters in high yields from pectin-based galactaric acid using a solid acid catalyst. The process resulted in up to 50 mol% FDCA methyl esters with total furancarboxylates yields of up to 90 mol%. Up-scaling of the synthesis from gram-scale to kilogram-scale was also demonstrated using batch reactors. Relatedly, initiatives are now also taken to investigate the potential of producing polymers from 2,5-bis- (hydroxymethyl)furan (BHEF), which can also be derived as a platform chemical from biobased feedstock (Post *et al.*, 2023).

2.4 Biobased (mono)ethylene glycol (MEG)

(Mono)ethylene glycol (MEG) is a versatile compound used in various industries, primarily as a key component in the production of plastics, resins, and antifreeze products. The traditional production of MEG involves the use of fossil-based feedstocks. However, growing interest in sustainable and renewable alternatives has led to the development of biobased MEG which is typically produced through conversion of plant-derived sugars. The sugars are then fermented into bioethanol and then dehydrated to bioethylene, which in turn is further processed through hydration or other processes to yield bio-MEG (Pang *et al.*, 2016), see Figure 8.

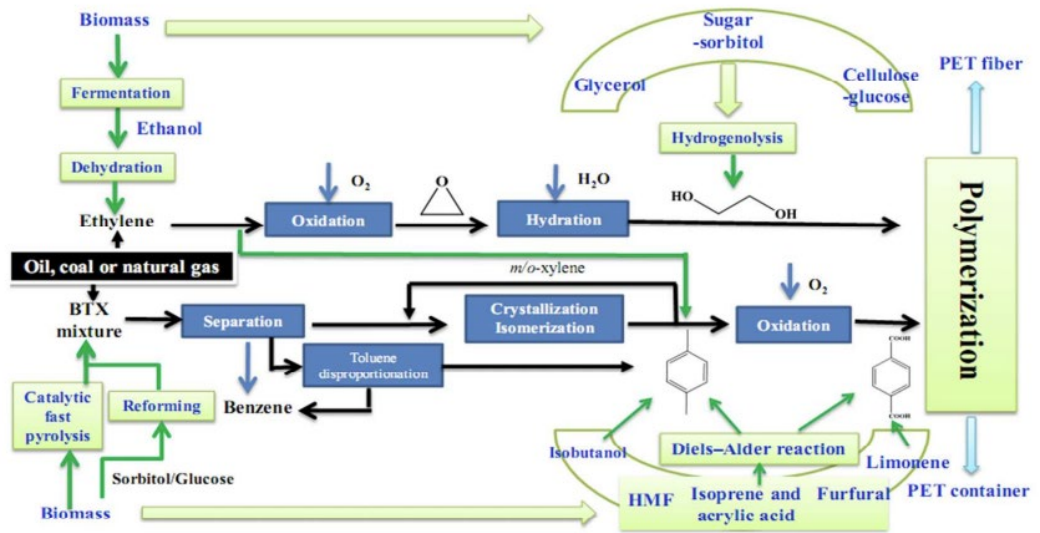


Figure 8. Drop-in replacement of fossil-based PET monomers from biomass (Pang *et al.*, 2016).

Several commercial actors have entered the market as suppliers of bio-MEG, such as DuPont Tate & Lyle BioProducts that produce bio-MEG from corn sugar, Toyobo is a Japanese company that produces bio-MEG under the name “Green Chemicals”, Myriant Corporation also produces bio-MEG from a renewable feedstock, and Changchun Dacheng Industrial Group Company in China produces MEG from sugars and sorbitol. Other initiatives for biobased MEG-production can be found in Table 3.

Table 3. Summary of different technologies for MEG production (Pang *et al.*, 2016).

Technology	Reaction Steps	Yield	Advantages	Disadvantages
India Glycols	1) Fermentation of sugars to bioethanol 2) Dehydration of ethanol to ethylene 3) Oxidation of ethylene to EO 4) Hydration of EO to MEG	> 90 %	High Selectivity	High cost of bioethanol
Avantium Ray Technology™	Catalytic hydrogenolysis of plant based sugars to MEG and MPG	N/a	One-step process	Low selectivity, harsh conditions
Haldor Topsoe MOSAIK™	Catalytic cracking of sugars followed by hydrogenation to MEG	N/a	Two-step process. High productivity	Harsh reaction conditions

Routes to also produce MEG from lignocellulosic biomass (i.e. secondary resources) have been presented in scientific literature (Mendieta *et al.*, 2022), see Figure 9.

Producing MEG from lignocellulosics is more challenging (and thus more expensive) compared to using primary feedstock as lignin acts as an inhibitor and limits the accessibility to the substrate for the microorganisms employed in the production of bioethanol.

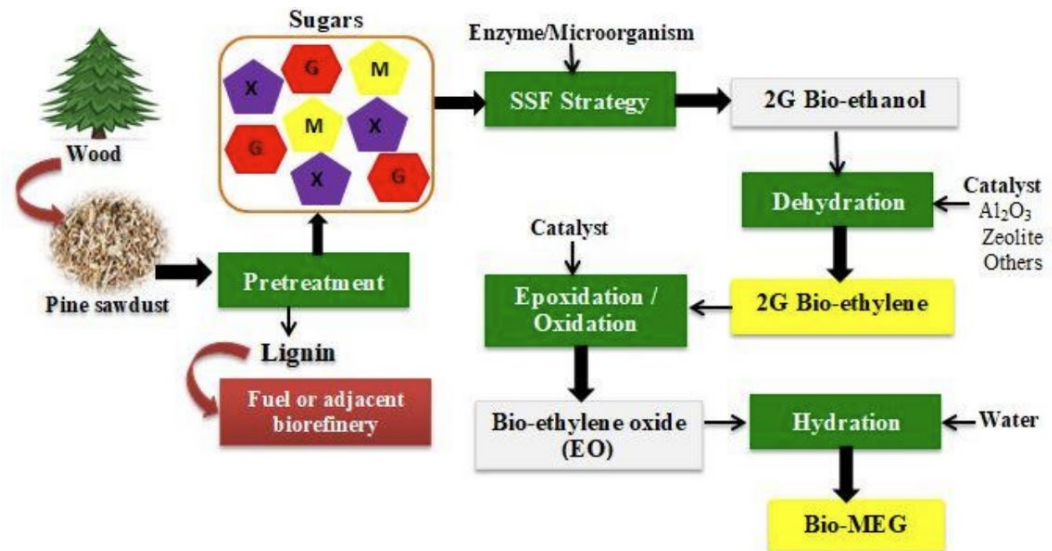


Figure 9. Route for MEG production from lignocellulosic biomass (Mendieta *et al.*, 2022).

Biotechnological production of MEG directly from sugars through synthetic metabolic pathways using the industrial microorganisms *Escherichia coli*, *Corynebacterium glutamicum* and *Saccharomyces cerevisiae* was reviewed by (Hwang *et al.*, 2020), see Figure 10. The best reported MEG production results were achieved via the Dahms pathway in an *E. coli* strain (Cabulong *et al.*, 2017). However, none of the pathways resulted in levels suitable for commercial production.

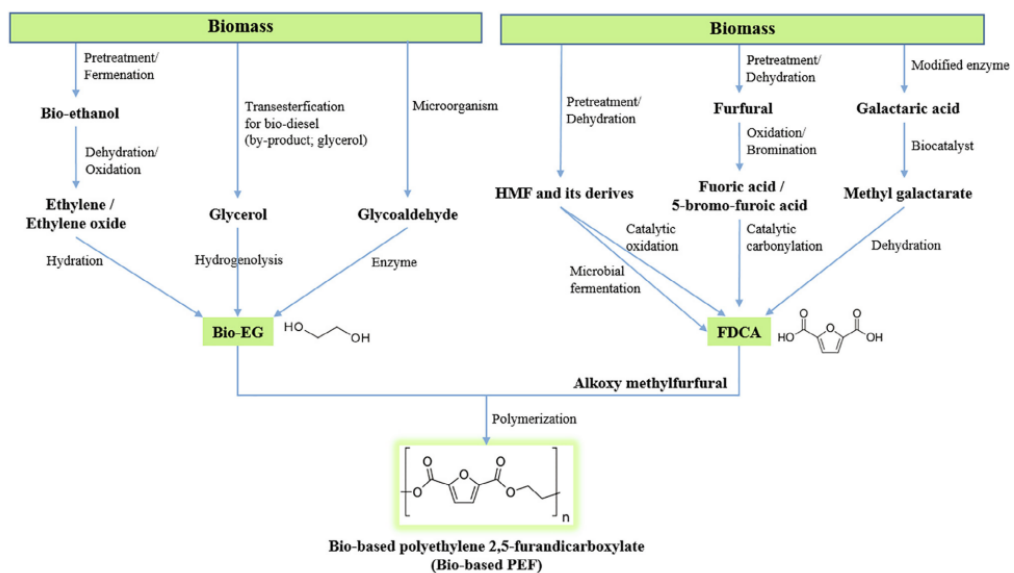


Figure 10. Production routes of PEF from biomass via EG and FDCA (Hwang *et al.*, 2020).

