

Replacing fossil based PET with biobased PEF; process analysis, energy and GHG balance

A. J. J. Eerhart,* A. P. C. Faaij and M. K. Patel

Received 26th August 2011, Accepted 4th January 2012

DOI: 10.1039/c2ee02480b

An energy and greenhouse gas (GHG) balance study was performed on the production of the bioplastic polyethylene furandicarboxylate (PEF) starting from corn based fructose. The goal of the study was to analyze and to translate experimental data on the catalytic dehydration of fructose to a simulation model, using the ASPEN Plus modeling software. The mass and energy balances of the simulation model results were then used as inputs for a process chain analysis (by application of the life cycle assessment methodology, LCA) and compared to its petrochemical counterpart polyethylene terephthalate (PET). The production of PEF can be divided into three main units: the production of fructose from corn starch; the conversion of fructose into Furanics and subsequent recovery and upgrading; and the oxidation to the monomer 2,5-furandicarboxylic acid (FDCA) and polymerization with ethylene glycol (EG) into PEF. The ASPEN Plus simulation model describes the conversion of fructose into Furanics, subsequent recovery and upgrading and a CHP unit. The production of fructose from corn starch and the oxidation and polymerization into PEF were based on the literature. In total, six model cases were analyzed, using different sets of underlying experimental data; four cases based on crystalline fructose and two cases on high fructose corn syrup (HFCS). Fructose can be converted into Furanics at efficiencies between 38% and 47%. The production of PEF can reduce the NREU approximately 40% to 50% while GHG emissions can be reduced approximately 45% to 55%, compared to PET for the system cradle to grave. These reductions are higher than for other biobased plastics, such as polylactic acid (PLA) or polyethylene (PE). With an annual market size of approximately 15 million metric tonnes (Mt) of PET bottles produced worldwide, the complete bottle substitution of PEF for PET would allow us to save between 440 and 520 PJ of non-renewable energy use (NREU) and to reduce GHG emissions by 20 to 35 Mt of CO₂ equivalents. If also substantial substitution takes place in the PET fibres and film industry, the savings increase accordingly. The GHG emissions could be further reduced by a switch to lignocellulosic feedstocks, such as straw, but this requires additional research.

Utrecht University, Copernicus Institute, Department of Science, Technology and Society, Budapestlaan 6, 3584 CD Utrecht, The

Netherlands. E-mail: a.eerhart@uu.nl; a.p.c.faaij@uu.nl; m.k.patel@uu.nl; Fax: +31 30 253 7601; Tel: +31 30 253 5144

Broader context

Within industry, the chemical industry is the most energy intensive sector, with organic chemicals and polymers being its most important products. In the last decade biobased plastics have been receiving increased attention, fueled by the potential they hold to reduce anthropogenic greenhouse gas (GHG) emissions and to increase the security of raw material supply through the transition from fossil feedstocks to sustainable biobased feedstocks. Another reason for this increased attention is the sustained high oil price. Most of today's biobased plastics are based on grain or sugar derived glucose and use microorganisms to produce monomers, which are subsequently converted to polymers. Examples are polylactic acid (PLA), polyhydroxyalkanoates (PHA's) and polyethylene (PE). Since not all bio-based polymers are attractive in terms of the energy use for their production, the greenhouse gas emissions and the land required (including the indirect impacts caused), there is urgent need for R&D into new monomers and polymers. Earlier analysis pinpointed the compound 2,5-furandicarboxylic acid (FDCA) as a potentially interesting candidate. FDCA is considered the biobased alternative to purified terephthalic acid (PTA), one of the fossil based monomers of polyethylene terephthalate (PET), which is the fifth largest bulk plastics worldwide. Against this background this paper presents an assessment whether the substitution of polyethylene furandicarboxylate (PEF) for PET could bring about significant reductions in non-renewable energy use and greenhouse gas emissions.

1. Introduction

Biobased plastics have been receiving increased attention in the last decade. This development is fueled by the potential biobased plastics hold to reduce anthropogenic greenhouse gas (GHG) emissions and to increase the security of raw material supply through transition from fossil feedstocks to renewable and sustainably exploited biobased feedstocks. Another reason for this increased attention is the sustained high oil price.

There are several different production routes to bioplastics, which can be divided into three categories:

(1) Thermochemical and catalytic conversion of the biobased feedstock to monomers, which are combined to polymers in a second step.

(2) Fermentation of the biobased feedstock to monomers, which are converted into polymers in a second step.

(3) Modification of naturally occurring polymers, which in essence remain intact.

Biobased plastics that fall in the third category have a long history and predate petrochemical plastics.¹ These were typically cellulose derived plastics, such as celluloid.² The research into biobased plastics has mainly focused on the second category, with clear examples being polylactic acid (PLA) and biobased polyethylene (PE).

This study focuses on polyethylene furandicarboxylate (PEF), which falls into the first category and is considered a biobased alternative to the petrochemical based plastic polyethylene terephthalate (PET). The PET bottle market amounts to about 15 Mt[†] which is equivalent to 5.9% of the global plastics production[‡] and represents roughly 0.2% of the global primary energy consumption[§]. The main component of PET is purified terephthalic acid (PTA)[¶], which could be replaced by biobased 2,5-furandicarboxylic acid (FDCA).⁵

In 2004, FDCA was identified by the U.S. Department of Energy (U.S. D.o.E.) as one of the twelve sugar-based building blocks which hold the greatest potential for the production of biobased chemicals and materials.^{6,7} These twelve building blocks are commonly referred to as the bioplatform chemicals and have attracted increased amount of interest in recent years as a replacement of petrochemical products in a wide range of application areas.^{6,7}

FDCA can be produced *via* the catalytic oxidation of 5-hydroxymethylfurfural (HMF),^{8–10} which in turn is produced by acid-catalyzed dehydration of fructose.^{9–12} As such HMF can be seen as a key contributing intermediate for the transition from fossil based industrial chemistry to biobased carbohydrate industrial chemistry.¹³ However, despite its application potential described in the literature, HMF is not produced on a commercial scale. The main barrier to commercial production of HMF is that it is not stable under the acidic conditions needed for its

formation and that it further reacts to form levulinic acid (LA) and formic acid (FA)||¹⁴. Two attempts to commercially produce HMF at a pilot-plant scale are described in the literature. Roquette Frères in France employed a bi-phase process approach, in which the HMF is extracted from the reactive phase directly after its formation.¹⁵ Südzucker in Germany focused on conditions that maximized HMF selectivity in a solvent consisting of water and dimethylsulfoxide (DMSO).^{16,17} Both approaches had their disadvantages and their further commercialization was abandoned.

In 2006, Dumesic *et al.* reported a process that achieved high fructose conversions and good HMF selectivities (80% HMF selectivity at 90% fructose conversion).²⁴ The process involves a bi-phasic reactor, in which sugar dehydration occurs by means of an acid catalyst in the aqueous phase and DMSO present to suppress undesired side reactions, such as the formation of LA and FA. The suppression of undesired side reactions is a similar approach to that of Südzucker, while the continuous extraction of the HMF formed in the organic phase (consisting of methyl-isobutylketone) is a similar approach to that of Roquette Frères.

Also in 2006, a breakthrough was made by Avantium Chemicals B.V. regarding the prevention of non-selective HMF decomposition to LA and FA. It was found that the problem of HMF degradation could be suppressed by the *in situ* formation of HMF ethers, which are formed when an alcohol is used as a solvent, thus ensuring good selectivities and yields of HMF and its corresponding ether (R-MF in Fig. 1).^{19,20} Avantium used their heterogeneous catalyst screening methodology to optimize the process.^{19,20} Their process is designed to maximize the yield of HMF and HMF ethers and preventing the decomposition to LA and LA esters. Next to these four compounds, a small part of the fructose is converted into furfural and formaldehyde.

HMF, HMF ethers, LA, LA ester, furfural and formaldehyde can further react with each other to form a humins molecule. Humins is the general term for a dark, poorly soluble condensation product often found when dehydrating sugars. The exact structure and formation process of humins are unknown, however, it can be theorized that the formation of humins involves multiple (aldol) ketalization, hydroxyalkylation and dehydration reactions.