2.5 Polymerization to PEF

The polymerization reactions to produce PEF are analogous to PET-polymerization, but with FDCA instead of TPA (Louw, 2024). The reaction temperatures for FDCA and MEG is lower, and the reaction times are somewhat shorter compared to TPA and MEG, which could imply a lower production cost. Polymerization of PEF is performed in two steps, i.e. esterification (into bis(2-hydroxyethyl)-2,5-furandicarboxylate (BHEF)) and polycondensation. Polycondensation is typically conducted in two phases; melt phase polymerization (MPP) followed by solid-state polymerization (SSP) to increase the molecular weight of the polymer. During polycondensation, MEG and water is continuously released and removed using vacuum, see Figure 11.

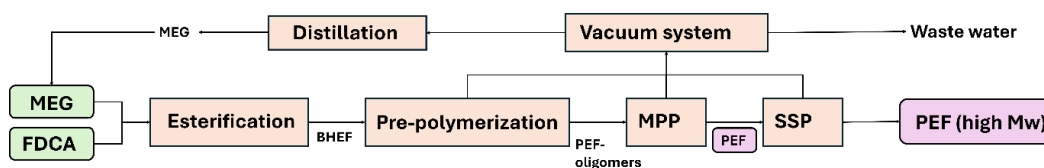


Figure 11. Simplified process scheme for PEF polymerization (adapted from Louw, 2024).

A summary of syntheses based on FDCA and thermal properties of a variety of furanoate-based polyesters, including PEF were reported by (Papageorgiou *et al.*, 2016). The paper covers different melt polycondensation methods as well as solution methods, and apart from PEF, other polyesters, such as poly(propylene 2,5-furandicarboxylate) (PPF), poly(butylene 2,5-furandicarboxylate) (PBF) and poly(hexylene 2,5-furandicarboxylate) (PHF) are described and considered as viable candidates for the next generation of novel bio-based coatings, toners, binders, glues, bottles and wrapping materials.

In a study by Stanley *et al.* (Stanley *et al.*, 2023), comparison of using FDCA versus the derivative dimethyl 2,5-furan dicarboxylate (DMFD) for producing PEF showed that FDCA was more effective in generating PEF of high molecular weight.

As an alternative to polycondensation, ring-opening polymerisation (ROP) has also been proposed to avoid potential degradation and discoloration reactions and long reaction times (Rosenboom *et al.*, 2018), see Figure 12. The ROP process starts from cyclic PEF oligomers and by initiation in the presence of a high boiling and inert liquid plasticiser, the self-plasticising effect of the forming polymer can be exploited to form PEF with high molecular weight.

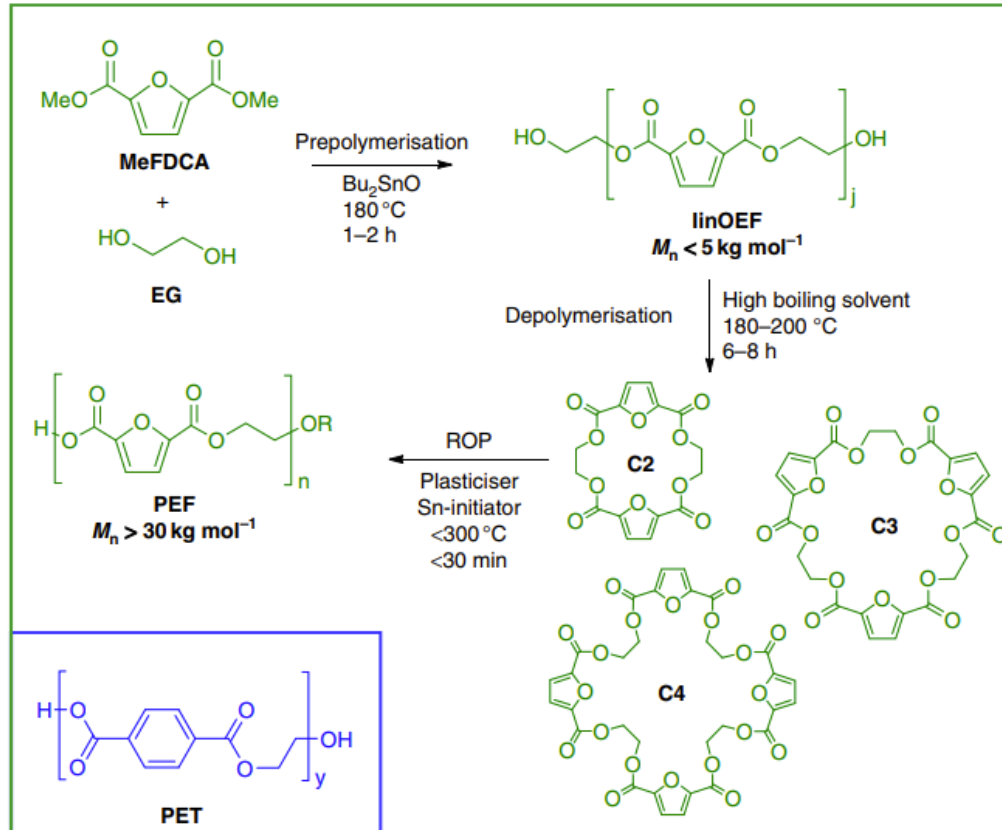


Figure 12. Synthesis of PEF via ring-opening polymerization (Rosenboom *et al.*, 2018).

ROP has shown to deliver bottle-grade PEF in relatively short reaction times and a preliminary comparison of the energy requirements shows that ROP resulted in similar values as polycondensation (Rosenboom, 2018). Thus, ROP seems an interesting alternative route, however the steps to produce the cyclic PEF oligomers probably need further development for an upscaled process.

2.6 Techno-economic analysis

As discussed in many papers, a process for biobased plastics need not only be technically viable but must also be cost-competitive. In a study by (Motagamwala *et al.*, 2018), a techno-economic analysis of FDCA production from fructose was performed and it was found that their process can deliver FDCA at a minimum selling price of 1490\$/metric tonne, which was competitive with the TPA selling price at the time (1445\$/metric ton).

A more recent and thorough techno-economic analysis of PEF production was presented by (Louw, Farzad and Görgens, 2023), where the mass, energy, and economic performance of PEF production in biorefineries, including integrated self-sufficient bioenergy, were evaluated. Three cases were simulated using different types of feedstocks: A-molasses (1G), sugarcane bagasse and trash (2G), or combinations of them (1G2G), see Figure 13. The 1G scenario was most profitable due to low capital cost and energy requirements associated with 1G conversion with a minimum selling price of 1.82\$/kg (approximately 77% higher than the market price

for fossil-based PET in 2019). The 2G scenario was the least profitable (4.26\$/kg) whereas the 1G2G scenario (2.39\$/kg) was more profitable due to economics of scale and other synergistic benefits of feedstock co-processing, such as increased sugar concentration which reduced the energy demands and the cost of downstream recovery. This highlights the importance of improving the efficiency and lowering of the capital cost of second generation biomass conversion.

The profitability of 1G PEF was most dependent on the total annual operational cost, highlighting the importance of feedstock cost for 1G PEF production and the significant risk involved due to market variability in sugar prices, which directly affects the price of A-molasses. It was concluded that future research should focus on investigating different routes for monomer production, best solvents for sugar dehydration, and direct routes to produce MEG from sugars (Louw, Farzad and Görgens, 2023).

Recently, commercialization challenges for PEF (and PHA) were specifically investigated, and the analysis was based on interviews and patent investigations to understand the technology trends for these bioplastics (Kunamaneni, 2023). For PEF, it was highlighted that a thin layer of PEF on a paper bottle could provide the high gas barrier properties needed for beverages such as beer and carbonated soft drinks. However, substituting complete glass or PET bottles with PEF has a much greater market uncertainty than adding value to a paper beverage bottle; as the cost of PEF is 8-10 times that of PET and even at economic scales it is predicted to be twice than that of PET. Presumably, the cost-performance of PEF for beverage bottles is not sufficient to overcome the cost-performance of PET even if all the PET was 100% biobased. Thus, some argue that PEF should be limited to added-value applications. (*“The importance of PEF is not the similarity to PET, but the difference. The attention should be focused on value-added applications where the barrier properties of PEF can be exploited”*).