The research described so far focuses on the production of HMF and HMF ethers. However, several companies, such as Biofine,²⁵ Segetis²⁶ and Shell²⁷ see great potential in LA, a decomposition product of HMF. LA and LA esters can be used as precursors to plasticizers, nylon-like polymers, synthetic rubbers and plastics. LA is also a versatile synthetic intermediate in the production of pharmaceuticals and is a precursor for chemicals such as methyltetrahydrofuran (MTHF), valerolactone and ethyl levulinate. The compounds have recently received more attention as potential biofuels.²⁷

1.1. Objectives

The focus of this study is the production of PEF using Furanics compounds as intermediates. The goal of this study is to determine the mass and energy balances, the non-renewable energy use (NREU**) and GHG emissions of the production of PEF

[†] The total PET production is about 50 Mt³ per year and also includes fibres (31 Mt),³ films and sheets (2 Mt)⁴ and packaging (0.4 Mt).³

[‡] The PET market is equal to 14.7 Mt per year for 2009, while total plastics production amounted to 250 Mt in 2009.⁴

[§] Based on a heating value of 69.4 GJ_{HHV} per tonne PET and a global primary energy consumption of 474 EJ.⁵

[¶] Based on carbon content, terephthalic acid (C₈H₆O₄) represents approximately 80% of the mass of PET (C₁₀H₈O₄), while ethylene glycol (C₂H₆O₆) represents 20%.

|| Formic acid is nowadays produced *via* petrochemical processes.

** NREU represents the total of primary fossil and nuclear energy.

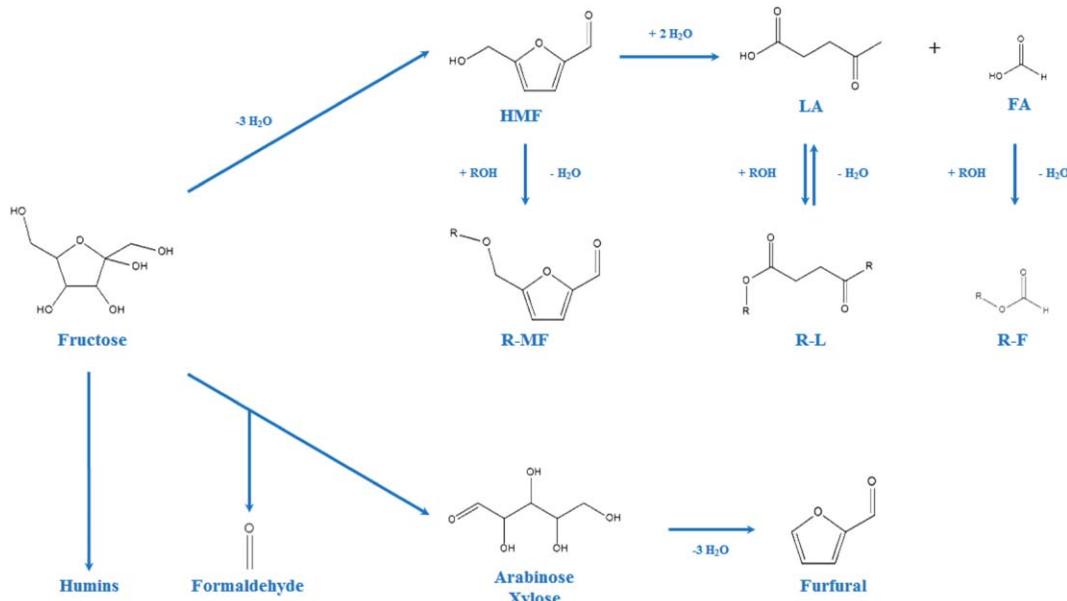


Fig. 1 Composite overview of Furanics reactions based on fructose.^{18–24}

compared to its petrochemical counterpart PET. Avantium reports conversion and yield data using H_2SO_4 as the catalyst in their patents and the most recent available data were used in this study.^{19,20} Experimental data on the catalytic dehydration of fructose were analyzed and translated to a simulation model using the ASPEN Plus modeling software. The result of the simulation model was then used as the input for a chain analysis of PEF.

The structure of this article is as follows: Section 2 describes the entire PEF production chain, including the ASPEN Plus simulation model at its center. In Section 3 the key assumptions and data are given, while in Section 4, the results of the PEF production chain analysis are presented. The results are discussed in detail in Section 5, followed by the conclusion presented in Section 6.

2. System overview

A simplified flowsheet to produce PEF from fructose and HFCS is given in Fig. 2. The production of PEF can be divided into six sub-processes:

- (1) The production of corn starch in the Corn Wet Milling (CWM) process.
- (2) The conversion of corn starch into fructose and HFCS.
- (3) The conversion of fructose and HFCS into Furanics.
- (4) The recovery and upgrading of Furanics into HMF and HMF ethers.
- (5) The oxidation of HMF and HMF ethers into FDCA.
- (6) The polymerization of FDCA and EG into PEF.

These six processes are divided into two levels: the ASPEN Plus simulation model, consisting of sub-processes 3 and 4; and the PEF chain analysis, which expands the ASPEN Plus simulation model to include sub-processes 1, 2, 5 and 6.

2.1. The ASPEN plus simulation model

The ASPEN Plus modeling part of the PEF production flowsheet consists of three processes:

- (1) The conversion of fructose and HFCS into Furanics.
- (2) The recovery and upgrading of Furanics into HMF, HMF ethers and HMF decomposition products.
- (3) A combined heat and power (CHP) plant to burn the unused products for onsite heat and power generation.

In total, six cases were modeled, based on experimental data received from Avantium Chemicals B.V., which are described in Tables 1–4. The main differences between the cases is the type of sugar used (Table 1), the total amount of water going into the Furanics reactor (Table 2) and finally the difference between the combined yield of HMF and HMF ethers and the combined yield of LA and ML (Table 3). Cases 1, 2 and 3 are optimized towards HMF and HMF ether production, while the last three cases are optimized towards the overall yield of products.

The ASPEN Plus modeling software has a standard database with physical property data on different components. HMF, HMF ethers, LA esters are not included in this standard database, but can be imported into the database *via* the ThermoData Engine.††

Humins are also not included in the standard database. In order to determine the molecular structure of a humins molecule, the experimental yields on fructose dehydration were used to solve the mass balance in terms of carbon, hydrogen and oxygen, with any remainder ending up as a humins molecule. It was determined that the general molecular structure of a humins molecule is $(C_xH_{2x}O_x)_n$. From the experimental results, it was also determined that the humins fraction has a very high boiling point and high viscosity, however, no component in the standard database with a structure of $(C_xH_{2x}O_x)_n$ has these properties. Therefore as a close approximation, a theoretical molecule with a molecular formula of $C_{23}H_{26}O_{12}$ was used to represent a humins molecule.

†† The ThermoData Engine software is to provide critically evaluated thermodynamic and transport property data based on the principles of dynamic data evaluation, published experimental data and predicted values based on molecular structure.²⁸

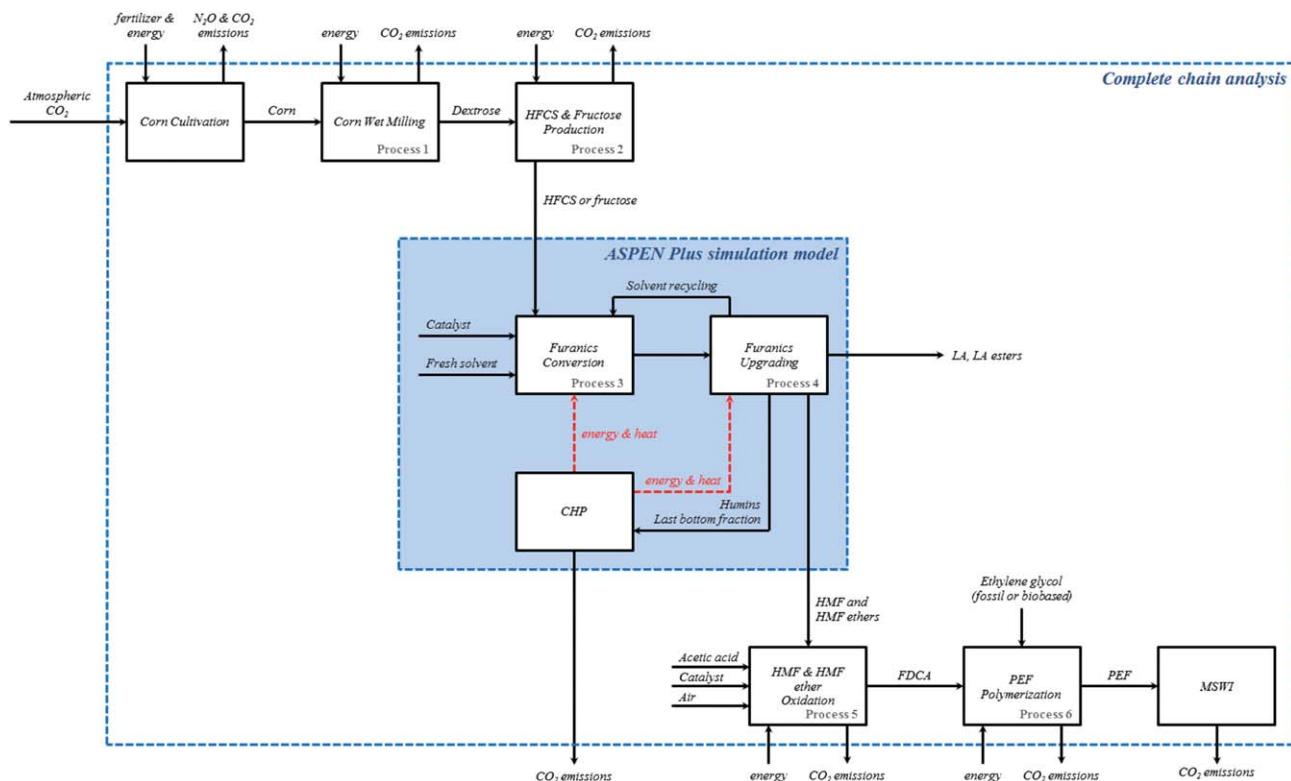


Fig. 2 System overview of the processes for the production of PEF from fructose and HFCS.

2.1.1. Furanics conversion. Fructose and HFCS are mixed with a catalyst and a solvent consisting of water and methanol (Fig. 3). This mixture enters the Furanics reactor, operating at 50 bars and temperatures between 200 °C and 220 °C.

Tables 1–4 present the underlying modeling input for the Furanics conversion.

With the different conversion and yields across the six cases analyzed, it was decided to fix the production of FDCA at 20 ktonnes per year, to represent a pilot scale plant. According to preliminary analyses scaling up the production does not yield significant process efficiency improvements^{‡‡}, while for economic reasons a substantial scale-up to 100 to 500 ktonnes per year would be desirable.

2.1.2. Recovery and upgrading. The effluent from the Furanics reactor is a mixture of the Furanics products, the solvent (water and methanol) and humins and is led to the recovery and upgrading section. This section consists of a series of eight distillation columns, where the pressure is gradually reduced in order to simplify the recovery of light end products, such as methanol, methyl formate (MF) and formaldehyde. The first five distillation columns are dedicated to the light ends recovery and operate between 25 and 1 bar (columns 1 to 5 in Fig. 4). After the light ends recovery, the final three distillation columns of the recovery and upgrading section are dedicated to the recovery and upgrading of HMF, HMF ethers, LA and LA esters and operate between 0.2 and 0.015 bar (near vacuum) and elevated temperature (columns 6 to 8 in Fig. 4). A neutralization step is needed to

Table 1 Operating conditions

Case	Sugar	Acidity/mM	Temperature/°C	Pressure/bar
1	Fructose	5.00	220	50
2	Fructose	5.00	200	50
3	HFCS	5.00	200	50
4	Fructose	10.0	200	50
5	Fructose	10.0	220	50
6	HFCS	10.0	220	50

neutralize the sulfuric acid catalyst used in the Furanics conversion in order to prevent the desired products from degrading to unwanted humins.

The humins that are formed during the Furanics conversion are recovered in the bottom fraction of the last distillation column, due to their high boiling point. Humins are free of water, since water is recovered in the previous distillation towers. The humins stream obtained has a very viscous consistency and a complex chemical structure and it cannot be used for further processing. Humins may still have value as fuel for a combined heat and power unit (CHP). Using a heating value based on the general formula $\text{C}_{23}\text{H}_{26}\text{O}_{12}$ obtained from the ASPEN Plus model the contribution to the overall process energy requirements can be determined (see Section 2.1.3).

2.1.3. CHP. The CHP unit consists of a boiler operating at atmospheric conditions and a steam cycle. The steam cycle consists of a water pump, heat recovery steam generator (HRSG), three steam turbines (high, medium and low pressure) and a condenser (Fig. 5). Humins are led to the boiler and combusted

^{‡‡} Scaling will have a significant impact on the economics of the process.

Table 2 Sugar inputs and recycle

Case	Sugar feed/gram	Sugar amount in feed/gram	H ₂ O amount in sugar feed/gram	H ₂ O in recycle/gram	MeOH in recycle/gram	Total recycle/gram
1	25.0	25.0	0.00	4.25	70.8	75.0
2	25.0	25.0	0.00	11.3	63.7	75.0
3	32.5	25.0	7.47	3.83	63.7	75.0
4	25.0	25.0	0.00	4.25	70.8	75.0
5	25.0	25.0	0.00	11.3	63.7	75.0
6	32.5	25.0	7.47	3.83	63.7	75.0

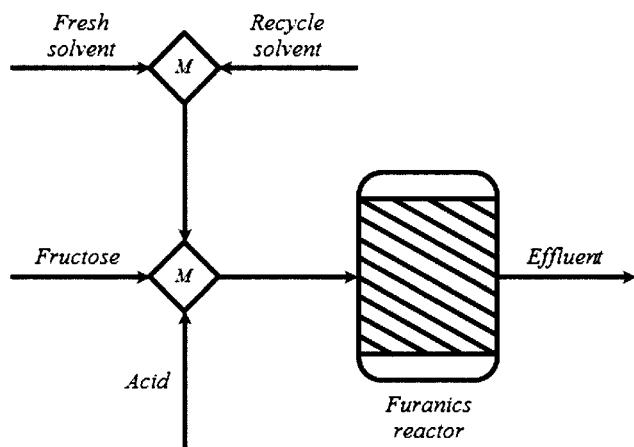
Table 3 Furanics product yields based on experimental data from Avantium Chemicals B.V

Case	Yield HMF/mol%	Yield MMF ether/mol%	Yield furfural/mol%	Yield LA/mol%	Yield LA ester/mol%	Yield MF/mol%	Yield formaldehyde/mol%
1	9.60	50.2	2.70	0.95	7.70	1.73	0.54
2	22.5	38.6	2.30	2.90	7.80	2.14	0.46
3	20.9	35.9	2.10	2.70	7.20	1.98	0.42
4	11.9	43.7	2.20	3.40	14.5	3.58	0.44
5	9.10	42.6	3.00	5.20	16.6	4.36	0.60
6	8.50	39.6	2.80	4.80	15.4	4.04	0.56

Table 4 Overall conversions and humins

Case	Total conversion/mol%	Yield sugar/mol%	Yield sugaroside ^a /mol%	Total products ^b /mol%	Yield humins/mol%	Total/mol%
1	99.7	0.00	0.30	73.4	26.2	100
2	99.3	0.70	0.00	76.7	22.6	100
3	92.3	0.70	7.00	71.2	21.1	100
4	99.7	0.30	0.00	79.7	20.0	100
5	99.8	0.20	0.00	81.5	18.3	100
6	92.8	0.20	7.00	75.7	17.1	100

^a Sugarsides are etherified sugars, where an alcohol group is attached to a sugar molecule. ^b Total products include HMF, HMF ethers, LA, LA esters, furfural, MF and formaldehyde, as shown in Table 3.

**Fig. 3** The Furanics conversion process (effluent containing Furanics, humins, methanol, water and H₂SO₄).

with air (combustion in a typical industrial boiler with current technology still needs to be confirmed). The exhaust gases are then led to the HRSG where pressurized water of 100 bars is converted into steam at 510 °C (Table 5). This high pressure steam is then expanded to 40 bar in the high pressure steam turbine. The

discharged steam, now referred to as medium pressure steam, is expanded to 12.5 bar in the medium pressure steam turbine. In order to ensure sound operation and maintenance of the low pressure steam turbine and reduce the effect of cavitation on the turbine blades, the discharged steam of the medium pressure turbine (at 12.5 bar) needs to be reheated to 410 °C (using heat from the combustion of humins), so that the liquid fraction of the discharged steam from the low pressure steam turbine does not exceed 10% (Table 6). Finally, to close the steam cycle, the low pressure steam needs to be condensed to 100% liquid, before being fed back to the water pump. Part of the medium and low pressure steam is used to meet the heat demands of the Furanics conversion and recovery and upgrading processes.