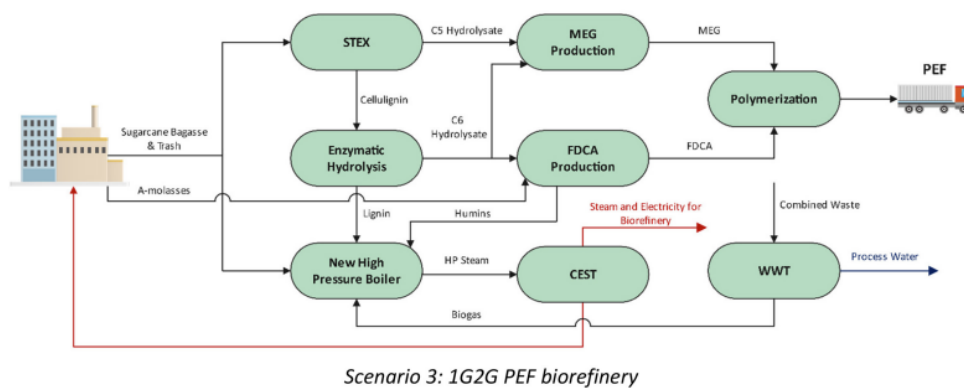
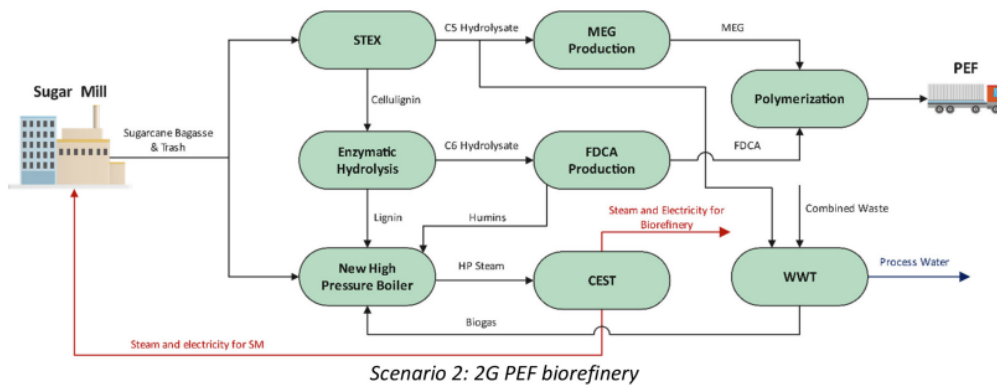
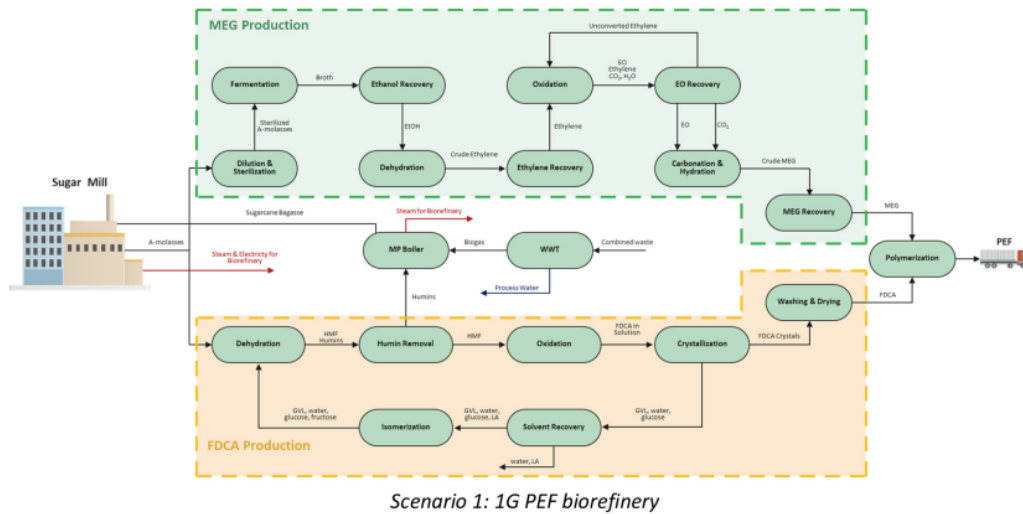


Figure 13. The three biorefinery scenarios analysed by (Louw, Farzad and Görgens, 2023). Note that production of MEG and FDCA in the 2G and 1G2G scenarios follow the same steps as illustrated in the 1G scenario.

Figure 14 below summarises strategies on how to mitigate the technical and market uncertainties for PEF and its building blocks. Collaborative alliances with public science institutions supported by government grants not only mitigates technical uncertainty but also market uncertainty for PEF because more efficient and sustainable routes to building blocks can lead to opportunities in biobased polymer markets in general. In addition, more cost-effective FDME can relieve technical and market uncertainties around FDCA to PEF that requires high-purity FDCA and therefore limits volumes.

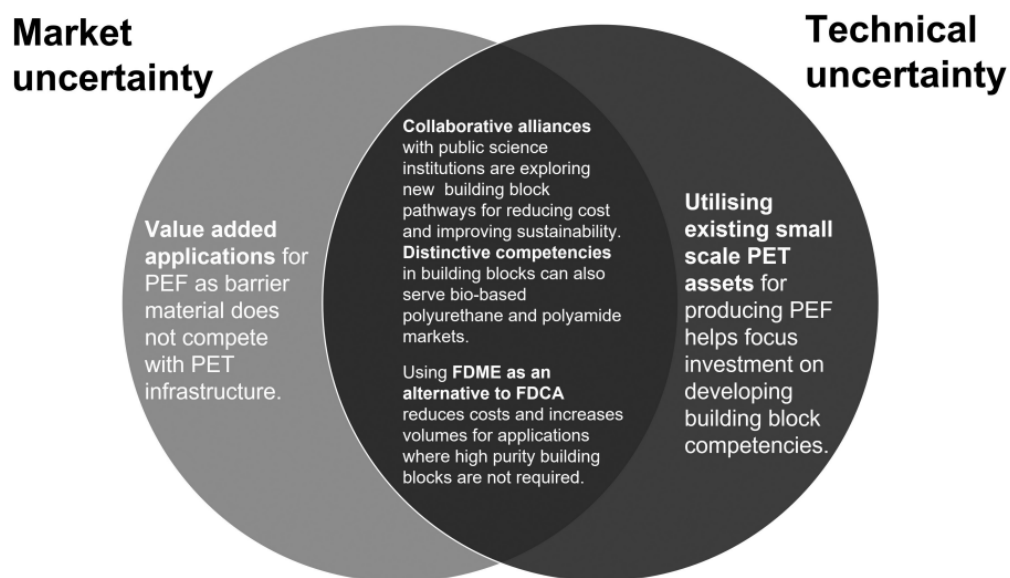


Figure 14. Strategies for mitigating technical and market uncertainties for PEF and its building blocks (Kunamaneni, 2023).

Another study presented a new process design for FDCA production from lignocellulosic biomass (Kim, Baek and Won, 2022). The economics of the process were optimized by applying an effective biomass fractionation method based on catalytic conversion and separation subsystems. Pinch analysis coupled with a heat pump was performed to reduce the heating requirement by 66%. A techno-economic analysis determined a minimum FDCA selling price of \$1520/ton, with the feedstock and reaction conditions being the principal cost drivers of the process.

3. Properties of PEF (compared to PET)

PEF has received wide recognition due to its resemblance to conventional PET and its suitability for many common applications, such as packaging and carbonated drinks, but also for films, fibres, and textiles. The main advantage, which is highlighted in most publications, is PEF's exceptional barrier properties. PEF has been shown to be approx. 16-20 times less permeable to CO₂ compared to PET (Burgess *et al.*, 2016), see Figure 15 and 16. Semicrystalline PEF exhibits reduced H₂O, O₂, and CO₂ uptake compared to amorphous PEF. The reason behind the enhanced barrier properties is explained by the energy difference among the amorphous and crystalline chains of PEF, which is higher than in PET and contributes to PEF's higher crystallization temperature. Several low-frequency vibrational mode measurements support the current view that PEF chains are less flexible than those of PET, posing greater resistance to gas penetration and resulting in improved barrier properties (Araujo *et al.*, 2018). It has also been shown, by viscosity measurements, that the conformational freedom of PET and PEF are similar but that the chain packing is lower for PEF due to the shorter bond length of FDCA, inducing a lower entanglement density (Van Berkel *et al.*, 2018).