2.2. PEF chain analysis

2.2.1. Corn cultivation, corn wet milling process, fructose and HFCS production. The process to produce PEF starts with corn production. The corn plant captures solar energy by photosynthesis, and fixes carbon, hydrogen and oxygen from water and carbon dioxide to form a carbohydrate (CH₂O). The non-renewable energy use and GHG emissions associated with corn cultivation can be divided into three categories.²⁹

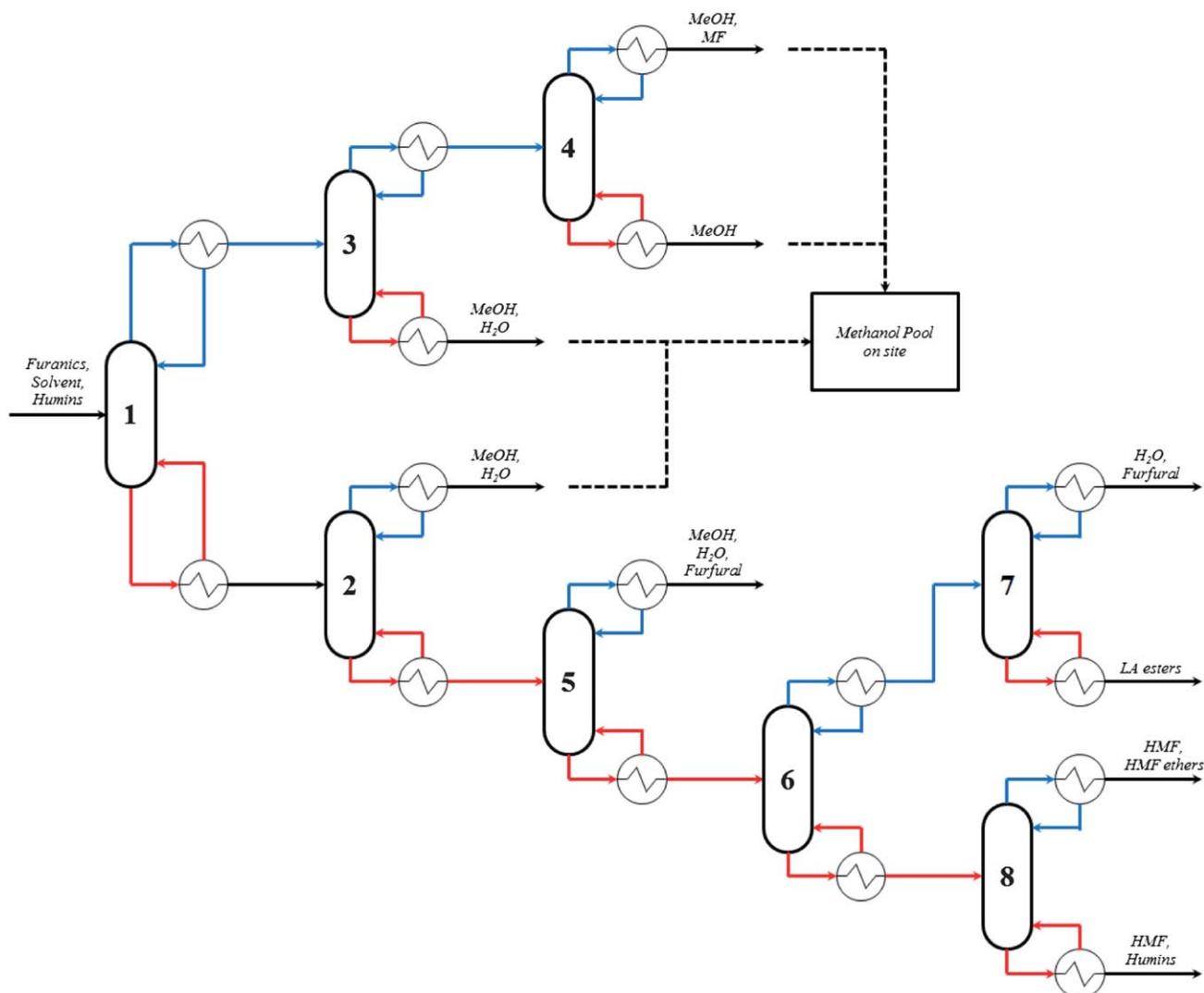


Fig. 4 The recovery and upgrading section (columns 1 to 5 are dedicated to the light ends recovery, while columns 6 to 8 are dedicated to the recovery of HMF, HMF ethers, LA and LA esters).

(1) Fertilizer production and application on the land (e.g. N₂O emissions derived from nitrogen based fertilizers).

(2) Agro-chemicals production (e.g. pesticides).

(3) Transportation of the harvested corn to the processing plant.

The data^{§§} on these three categories are based on the production of corn in the states of Iowa and Nebraska of the United States, using the DAYCENT model.³⁰ The assumption in this study was that the use of corn feedstocks does not cause adverse land use change, which will be further discussed in detail in Section 5.3.

After harvesting, corn is processed in a corn wet milling process to produce starch hydrolyzate (Fig. 6). This is hydrolyzed using enzymes into a mixture of dextrose and water. This mixture then undergoes enzymatic isomerization, after which excess water is evaporated, resulting in a mixture of dextrose and fructose (60% dry solids). This mixture is commonly referred to

as HFCS-42, indicating that 42% of the sugars are fructose (the other 58% are composed of 53% dextrose and 5% di- and oligosaccharides). HFCS-42 can be further processed *via* chromatographic separation by means of ion exchange resins, resulting in a fructose rich stream, commonly referred to as HFCS-90 and a dextrose rich stream which is recycled back to the isomerization stage.³¹ This HFCS-90 stream can then be further processed into crystalline fructose^{¶¶} (not shown in Fig. 6).

Several studies were prepared on the production of starch and dextrose from biomass, such as a study by NatureWorks for the production of polylactide from dextrose³² and a study by the U.S. Department of Agriculture.³³ The study by Vink *et al.* reports dextrose produced from corn to have a NREU of 6.2 GJ per tonne.³² However, to our knowledge, there are no

^{§§} The data used are explained in more detail in Table 7 in Section 3.

^{¶¶} The production of crystalline fructose involves the seeding of dry fructose crystals into HFCS-90, after which it is cooled down to crystallize pure fructose. The crystalline fructose is then removed by centrifugation and further dried, resulting in 99.5% pure fructose.³¹

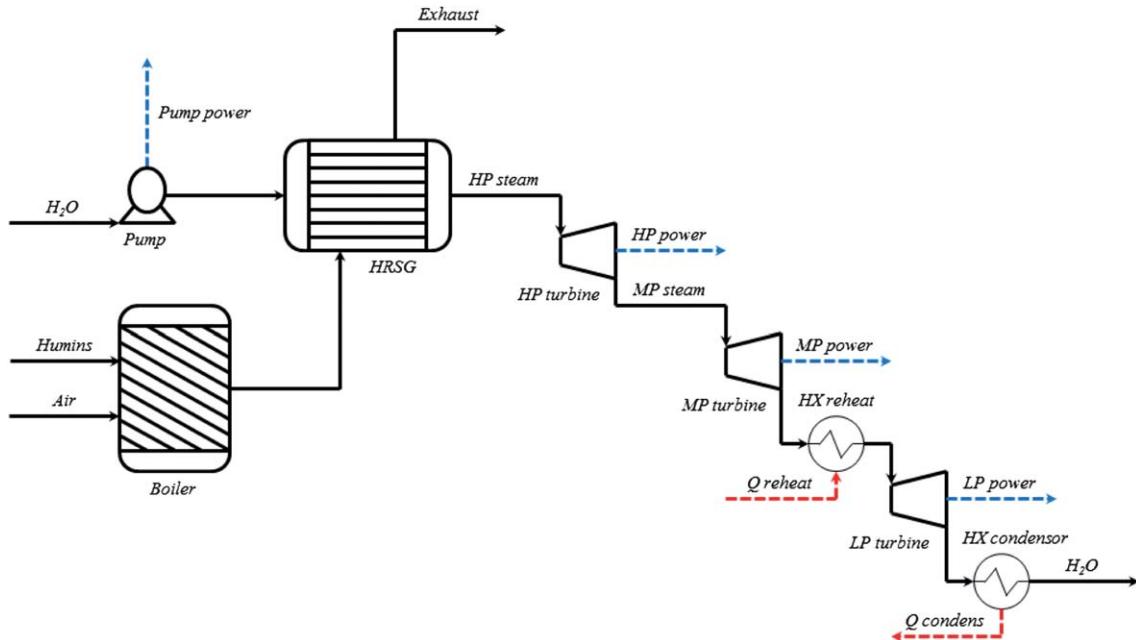


Fig. 5 The CHP section.

Table 5 Boiler and heat exchanger operating conditions

<i>Boiler</i>		
Heat duty	MW	0.00 (adiabatic)
Pressure	Bar	1.01325
<i>Heat exchanger</i>		
Steam outlet temperature	°C	510
Temperature approach (pinch)	°C	15
Type	—	Countercurrent

Table 6 Steam turbines operating conditions

<i>High pressure turbine</i>		
Type	—	Isentropic
Isentropic efficiency	%	85
Mechanical efficiency	%	100
Discharge pressure	Bar	40
Liquid fraction discharged steam	—	0.00
<i>Medium pressure turbine</i>		
Type	—	Isentropic
Isentropic efficiency	%	93
Mechanical efficiency	%	100
Discharge pressure	Bar	12.5
Liquid fraction discharged steam	—	0.00
<i>Low pressure turbine</i>		
Type	—	Isentropic
Isentropic efficiency	%	89
Mechanical efficiency	%	100
Discharge pressure	Bar	0.025
Liquid fraction discharged steam	—	0.10

publications on the environmental impacts caused by the production of crystalline fructose or HFCS from dextrose.

Typically, to produce 1 tonne of fructose, 1.06 tonne of dextrose is needed.³⁴ The most energy intensive process step is the evaporation of water after the isomerization step, requiring approximately 3.9 GJ of NREU per tonne of fructose (further energy

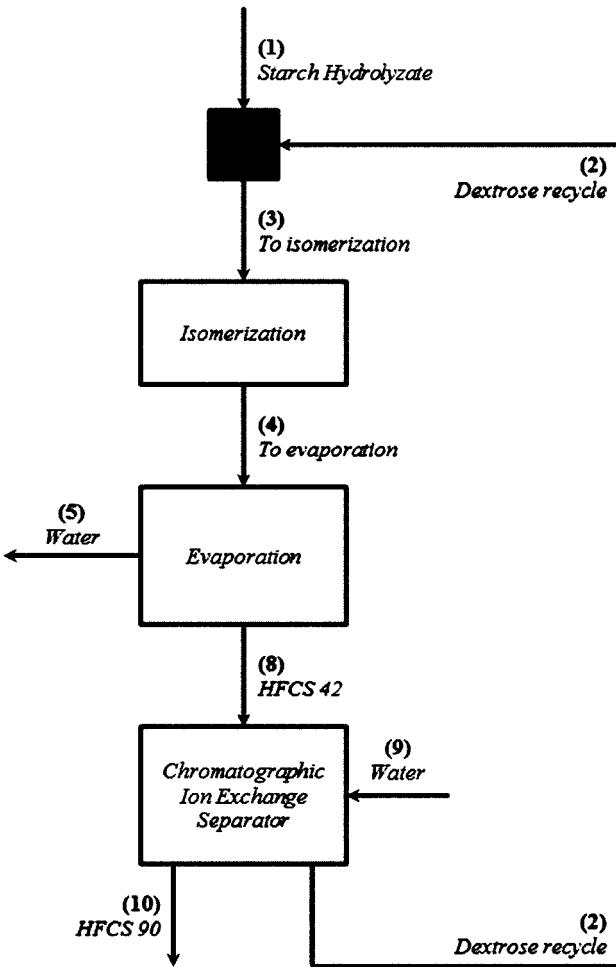
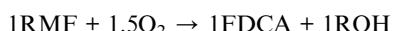
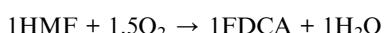


Fig. 6 Fructose and HFCS production overview.

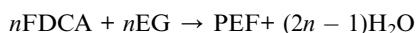
requirements, presumably only for pumping are estimated to be small and have been neglected). These factors, combined with the value of 6.2 GJ per tonne for dextrose production yield a total for the NREU of HFCS-90/fructose of 10.5 GJ per tonne of fructose.

2.2.2. Oxidation and polymerization. The production of PEF from HMF and HMF ethers follows similar process steps as the production of PET from *p*-xylene. The PET production process starts with the oxidation of *p*-xylene (using air) into terephthalic acid, which is then purified (purified terephthalic acid, PTA).³⁵ PTA in turn is polymerized with ethylene glycol (EG) to form PET. The alternative process using FDCA, a biobased alternative to PTA produced from HMF, results in the production of PEF. HMF and HMF ethers are oxidized with air into FDCA, which in turn is polymerized with EG to form PEF. In comparison with the conversion of *p*-xylene to PTA, HMF and HMF ethers require less air in the oxidation reaction to FDCA, as they already contain oxygen within their chemical structures (Fig. 7). With FDCA being a biobased alternative for PTA, the use of biobased EG (instead of petrochemical EG) allows the synthesis of PEF from biobased feedstocks only.

HMF and the HMF ether MMF are oxidized to FDCA according to the following reaction:



The polymerization of FDCA with EG occurs according to the following equation:



The conversion of HMF and HMF ethers into FDCA and the subsequent polymerization to PEF are expected to be more efficient than their petrochemical counterparts for the following reasons:^{36,37}

(1) Preliminary analysis has shown that the HMF and HMF ether oxidation to FDCA operates at lower temperatures (180 °C vs. 210 °C) and lower pressures (7 bar vs. 12 bar).

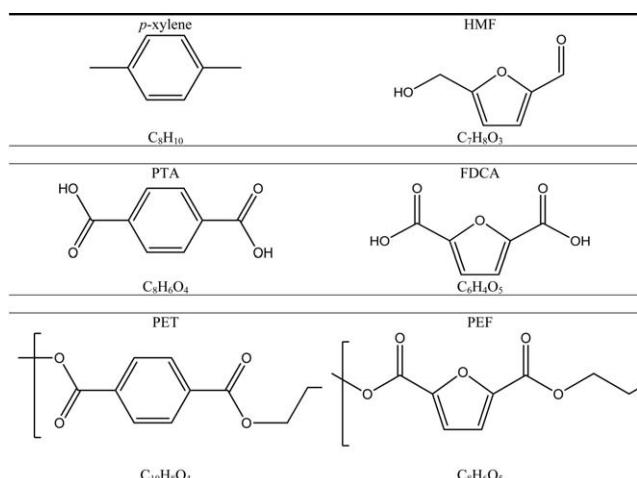


Fig. 7 Structural formulae of fossil PET and biobased PEF.

(2) Less acetic acid is oxidized to CO_2 , reducing the inputs of fresh acetic acid (acetic acid is recycled throughout the oxidation of HMF and HMF ethers).

(3) FDCA polymerization with ethylene glycol (EG) to PEF operates at ~30 °C or lower temperatures and twice as fast.

Based on the milder process conditions, lower process energy requirements can be expected and possibly also a purer product streams (due to less degradation processes). However, at the current stage of development, these benefits of PEF production could not be quantified yet. Also, as can be seen in the system overview (Fig. 2), the polymerization and oxidation to PEF are not modeled in ASPEN Plus and are instead estimated assuming equivalent energy requirements as for conventional, petrochemical production of PET from its monomers; this conservative approach is chosen in view of the rather small temperature differential, the lack of detailed process information (e.g. on yields and byproducts for long operation times) and in view of the many decades of optimization of PET polymerization.

3. Key assumptions and data

Table 7 presents an overview of the data for compounds and processes needed for the production of PEF, in terms of NREU and CO_2 emissions. The functional unit defined for this energy and GHG emissions study is 1 tonne of PEF (at the factory gate).

3.1. Energy and GHG balance methodology

When comparing the energy and GHG balance of PEF to petrochemical PET, it is important that the underlying methodologies are consistent for both products. The values for PET, as presented in Table 7, are based on the Eco-profile of PET published by PlasticsEurope.⁴¹ As pointed out by Reap *et al.*⁴⁵ the most critical aspects in LCA studies are the functional unit, allocation methodology, cut-off rules and system boundaries.⁴⁵ For PET, the functional unit is set at 1 kg of PET at the factory gate and for multi-product processes, allocation was performed based on mass (see Section 3.2 for further explanations). Cut-off rules were generally avoided when preparing the Eco-profiles of PlasticsEurope. A fully consistent approach was applied for PEF, with the chosen functional unit being 1 kg PEF||| and moreover, with mass allocation and the avoidance of cut-off. One difference between the PEF and PET analysis is the system boundaries as we now explain in more detail:

(1) The energy and GHG emissions of PEF refer to the system cradle-to-grave. The use phase is assumed to be stationary, which implies that no extra energy use is assigned to it (contrary to products which are, for example, part of a transportation means where the weight of the product influences the energy requirements in the use phase). Transportation of the raw materials used and of the products made is also excluded. After the PEF has been discarded by the consumer, it is assumed to be disposed of in a municipal solid waste incinerator (MSWI) without energy recovery (“grave”). Other options for solid waste management

||| One may argue that identical mass (1 kg of PET as compared to 1 kg PEF) does not ensure full comparability due to the differences in material properties. However, this approach is justified given the similar properties of PET and PEF (thermal, mechanical and barrier properties are similar or better).⁴⁷