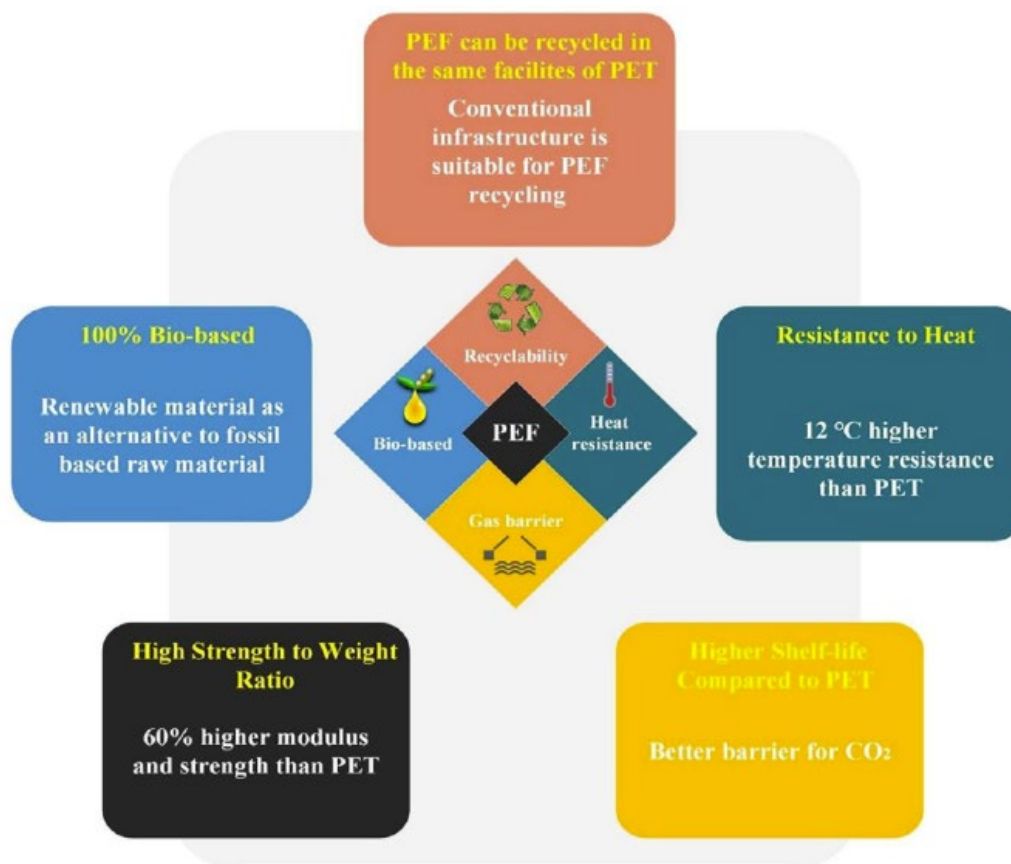


Figure 15. Enhanced properties of PEF compared to those of PET (Sahu, Thorbole and Gupta, 2024).

In a study by (Lightfoot *et al.*, 2022), computational techniques were used to further investigate the difference in barrier properties between PET and PEF. Oxygen diffusion was predicted to a high level of accuracy, at $3.24 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ for PET and $2.88 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ for PEF. Simulations quantifiably demonstrated the contributions of ring-flipping chain dynamics on oxygen diffusion, and novel Monte Carlo techniques revealed insights into the mechanism by which this occurs. Areas of accessible volume within the polymer matrix were seen to converge to facilitate lateral oxygen displacement. Infrequent convergences in PEF, due to subdued polymer chain dynamics and higher system density, accounted for the slower oxygen diffusion relative to PET. This implies that it is the asymmetric furan ring that is the main contributor to the barrier performance of PEF, and that the barrier properties are barely affected by humidity. Other polymeric barrier materials, like polyamides or ethylene vinyl alcohols, have higher oxygen permeability at high relative humidities³.

The mechanical properties of PEF have also been studied. In one paper where a high molecular weight PEF was prepared by a combination of melt polymerization and solid-state post condensation, PEF with absolute $M_n = 83,000 \text{ g mol}^{-1}$ was

³ See Table 3 "Oxygen transmission coefficient of various polymer films", Mitsubishi Gas Chemical, <https://www.mgc.co.jp/eng/products/ac/nmxd6/barrier.html>

obtained and the Young's modulus was determined to be 2450 ± 220 MPa and the maximum stress 35 ± 8 MPa (Knoop *et al.*, 2013).

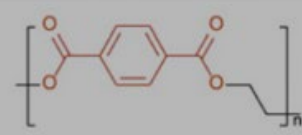
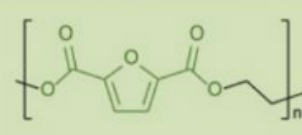
	PET	PEF
Structure		
GHG emissions (tonne / CO ₂ eq tonne)	4.44	2.05-2.38
NREU (GJ / tonne)	69.4	33.8-39.3
BIF amorphous polymers	x1	CO ₂ x19 O ₂ x11 H ₂ O x2.8
Typical thermal properties	T _m	245 °C
	T _g	80 °C
	T _{cc}	150 °C
Quiescent crystallization time	2-3 min	20-30 min
Elastic modulus	x1	~x1.5

Figure 16. Comparison between PEF and PET (Sousa *et al.*, 2021).

Previously, there were issues with discoloration of PEF and the factors that influenced the final colour of PEF was investigated, e.g., by (M. Gruter, Sipos and Adrianus Dam, 2011). It was found that it related to monomer purity and thermal stability, type of catalyst, and reaction conditions.

4. Applications

4.1 Plastic bottles and packaging, incl. films

One of the primary applications of PEF will likely be in plastic bottles due to the improved barrier properties, and research and industrial development is currently conducted on the processing parameters of both mono-material as well as multilayered packaging. The main advantage of this will be that the shelf-life of the products inside the PEF packaging is prolonged substantially.

Injection stretch blow moulding is a relevant technique for manufacturing plastic bottles of polyesters. The process involves strain-induced crystallization of the polymers, which is important for the strength and barrier properties. The differences between PEF and PET needs to be investigated and optimized for each polymer, and as PEF has a lower entanglement density, the amorphous regions need higher strains to deform before it hardens, i.e. higher stretch ratios are needed to reach the optimum mechanical and barrier properties (Forestier *et al.*, 2020).

A cost-effective approach to achieve better barrier properties is to use PEF as a layer in a multilayered, PEF-PET, bottle. It has been shown by Avantium that PEF can be processed in conventional multilayer co-injection moulding systems, and due to the similarities between PET and PEF there is a good interaction and thus a lower risk for delamination compared to current nylon barrier materials. However, it is of importance to have a good drying process and somewhat higher processing temperatures might be required.

In addition to research papers, there are plenty of patents for using PEF to produce packaging containers, bottles, films and fibres, a few examples; (Besson, Bouffand and Reutenauer, 2017)(Kriegel *et al.*, 2015)(Sipos *et al.*, 2016a, 2016b).

4.2 Textiles

Although the highest priority for PEF might be for packaging applications, a lot of research is also being directed towards using PEF for textiles. The differences in properties between PEF and PET (described in the previous section) also influence the behaviour of the polymer in the textile processes. PEF has a stiffer polymer chain with more chain interaction due to the shorter repeating unit and the unsymmetric as well as polar furan ring of the PEF monomer, which leads to more interference between ring and carbonyl oxygen groups.

Thermoplastic polymers, e.g., PEF and PET, can be melt spun into filaments, which in turn are formed into yarn and finished fabrics. The melt spinning process is dependent on how the polymers react to heat and shear, which is often studied through rheology and practical experiments. Since there are structural differences between PEF and PET, this will affect the process conditions during melt spinning. One such difference is that PEF has a lower entanglement density, which results in a stronger shear thinning due to less hindrance of entanglements. The implementation for fibre spinning is then that it is possible to achieve a higher orientation at lower temperatures for PEF. It also means that amorphous regions of PEF need to deform to higher strains before sufficient orientation has been built up to address the network contribution, i.e. PEF will strain harden at larger strains compared to PET when stretched at comparable conditions (Forestier *et al.*, 2020)(Van Berkel *et al.*, 2015). During stretching, the orientation of the amorphous phase can lead to formation of strain induced crystals (SIC). There is some scientific debate as to whether the SIC have the same organisation as thermally induced crystals (Forestier *et al.*, 2019, 2020)(Stoclet *et al.*, 2018). The formation of crystals in PEF and different conditions of stretching was studied by (Menager *et al.*, 2018), who found that PEF can, in a rubbery-like state, develop SIC involving crystallinity ratios up to 20% and that SIC is improved by annealing steps. The crystals in PEF are formed in a way, where there is less interaction between the crystalline and amorphous phase which results in a less rigid amorphous fraction. (Codou *et al.*, 2016). The strain rate and the stretching temperature is related to an equivalent strain rate on a master curve, and the mechanical response is equal for all conditions with the same equivalent strain rate (Forestier *et al.*, 2021). It is also possible to influence the stretching behaviour by

modifying the molecular weight of the polymer or make changes in the moisture content. For both PET and PEF, it is known that a higher moisture content reduces the dipole moment and thus the intermolecular interactions, which results in lower drawing stresses (i.e. water acts as a plasticizer for these polymers).

Current development of commercialization of PEF at Avantium have provided demonstrators of PEF textiles, both for clothing and apparel as well as for nonwovens. During summer 2024, Avantium announced a new partnership with leading textile innovators Auping, Monosuisse and Antex to develop mattresses using PEF-based yarns⁴.

PEF has also been shown to have better performance than PET in 3D-printing and could be recycled for the same use several times without noticeable loss of 3D-printing properties (tested four cycles) (Kucherov *et al.*, 2017).

5. Regulatory

In the EU, the plastic policymakers give surprisingly little attention towards the fossil dependence of plastics production (Palm *et al.*, 2022). There are several arguments to why this is the case, and one is the uncertainty surrounding the environmental benefits of changing the plastics feedstock from fossil oil to biomass. According to Palm *et al.* (2022), this is linked to the fear of repeating the oversights made with the EU renewable energy directive (2009/28). That policy aimed to introduce biofuel to lower the climate impact of the transport sector. However, the methodological guidance presented by the EC unintentionally resulted in the promotion of biofuels with a negative CO₂ balance. To address this mistake, the renewable energy directive (2015/1513) was updated with a clarification of the sustainability criteria for biofuel, putting special emphasis on indirect land use change. Since the plastics strategy was developed at approximately the same time, the influence of that experience is claimed to have influenced policymakers to avoid advocating for biobased products.

Currently, biomass used to produce biobased plastics must meet the EU sustainability criteria for bioenergy. As proposed by the Commission under the review of the Renewable Energy Directive (REDIII) of July 2021, these criteria include measures related to forest biomass and to biofuels with high risk of direct and indirect land-use change (European Commission, 2022). Regarding GHG emissions, the bioenergy framework cannot be directly applied to biobased plastics as these are not used to generate energy. Methodologies to assess the impacts of biobased plastics compared to fossil-based plastics from a life-cycle perspective are still under development (as of 2022). The most harmonised methodology currently available is the framework developed by the Commission's Joint Research Centre, referred to as the 'Plastics LCA method', which builds upon the EU Product Environmental

⁴ Press release, 2024, <https://newsroom.avantium.com/avantium-partners-with-leading-textile-innovators-to-create-pef-fabrics-for-auping-mattresses/>

Footprint method. In the EU policy framework, it is also stated that further scientific advancement is needed to incorporate in the assessment the accounting of biogenic carbon uptake and release from products during their lifespan and discussions to this end are ongoing in the context of the UN Life Cycle Initiative. It is also written that only biobased plastic products with a long lifetime that are not incinerated when they become waste can have beneficial carbon storage effects.

In summary, the focus of the policies on plastics in EU is generally positive towards biobased plastics, however there is currently more focus on recycling of plastics. In Sweden, the Swedish Environmental Protection Agency follows the developments on the EU-level and the national guidelines are much in line with those in EU. As an example, in the finalized government assignment “Rätt plast på rätt plats – redovisning av regeringsuppdrag” (Swedish Environmental Protection Agency, 2024) summarized that a more resource-efficient use of plastics should be prioritized in the following order: 1.) Use plastics more resource-efficiently, i.e. use less, increase product life length, increase repairability, 2.) Use recycled resources before virgin, and on third place, 3.) Replace fossil-based resources with biobased.

A summary of relevant policy documents and regulations is visualised in Figure 17, prepared by European Bioplastics.

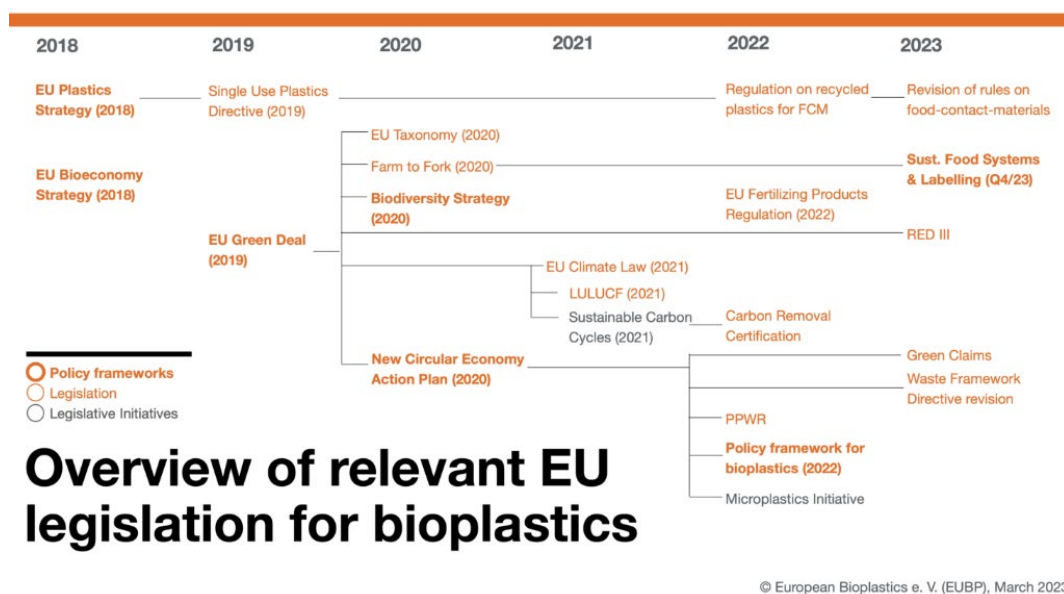


Figure 17. Overview of relevant EU legislation for bioplastics, European Bioplastics, 2023.

5.1 Safety

The scientific opinion of the EFSA Panel on Food Contact Materials, Enzymes, Flavourings and Processing Aids concluded that the substance FDCA does not raise a safety concern for the consumer when used as a monomer in the production of PEF and the migration of the substance itself does not exceed 5 mg/kg food. (European Food Safety Authority, 2014) However, there are studies showing that

PEF can contain oligomers, mainly of the FDCA and MEG units, which potentially could migrate to foods (Hoppe, De Voogt and Franz, 2018).

6. Life Cycle Assessment (LCA)

Assessing biobased feedstocks in life cycle assessment (LCA) presents several difficulties due to the complexity and variability of biological materials and their production processes. One significant challenge is the accurate accounting of land use changes, including direct and indirect impacts on biodiversity, soil health, and carbon sequestration. These factors can significantly influence the environmental profile; however, they are often difficult to quantify reliably. Additionally, biobased feedstocks can vary widely in terms of cultivation practices, geographic conditions, and crop yields, leading to inconsistencies and uncertainties in data collection and impact assessment. The allocation of environmental burdens between multiple outputs of agricultural systems, such as food, feed, and biobased products, further complicates the LCA. Moreover, biogenic carbon accounting, which involves tracking the carbon dioxide absorbed and released by plants, adds another layer of complexity, requiring robust methodologies to ensure accuracy. Thus, biobased polymers can sometimes have higher environmental burdens than fossil-based counterparts, depending on method and which parameters that are analysed, e.g., bio-PET, PTT and PLA was found to not offer advantages over conventional PET in a study by (Ivanović, Hirschler and Som, 2021). This complexity and the decisions made during the assessment was further shown in a review where 39 fossil-based and 50 biobased case studies were compared, where the results showed significant variation in impact between polymers across the seven impact categories (energy use, ecotoxicity, acidification, eutrophication, climate change, particulate matter formation and ozone depletion) for which sufficient data was available, both between fossil-based and bio-based categories, between individual polymers within each category, and between different studies of the same polymer (Walker and Rothman, 2020). In the end, it was not possible to draw conclusions on which polymer type having the least environmental impact in any of the categories.

When it comes to PEF, an energy- and greenhouse gas (GHG) study was conducted already in 2012 where six different model cases were compared, all starting from corn-based fructose (Eerhart, Faaij and Patel, 2012). It showed that PEF, in comparison to PET, could reduce GHG emissions by approx. 45-55% in a cradle-to-grave system. More recently Kim et al. (Kim *et al.*, 2022) provided a comparative LCA, cradle-to-gate, where PEF was compared to PET. The impact factors in focus were GHG emissions, water, and fossil fuels consumption. PEF was assumed to be produced from wheat straw and three different pathways were evaluated for the furanics conversion (route 1 used ethanol as solvent for pretreatment, while route 2+3 used methanol, route 3 had its pretreatment step consolidated with its hydrolysis step). The system boundaries included feedstock farming, pretreatment, hydrolysis, conversion to furanics, polymerization into PEF and on-site combined heat and power generation, see Figure 18.