Table 7 GHG emissions of the main inputs and process steps (data for the compounds refer to the system cradle-to-factory gate while data for the two processes refer to the process step only)

	NREU/GJ per tonne	GHG emissions/tonne CO ₂ eq. per tonne	Source
<i>Compound</i>			
Fructose/HFCS	10.48 ^a	0.63	Calculated
Methanol	^a	0.75	38
Sulfuric acid (H ₂ SO ₄) ^b	^a	0.14	38
Ethylene glycol			
Petrochemical ^c	^a	1.61	38
Biobased ^d , from maize ^e	27.2	1.39	39
Biobased ^d , from sugarcane today ^f	4.4	0.36	39
Biobased ^d , from sugarcane future ^g	-5.87	-0.51	39
Natural gas	58.3	3.24 ^h	40
PET ⁱ	69.4	4.44	41
<i>Process</i>			
HMF oxidation ^j	11.8	0.68	Calculated
PEF polymerization ^j	10.2	0.61	Calculated

^a For copyright reasons, no NREU data are presented for the EcoInvent data extracted from the Simapro tool. The EcoInvent GHG emissions have been reported in the CCaLC model.³⁸ ^b Reliable data were available for the model catalyst H₂SO₄; industrial process conditions might generate slightly different results. ^c Ethylene is oxidized to ethylene oxide (EO), which in turn reacts with water to form EG (0.6 tonnes ethylene per tonne EG). Typical production plants are integrated to produce EO and EG combined on-site. ^d Corn maize is converted into bioethanol, which in turn is converted into ethylene (1.65 tonnes ethanol per tonne ethylene). Ethylene follows then the same process as mentioned in (b). ^e The underlying data set in Patel and Chen³⁹ is based on the BREW study, which in turn is based on a study done by Vink in 2004 for the production of corn in Iowa and Nebraska, using the DAYCENT model.³⁰ The study by Vink is confidential, therefore only an aggregated CO₂ eq. value was presented in BREW.³⁰ ^f N₂O emissions are included in the calculation of the GHG emissions.³⁹ The underlying data set on sugarcane used by Patel and Chen³⁹ is based on Macedo *et al.*⁴² ^g The values for biobased EG from sugarcane future represent potential future process improvements in the Brazilian sugarcane industry. N₂O emissions are included in the calculation of the GHG emissions.^{39,42} ^h Calculated based on heating value (54.0 GJ HHV per tonne),⁴³ CO₂ emissions from combustion (56 kg CO₂ per GJ natural gas) and 7% Energy Requirement for Energy (ERE). ⁱ These values represent an updated study on PET by PlasticsEurope.⁴¹ There remains uncertainty about these values compared to the 2005 values of 80.75 GJ per tonne and 5.59 tonne CO₂ eq. per tonne.⁴⁴ This will be discussed further in Section 5. ^j By analogy with PTA/PET production. The EcoInvent database is used for one product, in this case PTA, to calculate NREU and CO₂ emissions from cradle to grave. By removing the inputs of raw materials and energy use from the calculations, it is possible to determine the NREU and CO₂ emissions of the oxidation and polymerization steps.

such as an MSWI with energy recovery or mechanical recycling would lead to lower environmental impacts by replacing grid electricity and heat, which would otherwise be produced from fossil fuels.⁴⁶ With the calorific values of PET and PEF being comparable (10–20% deviation²³), the benefits of a MSWI with energy recovery or mechanical recycling would hardly differ for both products.

(2) In order to ensure comparability with the chosen system boundaries for PEF, the system boundaries of PlasticsEurope's analysis for PET, which are set to "cradle-to-factory gate" in the original source,⁴¹ have been expanded to include the release of fossil CO₂ embodied in PET. This cradle-to-grave framework provides an objective and fully consistent basis for comparing PEF with its fully petrochemical counterpart PET.

When comparing PEF with PET, it is important to distinguish between fossil and biogenic GHG emissions. For petrochemical products, such as PET, the method for determining GHG emissions is broadly accepted. Accounting for CO₂ emissions arising from biobased products is more complex as there are two concepts which can be considered, *i.e.* carbon neutrality or carbon storage***.⁴⁸ However, these two methods yield the same result for the system cradle-to-grave which has been chosen in this

paper; therefore, we do not discuss here possible further implications and instead refer the reader to Pawelzik and Patel.⁴⁸

3.2. Allocation and partitioning

The Furanics conversion process yields not only HMF and HMF ethers, but also significant quantities of LA and LA esters, which justify their recovery and upgrading. According to the ISO standards for life cycle analysis (LCA),^{49,50} allocation, henceforth referred to as partitioning, should be avoided by either dividing the unit process into sub-processes or by system expansion. However, in this energy and GHG emissions study, this cannot be realized because further division of the unit process into sub-processes is not possible (because the model already represents the unit processes) and system expansion is not plausible because there are currently no dedicated commercial processes that produce LA and LA ethers at large scale. Partitioning can be implemented on the basis of mass, energy and economics. Partitioning based on energy would only be relevant if all products were used for energy production or energy carriers (*e.g.* fuels), while partitioning on economic value is not reasonable at this point in time as HMF and HMF ethers are not produced on a commercial scale and therefore do not have a (bulk) market price.

Against this background and to align our methodology with that of PlasticsEurope, we chose to perform the partitioning based on mass. It is a characteristic of mass partitioning that each product in the product basket has the same NREU value per kg of product and the same also holds for GHG emissions. The product basket in this analysis is defined as the four main products after the recovery and upgrading section: HMF,

*** The carbon neutrality concept assumes a closed loop for biogenic CO₂ that is sequestered (or fixed) by photosynthesis in the biobased feedstock and released back into the atmosphere. The carbon storage concept assumes that biogenic CO₂ is sequestered by photosynthesis thus "storing" CO₂ within the biobased product. There are several methodologies on how to account for carbon stored available in the literature, which are discussed in more detail by Pawelzik and Patel.⁴⁸

Table 8 Mass balance of the six cases analyzed (see Tables 1–4 for specification of the cases)

		Case					
		1	2	3	4	5	6
<i>Inputs</i>							
Sugar type		Fructose	Fructose	HFCS	Fructose	Fructose	HFCS
Sugar source	Tonnes per year	51,100	66,450	71,448	58,695	60,211	64,772
Ethylene glycol	Tonnes per year	7954	7954	7954	7954	7954	7954
<i>Outputs</i>							
HMF	Tonnes per year	1545	4711	4705	2201	1726	1734
HMF ethers	Tonnes per year	17,960	17,960	17,960	17,960	17,960	17,960
LA	Tonnes per year	282	1118	1117	1158	1817	1803
LA esters	Tonnes per year	2558	3371	3347	5534	6500	6486
Product basket	Tonnes per year	22,346	27,160	27,131	26,854	28,003	27,985
FDCA	Tonnes per year	44%	41%	38%	46%	47%	43%
PEF	Tonnes per year	20,000	20,000	20,000	20,000	20,000	20,000
		23,340	23,340	23,340	23,340	23,340	23,340

Table 9 Energy balance of the six cases analyzed

		Case					
		1	2	3	4	5	6
Condenser	MW	-12.5	-18.7	-19.4	-14.5	-16.6	-17.6
Reboiler	MW	9.7	16.7	17.4	12.3	13.5	14.3
CHP	MW	-17.2	-18.6	-19.3	-15.6	-14.9	-14.7
Total utilities	MW	-19.9	-20.6	-21.3	-17.8	-18.0	-18.0

HMF ethers, LA and LA esters. In order to become economically viable, prices of the four products would probably need to be in the same order, which would result in the similar NREU (GJ per tonne) and GHG emissions in the case of economic allocation.

4. Results

4.1. Material and energy balance

The mass balances of the six cases analyzed are shown in Table 8. Interestingly, there is no significant difference between using fructose or HFCS in terms of mass yield of overall products. The mass yields of the Furanics product basket (defined as HMF, HMF ethers, LA and LA esters) are around 50% of the sugar

input; this is clearly better compared to some other biobased monomers, such as maize based polyethylene (30%).³⁹

4.2. Environmental impacts

The NREU of the six cases is calculated in several steps. First, the NREU and CO₂ emissions of the product basket are calculated, using the mass and energy flows from the ASPEN Plus model, shown in Tables 8 and 9. The values for HMF and HMF ethers are then used to calculate the NREU and CO₂ emission for production of FDCA and subsequently PEF, using the stoichiometric formula in Section 2.2.2 and the values for the oxidation and polymerization processes presented in Section 3.