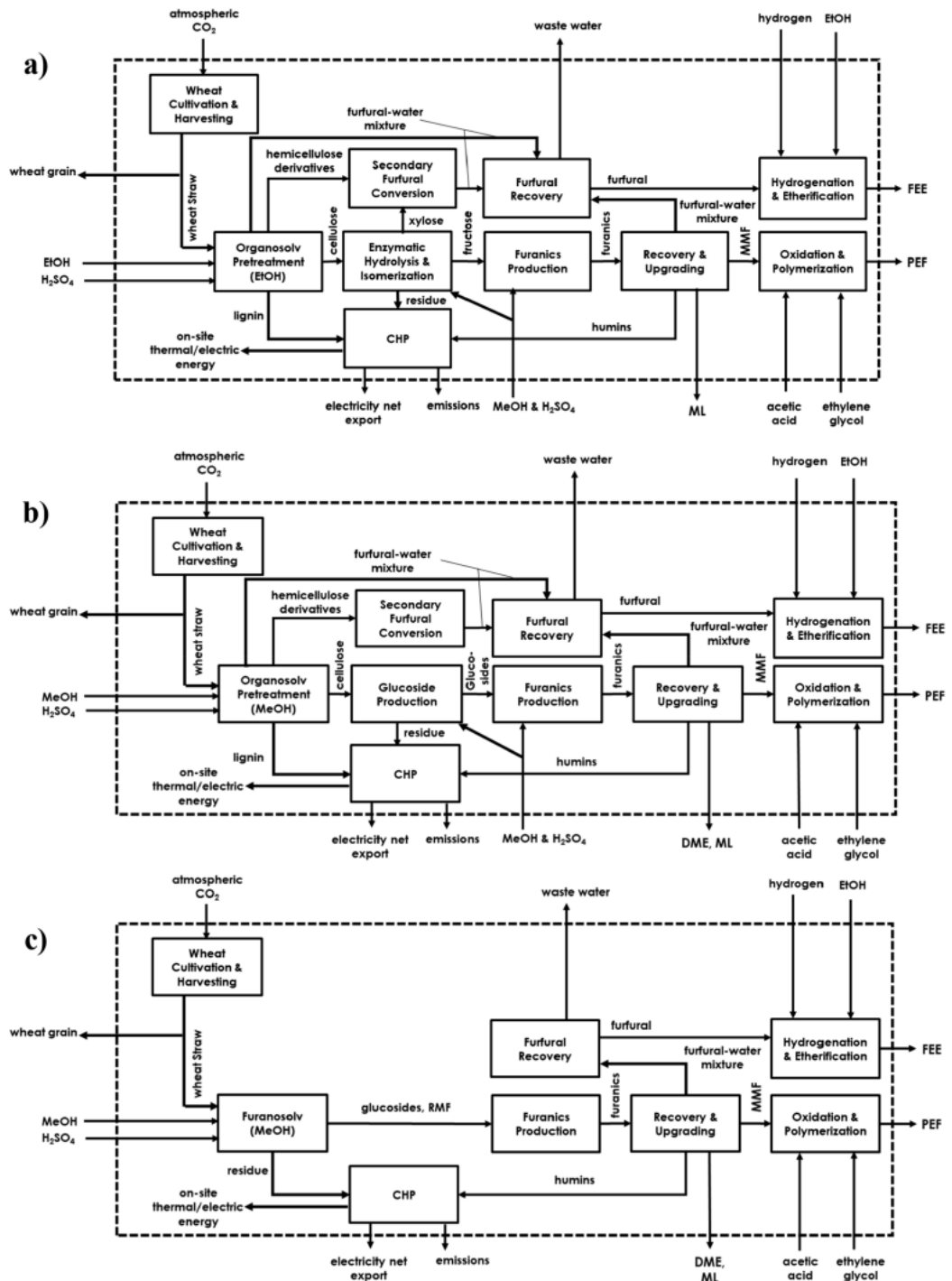


Figure 18. System boundary for PEF production (a) route 1, (b) route 2, and (c) route 3 from (Kim *et al.*, 2022) Abbreviations: ML: methyl levulinate, FEE: furfuryl ethyl ether, MMF: methoxymethyl furfural, DME: dimethyl ether, MeOH: methanol, CHP: combined heat and power.

All three PEF routes resulted in significant GHG reductions relative to PET (134, 139 and 163% respectively). Fossil fuel consumption was also reduced in all three scenarios (79, 57, and 53% reduction), while water consumption was increased for routes 1 and 2 (168 and 79%) whereas route 3 achieved a reduction of 77% relative to fossil-PET.

Another systematic LCA which included multiple recycling trips were assessed for different end-of-life (EoL) scenarios of PEF in the Netherlands (Stegmann *et al.*, 2023). The study focused on quantifying the potential global warming impacts of plastic bottles; 250 mL fossil-based PET and bio-based PEF and included four different waste management cases: A). waste management system for small plastic bottles in the Netherlands until 2021, based on post-separation, source-separation, mechanical recycling (MR) and incineration with energy recovery (ER). B). waste collection predominantly based on a deposit system combined with MR and ER. C). waste collection predominantly based on a deposit system combined with chemical recycling (CR) and ER. D). non-circular scenario, assuming the complete incineration of the bottles with energy recovery. The cradle-to-grave net GHG emissions for one bottle after one recycling trip are illustrated in Figure 19.

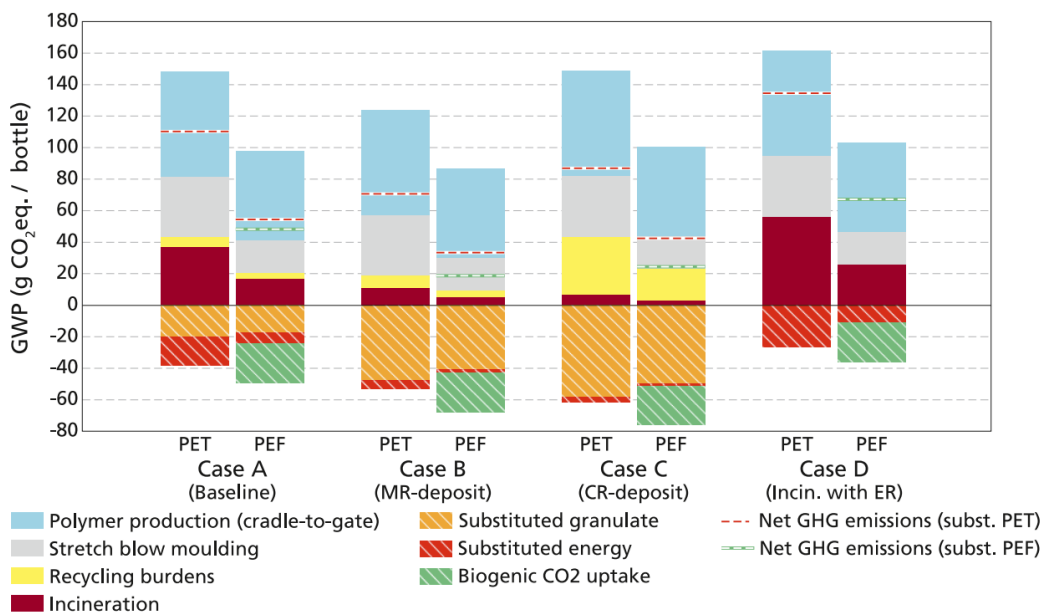


Figure 19. Global warming potential (GWP) for the different cases in the study by (Stegmann *et al.*, 2023).

For multiple recycling trips, both case B and C gain GHG saving benefits. For PEF-to-PEF recycling, case C even becomes the best option starting with the 8th recycling trip. However, case B stays the cumulatively best performing option for the entire number of recycling trips for both systems substituting PET.

There is somewhat of a trade-off between climate change and circular economy; the high recycling yield and substitution factor favours chemical recycling in terms of material utility (keeping more plastics in the loop for a longer period of time). However, high energy requirements hinder its performance when looking at GWP impact. Deposit-based mechanical recycling (case B) shows lowest net GHG emissions. In the long term, combining mechanical- and chemical recycling could be a promising synergy between material utilization and GWP. Overall, the study shows that switching from PET to PEF is a robust strategy to reduce the GHG emissions of small plastic bottles. This is in line with the LCA that nova Institute and Avantium has

performed for PEF plastic bottles (based on Avantium's process) (Puente, de Jong and Stratmann, 2022).

There has also been a study investigating early-stage LCA of the TERRA electrochemical process (Zuiderveen *et al.*, 2021), which identified the process including the electrochemical reactor to be the most crucial contributor to the environmental impacts. It can also be concluded that future scenarios, with more green energy, will result in different impacts.

7. Recyclability

As described in the section on LCA, the different end-of-life scenarios (see Figure 20) will have a significant impact on the total environmental impact of PEF. Some studies have investigated questions related to the recyclability of PEF. In Silverwood *et al.* (2024), it is stated that one of the factors that could slow the adoption of PEF separation into recycling streams is the initial low fraction of PEF, while it is still breaking into the market (Silverwood *et al.*, 2024). During this time, it may not be profitable to invest in the required equipment for such a small volume. Interestingly, low concentrations of PEF (<5%) have been shown to have little effect on the quality of mechanically recycled PET (rPET). In 2017, the European PET bottle platform (EPBP) reported that a 2% PEF concentration in rPET did not exhibit any negative effect on colour, haze and other properties of the resulting material. In 2022, a second investigation drew similar conclusions from tests incorporating a 5% concentration of PET/PEF multilayer bottles containing 10% of PEF into the PET recycling stream. These results suggest that, while the fraction of PEF in waste streams is still low, simply leaving PEF in PET recycling streams could provide an acceptable end-of-life pathway. In this context it is relevant to mention that Avantium has obtained a conditional 'approval' for market entrance from EPBP, which states that until a market penetration of 2% is reached there will be no issues with PEF ending up in PET streams. For larger market penetrations, either additional tests or the development of a separate collection and recycling system for PEF bottles will need to be in place to further anticipate any negative impact on rPET quality.

If a higher amount of PEF ends up in the waste stream, mechanical recycling of solely PEF could be a viable end-of-life option. However, many challenges will have to be solved, such as chain scission reactions and formation of chromophoric groups which can alter the mechanical properties and colour of the polymer over several reprocessing cycles. Those phenomena could be reduced by the optimisation of the reprocessing conditions and a post-reprocessing step that increases the molecular weight. Additionally, several studies reported the chemical recycling of PEF with high yield, but these processes are yet to be demonstrated as suitable for industrial scale.

Incineration is another probable (at least in some cases) end-of-life scenario. Even if this scenario should be avoided, a LCA showed that it would result in a lower GWP compared to the incineration of PET (Stegmann *et al.*, 2023).

In a paper by Alaerts et al. (2018), three elaborated case studies using data and information retrieved through an extended literature search evaluated risks related to recycling of various biobased plastics (Alaerts, Augustinus and Van Acker, 2018). No overall risks were revealed for biobased plastics as a group; rather, every biobased plastic is to be considered as a potential separate source of contamination in current recycling practices. For PLA (polylactic acid), a severe incompatibility with PET recycling is known; hence, future risks are assessed by measuring amounts of PLA ending up in PET waste streams. For PHA (polyhydroxyalkanoate) there is no risk currently, but it will be crucial to monitor future application development. For PEF, it was found that PEF and PET are not easily separated by visual appearance or flotation, however if NIR technology is available for detection of PET bottles, it is probable that most of the PEF bottles would be separated. Thus, a particular approach for contamination-related issues were included in the upcoming market introduction and to further assess the impact of PEF on rPET.

In 2023, the European Union funded Avantium's Rebiolution project, conducted by a consortium of nine partners from different European countries. Rebiolution stands for "novel biodegradable, REcyclable, BIO-based and safe plastic polymers with enhanced circuLar properties for food packaging and agricUltural applicaTION". This project may provide new insights about the end-of-life of PEF or its derivatives.

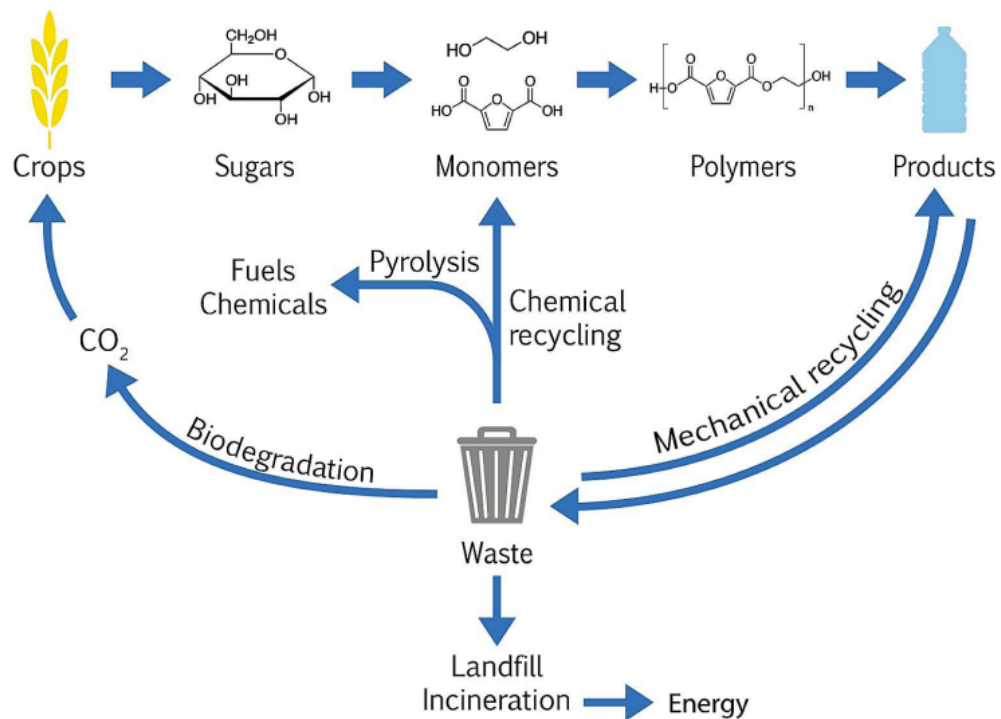


Figure 20. Production of PEF and the main end-of-life scenarios (Silverwood, Mottoul and Dumont, 2024).

7.1

Chemical recycling

Chemical glycolysis of PEF has been investigated by Gabirondo et al. (Gabirondo et al., 2021). They produced PEF-films and then resynthesized the polymer from the recycled monomers. The PEF-films were placed with bio-MEG in the presence of the

ionic liquid 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and benzoic acid, and was heated to 180°C for 2h under vigorous stirring and atmospheric pressure. The resulting monomers were analysed and confirmed to be bis(2-hydroxyethyl)-furan-2,5-dicarboxylate (BHEF), which were possible to repolymerise using melt polycondensation followed by solid-state polymerization (SSP) to virgin-like PEF.

The incorporation of spiroacetal units in polyester backbones could be considered as a factor to facilitate the molecular design toward enhanced chemical and biological recyclability. Acid hydrolysis of these polyesters under mild conditions could completely break the acetal bonds while leaving the ester bonds basically intact. The produced telechelic oligomers with aldehyde functional groups, can be repolymerized back to the initial polymer. This demonstrated the feasibility of using spiroacetal units as a structure element for the design of polyesters with the possibility for shorter loop chemical recycling (Mankar, 2023).

7.2 Biological recycling

Another possible recycling pathway would be to utilize enzymes to break down PEF into its monomers, which has been shown for various molecular masses and particle sizes of PEF (Weinberger *et al.*, 2017). It was shown that hydrolysis was slower for higher molecular weights and higher levels of crystallinity. However, 100% hydrolysis of amorphous PEF films was achieved after only 72h of incubation in 1M potassium phosphate (KH₂PO₄) at pH 8 and 65°C when using cutinases from *Humicola insolens*. Enzymatic depolymerization has also been studied for PET using engineered cutinase (Cut190) (Kawai *et al.*, 2022). Their findings conclude that accessibility for the enzymes, i.e., high surface area is of great importance. It was also shown that the use of a cationic surfactant (dodecyltrimethylammonium chloride) promoted PET degradation while it had an opposite effect for PEF.

7.3 Biodegradability

According to an ASTM D 6400-04 standard, PEF is not compostable, even if it decomposes faster in industrial composting conditions than PET.

Enzymatic studies have shown that PEF films degrade 1.7 times faster than PET ones, however further studies in soil under accurately controlled conditions are necessary to assess and compare the two plastics (Loos *et al.*, 2020).

8. PEF on its way to commercialization

8.1 Avantium

Avantium is a Dutch company that has taken a prominent role in the emerging industry of renewable and sustainable chemistry. Avantium is headquartered in Amsterdam, employing approximately 200 people, with R&D laboratories and three pilot plants in Geleen and Delfzijl, the Netherlands. The company is developing and commercializing technologies to produce chemicals from renewable sources and circular plastic materials used for a variety of consumer products. The main product

is PEF, which is expected to have potential in the packaging, textiles and film sectors, with growing markets worth over \$200 billion (de Jong *et al.*, 2022). The Avantium technology is based on a chemical catalytic process to produce 5-(methoxymethyl) furfural) with a certain amount of HMF which is subsequently converted to FDCA, using the YXY® Technology.

Avantium has ongoing partnerships to develop, scale and commercialize this technology with multiple players throughout the value chain, from feedstock providers to converters and global consumer brands. An example is the collaboration in the EU-project PEFerence, a consortium of organizations aiming to replace a significant share of fossil-based polyesters with PEF. Another example is the Paper Bottle Project (Paboco®), an innovation community joining leading brands who wish to develop a paper bottle. PEF will provide the Paper Bottle with the high barrier properties needed for beverages such as beer and carbonated soft drinks. Avantium also launched a new PEF Textile Community in June 2022, together with Antex (a producer of yarns made from PEF) and four other partners who will use Antex's yarn to develop PEF fabric applications in different market segments, including industrial fibres, sportswear and fashion clothing.

The YXY® Technology is currently the leading commercial production process of FDCA, which will be produced at the FDCA Flagship Plant in Delfzijl in 2024. The final polymerization into PEF will happen at the assets of specialty polyester firm Selenis in Portugal⁵. Avantium has built a strong ecosystem of partners throughout the PEF value chain for the Flagship Plant. To date, Avantium has secured 14 offtake commitments. Contracts were signed with 1. specialty chemical company Toyobo (Japan), 2. specialty polyester film producer Terphane (US), 3. beverage bottling company Refresco (Netherlands), 4. international rigid packaging supplier Resilux (Belgium), 5. masterbatch producer Sukano (Switzerland), 6. leading beer brewing company Carlsberg Group (Denmark), 7. AmBev, the world's leading brewing company – part of the AB InBev Group (Brazil), 8. world luxury goods leader LVMH Group (France), 9. Monosuisse, a leading producer of a wide variety of synthetic monofilaments for industrial use (Switzerland), 10. Henkel, a global leader of adhesives, sealants and functional coatings (Germany), 11. Origin Materials, leading sustainable materials company (USA), 12. Kvadrat, a leader in design innovation, producing quality contemporary textiles (Denmark), and 2 undisclosed brand owners.