In all cases PEF has a significantly lower environmental impact than PET (Table 10 and Fig. 8). This is primarily caused by a lower NREU and CO₂ emissions of the product basket, while the conversion of HMF and HMF ethers to PEF is modeled by analogy with the conversion from *p*-xylene to PET (see Section 2.2.2). As Fig. 8 shows, the NREU reduction is roughly in the same range (42% to 52%) for all PEF cases. This effect is caused by the chosen partitioning method (as explained in Section 3.2): despite the different yields for HMF, HMF ethers, LA and LA esters for each case, this effect is largely cancelled out as a consequence of mass partitioning methodology applied for the NREU and GHG emissions.

Table 10 Results of the environmental impact analysis for the system cradle to grave (see Tables 1–4 for specification of the cases)

		Case					
		1	2	3	4	5	6
<i>NREU/GJ per tonne</i>							
NREU product basket		-1.54	3.68	4.83	3.89	3.91	5.57
NREU FDCA		10.4	15.0	16.0	15.3	15.3	16.8
NREU PEF		33.8	37.8	38.6	38.0	38.0	39.3
NREU PET		69.4	69.4	69.4	69.4	69.4	69.4
NREU reduction PEF vs. PET		51%	46%	44%	45%	45%	43%
<i>GHG emissions/tonne CO₂ eq. per tonne</i>							
GHG emissions product basket		-0.09	0.22	0.29	0.23	0.23	0.33
GHG emissions FDCA		0.59	0.87	0.93	0.88	0.88	0.97
GHG emissions PEF		2.05	2.29	2.34	2.30	2.30	2.38
GHG emissions PET		4.44	4.44	4.44	4.44	4.44	4.44
GHG emissions reduction PEF vs. PET		54%	48%	47%	48%	48%	46%

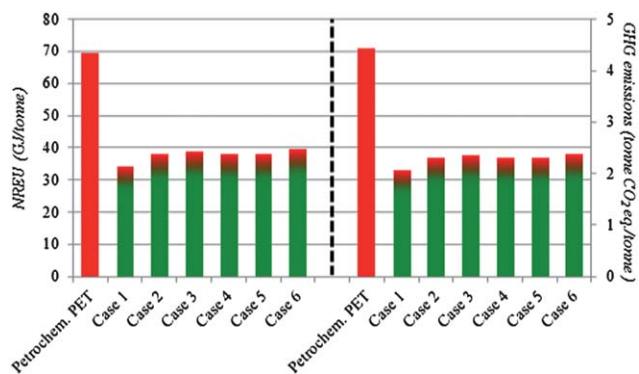


Fig. 8 Results of the environmental impact analysis for the system cradle to grave (see Tables 1 to 4 for specification of the cases). (Petrochemical components are presented in red, while green refers to a biobased component. The red top for case 1 to 6 represents petrochemical EG.)

The production of humins is the major by-product in the Furanics conversion. Since humins are not considered sellable products, they are used for on-site power production in the CHP and thus provide enough power and steam to make the core of the process, the Furanics conversion, self-sufficient. Excess energy (heat and electricity) is used in the fructose production or is fed to the grid, in which case a credit is given, based on primary energy†††. The CO₂ emissions caused by the combustion of humins are considered carbon neutral and are not included in the overall GHG emissions caused by the PEF system.

During the polymerization of FDCA, ethylene glycol is needed. EG can be produced *via* petrochemical processes, which is the base assumption of this study. However, EG can also be produced from biobased feedstocks, such as maize and sugarcane (today and expected future values) and are reported in Section 3. The influence of using biobased EG can be seen in case PEF+ (a) and PEF+ (b) in Fig. 9.

When comparing PEF with other biobased plastics, it can be seen that its performance for reducing environmental impacts is significantly better compared to other biopolymers (Fig. 10). PEF+ has the lowest environmental impact and is actually followed by petrochemical based high density polyethylene (HDPE) in terms of CO₂ emission reductions. HDPE is followed by biobased (maize) polyethylene (PE), with a factor two higher for CO₂ emission reductions when compared to PEF+ (Fig. 10).

5. Discussion

5.1. Discussion regarding modeling assumptions

One of the main uncertainties in the ASPEN Plus modeling is the burning of the humins fraction in a CHP unit. To the authors' knowledge, no commercial application currently exists, but it is expected that it should be technically possible. Humins are expected to be an excellent fuel for a CHP unit, since they are free of water. The consistency resembles viscous heavy crude oil. As the results of the model show, the energy benefits of using the humins fraction for onsite heat and power cannot be neglected,

††† If heat is exported, the credits are calculated based on 85% efficiency of fossil based feedstocks to heat. If electricity is exported, the credits are calculated based on 35% efficiency of fossil based feedstocks to electricity.

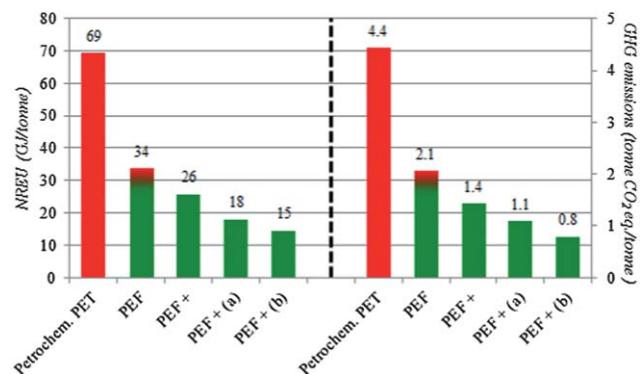


Fig. 9 The influence of biobased ethylene glycol (cradle-to-grave). (Petrochemical components are presented in red, while green refers to a biobased component.) (PEF = use of petrochemical EG; PEF+ = use of EG from maize; PEF+(a) = use of EG from sugarcane today; PEF+(b) = use of EG from sugarcane 2020.)

for it makes the system self-sufficient in terms of energy use, achieving significant reductions in NREU. Therefore the need arises to demonstrate that humins can be burned effectively in a CHP unit, through pilot and demonstration plants.

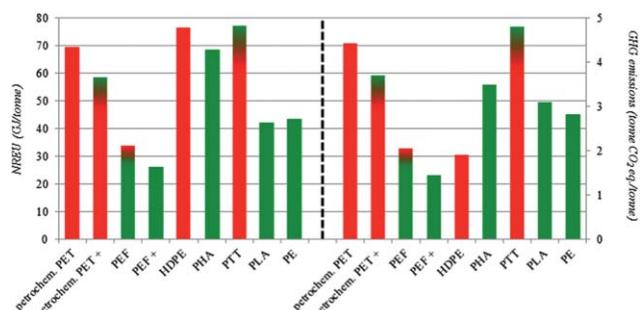


Fig. 10 Comparison of petrochemical PET and biobased PEF with other biobased plastics from maize for cradle-to-grave. (Petrochemical components are presented in red, while green refers to a biobased component.) (PET = petrochemical PTA and petrochemical EG;⁴¹ PET+ = petrochemical PTA⁴¹ and biobased EG from maize (best practice today);³⁹ PEF = biobased FDCA (results according to this paper) and petrochemical EG;⁴¹ PEF+ = biobased FDCA (results according to this paper) and biobased ethylene glycol from maize (best practice today);³⁹ HDPE = petrochemical HDPE;⁵¹ PHA = biobased (maize) PHA;⁵² PTT = petrochemical PTA⁴¹ and biobased (maize) 1,3-propanediol (PDO);³⁰ PLA = biobased (maize) PLA;³² PE = biobased PE³⁰.)

Table 11 Status of the plastics presented in Fig. 10

Plastic	Status	Source
PET	Fully commercialized industry	
PET+	Commercial bottle by Coca Cola company	53
PEF	Pilot scale	54
PEF+	Lab scale	23
HDPE	Fully commercialized industry	51
PHA	Demonstration/pilot plant phase	52,55
PTT	First commercial plant in operation (SORONA, DuPont)	56
PLA	First commercial plants in operation (NatureWorks, PURAC)	55
PE	First commercial plant in operation (Braskem)	55

The NREU and CO₂ emissions of fructose and HFCS had to be estimated since no process data from industry processes could be found. Further research should elucidate the actual NREU demand also taking into account the potential energy surplus realized by the CHP unit further in the Furanics process. In an integrated process, the production of fructose and HFCS could be coupled with a PEF plant, integrating heat demands across the entire plant, *e.g.* excess heat from the CHP could be used for the evaporation of the water in the HFCS process.