8.2 Stora Enso

Stora Enso is a Finnish and Swedish forest industry company that produces and develops various renewable materials and products. The focus is on cellulose-based materials; however, the product portfolio is broad and as there is a huge and growing demand for plastics, especially for packaging applications. Thus, there are also development of biobased plastics and Stora Enso has initiated development of FuraCore®, which is a patented process for production of FDCA, see Figure 21.

⁵ <https://www.selenis.com/>

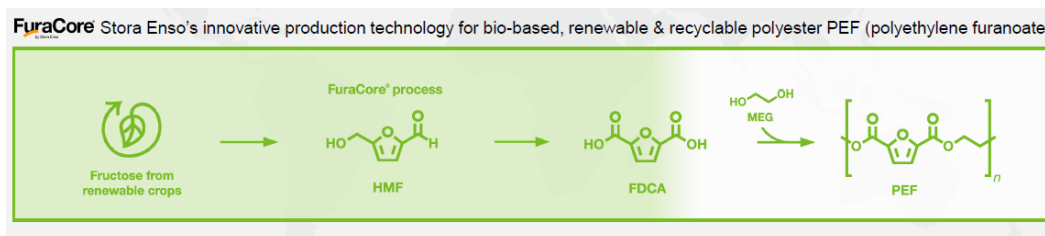


Figure 21. Stora Enso's process for production of PEF called FuraCore⁶.

The three main benefits of the FuraCore® process are the use of a single solvent (that can also be recycled), an efficient removal step of the by-product humins, and the fixed-bed oxidation process.

In 2023, Stora Enso presented their pilot FDCA facility in the Langerbrugge mill, which has a capacity of approx. 8 ton/year (1kg/h) and is used to validate the process and the quality of the FDCA, as well as to test the FDCA in various applications together with potential customers and partners along the whole value chain (e.g., feedstock companies, chemical companies, polymer producers, converters, brand owners and recycling companies).

FDCA with less than 200 ppm combined impurities has successfully been produced at the pilot plant, and further optimization is ongoing. The plans are to scale-up the process and construct a first commercial facility with a capacity of 50-70 kton per year, with sales into niche/speciality applications (and later to full commercial scale, ca. 300-500 kton/year).

Currently (2024), the aim is to find demand for approx. 60 kton of PEF at about 4-5 €/kg, however the PEF pricing is speculative at the current state of development, and it can be expected that there will be cost reductions later on driven by the maturity of technology and benefits from economy of scale (as was the case also for PET). A contract is also signed with South Korean company Kolon Industries to develop biobased plastics together⁷.

8.3 Origin Materials

Origin Materials is an American materials company with a mission to enable the world's transition to sustainable materials. The company was founded in 2008 and has during the past 10 years developed a platform of different materials based on biomass, from initial proof of concept to pilot demonstration and beyond. In 2016, Nestlé Waters and Danone formed an alliance with Origin to commercialize the platform's first product, plant-based PET plastic with a low carbon footprint. PepsiCo joined the NaturALL Bottle Alliance in 2018. In April 2024, Origin Materials announced their first commercial plant (Origin 1) in Sarnia, Ontario, Canada. The process starts with sustainably sourced wood residues, which is converted into chloromethyl furfural (CMF) via hydrothermal carbonization (HTC) together with oils and extractives. The different intermediates are then separated into pure fractions,

⁶ <https://www.storaenso.com/sv-se/products/bio-based-materials/furacore-fdca>

⁷ <https://www.kedglobal.com/chemical-industry/newsView/ked202303220021>

which can be used for various products such as textiles, plastics, tires and automotive components, as well as fuels and high-performance polymers.

The Origin 1 plant is an asset used to support Origin market development, including customer materials testing and formulation in preparation for future technology scale-up. With the plant's wood handling system activated and the conversion of wood residues into intermediates, including CMF, HTC, and oils and extractives, the company's biomass conversion technology currently performs as expected and supports market development activities.

Origin Materials process starts with mixing lignocellulosic biomass with HCl gas in a fluidized bed reactor for a quick first hydrolysis. The subsequent step comprises washing with a Lewis acid (e.g. LiCl and CaCl₂) in dichloromethane to produce CMF. This differs from the process developed by Avantium (DAWN technology) in which milder conditions for hydrolysis (ambient pressure and room temperature) allow for a first selective saccharification and separation from lignin. Later, the excess of HCl present in the acidic sugar solution is enough to produce CMF in high yields using halogenated organic solvents (e.g. chlorobenzene) in biphasic reactors.

A similar process has been described in scientific literature where CMF is produced from lignocellulosic biomass (Bueno Moron, van Klink and Gruter, 2023). The first step was acid hydrolysis of biomass into sugars followed by conversion of saccharides in HCl to furanics, which were extracted and separated in good yield using immiscible organic solvents (e.g. fluoro- and chlorobenzene). Halogenated analogues of HMF have a longer shelf storage compared to their hydroxy analogue, and HMF quickly interconverts to CMF in presence of concentrated HCl. HMF and CMF coexist in equilibrium and can interexchange in the presence of water and HCl. It is suggested that a quick removal of HMF from HCl_{aq.} solution protects it from side-reactions that lead to the formation of levulinic acid, formic acid and polycondensation compounds such as humins.

Mascal (2019) concluded that the main advantage of CMF over HMF is that it can be produced in high yield under mild conditions directly from raw biomass (Mascal, 2019). Examples of commercial markets that can be unlocked by synthetic manipulation of CMF are broken down into two derivative manifolds, furanic and levulinic, which are distributed over three product family trees: renewable monomers, fuels, and specialty chemicals.

8.4 Other initiatives

AVA Biochem AG is the global leader in the industrial production and sale (including corresponding development services and licensing) of the biobased platform chemical HMF. Since 2014, Swiss-based AVA Biochem has been producing high-purity HMF for research purposes and speciality chemicals markets, as well as technical-grade HMF for bulk chemistry applications.

Dupont - Together with the agriculture company Archer Daniels Midland, Dupont announced a process for making furan dicarboxylic methyl ester (FDME) from fructose. The companies plan to react FDME with 1,3-propanediol to make a new biobased packaging polymer; polytrimethylene furandicarboxylate (PTF). FDME is the methyl ester of FDCA, thus the properties of the two compounds are very similar, and just like PEF, PTF has superior barrier properties compared to PET. Whereas both PTF and PEF offer better barrier properties compared to PET, PEF is a better choice for rigid packaging, such as bottles, and PTF may be a better choice for flexible packaging. FDME can also form PEF if reacted with MEG.

The companies plan to build a 60 kton demonstration facility at ADM's complex in Decatur, Illinois. This product line has now been divested to IFF.

International Furan Technology (South Africa)⁸ – uses bagasse (the fibers that are left over once the sugar from sugarcane has been extracted) to produce furfural. The worldwide leading manufacturer of this renewable chemical, Central Romana Corporation, is in the Dominican Republic, conveniently situated near where the sugarcane is grown.

BASF has been involved in research and development efforts related to furfural production from biomass. The company explores various biomass conversion technologies, including acid-catalyzed processes and enzymatic methods, to produce furfural as a precursor for renewable chemicals and materials.

There are also several Chinese companies engaged in the production of furfural and furfuryl alcohol from agricultural residues such as corncobs and bagasse.

⁸ <https://www.furan.com/>

9. Concluding remarks

Polyethylene furanoate (PEF) is a polymer that can be produced from 100% biobased feedstock and has undergone extensive development during later years. The close resemblance to conventional PET has several advantages, e.g., that processing equipment can be used for both plastics. PEF is also allowed to follow the PET recycling stream up to a market penetration of 2% (and given the large production volumes of PET, this means that PEF can be recycled alongside PET for a long period of time, given that it will take time before production volumes of PEF increases to those volumes). At the same time, PEF offers some unique advantages over PET, with its high barrier properties for oxygen and carbon dioxide that can result in more lightweight and resource-efficient products.

The main challenge for PEF is related to economics as it will be more expensive to produce than conventional PET. It will also be of importance to continue working on the shift from primary biobased feedstock to secondary resources, with more efforts and investments in biorefinery research. Finally, it is important to keep developing the systems for recycling and to contribute to the circular economy, which aims to avoid waste and to keep the value of resources for as long as possible.

10. Acknowledgements

The careful proofreading, comments and additional references added by Prof. Rajni Hatti-Kaul, Lunds University, is gratefully acknowledged.

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