As presented in Section 2.2.2, preliminary experimental results show several advantages of HMF and HMF ether oxidation and polymerization into PEF, as compared to PET.^{36,37} However, as presented in the system overview, the oxidation and polymerization processes into PEF are not modeled in ASPEN Plus. The improvements presented in the literature, such as lower temperatures and pressures, as well as reduced acetic acid oxidation to CO₂ need to be quantified and verified by process data. If the benefits of PEF oxidation and polymerization over the production process of PET could be quantified and accounted for in the ASPEN Plus model, this would most likely reduce the energy needed and the related GHG emissions.

5.2. Discussion regarding allocation methods and PEF chain analysis

Because the Furanics process produces a range of products of interest, the NREU and CO₂ emissions had to be partitioned over HMF, HMF ethers, LA, LA esters and others (MF, furfural, humins). This partitioning was done on mass basis, as explained in Section 3.2. However, with large scale commercialization and an established market, economic partitioning based on market prices would be preferred.

The key characteristic of economic partitioning is that the compound with the highest value per tonne in the product basket will have the biggest share of the environmental impact, as shown in the following tables (Tables 12–14).

There is an interesting effect when the NREU of the process is negative (in this study only case 1, see results in Table 10). Normally the environmental impacts have to be distributed and the most expensive product, *i.e.* the product for which the process is primarily optimized, receives the biggest share of these impacts. As can be seen in Table 12, LA is the most expensive product, thus receiving the biggest share of the environmental impacts (14.95 GJ per tonne LA), even though the amount produced is the smallest.

However, if the process produces a credit, for example by producing excess power that can be transported to the grid, this credit has to be distributed across the outputs as well. Thus, again, the most expensive product, in this case LA, receives the biggest share of these credits (−5.76 GJ per tonne LA).

When comparing the two different allocation options for case 1, it can be seen that the difference in NREU and GHG emissions is not that significant and differs by 4% to 8% (Table 14).

In this energy and GHG emissions study, the assumption was made that PEF is disposed in a MSWI without energy recovery. The results could potentially be more favorable if a MSWI with energy recovery was assumed and credits for heat and power production were to be allocated to PEF, as discussed in Section 4.2. Another option that can reduce the NREU and GHG emission is to assume PEF is recycled. A study by Shen *et al.*⁵⁸ found that PET recycling to produce PET fibers can reduce the NREU by 40% to 85% and GHG emissions by 25% to 75%, compared to virgin PET fibers and depends on the recycling technology used, allocation methods and system boundaries.⁵⁸

Table 12 Results of the economic allocation, normalized to 1 tonne fructose input

Outputs	Yield/tonne	Price/€ per tonne	Total value/€	Economic share (%)	Economic partitioning/GJ per tonne output	Economic partitioning/GJ per tonne output
HMF+HMF ethers	0.42	1775.00 ^a	752.92	88%	3.52	8.29 GJ per tonne HMF + HMF ethers
LA	0.01	3200.00 ^b	19.60	2%	0.09	14.95 GJ per tonne LA
LA esters	0.06	1500.00 ^c	83.45	10%	0.39	7.01 GJ per tonne LA esters
Water	0.30	0.00	0.00	0%	0.00	0.00 GJ per tonne water
Others: (MF, furfural, humins)	0.21	0.00	0.00	0%	0.00	0.00 GJ per tonne others
Total	1.00		855.97	100%	4.00	

^a Based on the spot price of *p*-xylene. ^b Based on A.D. Patel *et al.*⁵⁷ ^c Based on Avantium Chemicals B.V.²³

Table 13 Results of the economic allocation, normalized to 1 tonne fructose input and a negative process NREU

Outputs	Yield/tonne	Price/€ per tonne	Total value/€	Economic share (%)	Economic partitioning/GJ per tonne output	Economic partitioning/GJ per tonne output
HMF HMF ethers	0.42	1775.00	752.92	88%	−1.35	−3.19 GJ per tonne HMF + HMF ethers
LA	0.01	3200.00	19.60	2%	−0.04	−5.76 GJ per tonne LA
LA esters	0.06	1500.00	83.45	10%	−0.15	−2.70 GJ per tonne LA esters
Water	0.30	0.00	0.00	0%	0.00	0.00 GJ per tonne water
Others: (MF, furfural, humins)	0.21	0.00	0.00	0%	0.00	0.00 GJ per tonne others
Total	1.00		855.97	100%	−1.54	

Table 14 Comparison of mass and economic allocation for case 1 and its effect on the NREU and GHG emissions of PEF

		Economic Positive NREU	Mass	Economic Negative NREU	Mass
HMF + HMF ethers	GJ per tonne HMF + HMF ethers	8.29	4.00	-3.19	-1.54
FDCA	MJ per kg FDCA	19.19	15.37	8.97	10.44
PEF	MJ per kg PEF	41.34	38.07	32.58	33.84
FDCA	Tonne CO ₂ eq. per tonne FDCA	1.12	0.89	0.51	0.59
PEF	Tonne CO ₂ eq. per tonne PEF	2.50	2.31	1.98	2.05

In Section 3, we reported NREU and CO₂ emissions for petrochemical PET to be 69.4 GJ per tonne and 4.44 tonnes CO₂ eq. per tonne.⁴¹ This is in contrast with the data reported in 2005, where PlasticsEurope reported NREU and CO₂ emissions of 80.75 GJ per tonne and 5.59 tonnes CO₂ eq. per tonne, respectively^{†††}. The values for 2010 thus represent a reduction of 14% in NREU and 20% in CO₂ eq. emissions. These reductions are intriguing and according to PlasticsEurope are related to improvements in PTA production.⁵⁹ Further analysis is required in order to understand the effects of technological progress in individual steps and of process and heat integration. The results of the PEF analysis are consistent with the 2010 values of PET (69.4 GJ per tonne, 4.44 tonne CO₂ eq. per tonne). If the 2005 values of PET are used (80.75 GJ per tonne, 5.59 tonne CO₂ eq. per tonne), a 7% increase in reduction is realized for NREU and 11% for GHG emissions.

5.3. Land use, direct and indirect land use change emissions

The production of PEF starts with the production of corn derived dextrose for its monomer FDCA. Typical land use for dextrose production is 0.13 ha per tonne of dextrose after partitioning.³⁰ Starting from 1 tonne of dextrose, 0.56 tonne of PEF is produced^{§§§}, which results in an associated land use of 0.23 ha per tonne of PEF.

The use of corn feedstocks to produce PEF opens the door for the emissions caused by indirect land use change. Most GHG emission studies on biobased products (biofuels or bioplastics) show that overall GHG emissions can be reduced compared to fossil based products, by harnessing carbon dioxide sequestration from the atmosphere as a consequence of photosynthesis during plant growth.⁶⁰ In 2008, Searchinger *et al.* introduced the carbon cost concept: the accounting for the loss of carbon stored in the biosphere as a consequence of land use change (LUC). He distinguished two types of LUC emissions: (1) emissions caused by direct land use change (dLUC^{¶¶¶}) and (2) emissions caused

^{†††} A study by Worrell *et al.* reported NREU to be 78.2 GJ per tonne PET, based on the Witten DMT process, where dimethyl terephthalate (DMT) is polymerized with ethylene glycol.⁶¹ This process is being phased out due to superior qualities of the PTA route in terms of conversion efficiency and capital investments. However, DMT is still used in the production of PET films, which makes up less than 10% of the PET market.

^{§§§} The remainder of 0.44 tonne consists of LA and LA esters, as well as a large humins fraction, which is burned in the CHP for onsite heat and power.

^{¶¶¶} dLUC refers to the process of creating new agricultural acreage for the production of feedstocks for biobased products (fuels and plastics), thus displacing prior land use, *e.g.* the conversion of rain forests to sugarcane plantations.

by indirect land use change (iLUC^{|||||}). iLUC emissions also include CH₄ emissions^{****} caused by a loss in the oxidation potential of CH₄ in aerobic soils, next to the release of (biobased or fossil) methane from technical systems^{62,63} and N₂O emissions by increased use of fertilizers and organic matter decomposition in soils.⁶³ It also accounts for the carbon debt^{†††††} left by clearing virgin forests and grasslands (either through dLUC and/or iLUC).

Since the publication by Searchinger *et al.*,⁶⁰ the debate about GHG emissions caused by dLUC and iLUC for the production of biofuels and bioplastics has gained momentum. Searchinger *et al.* reported an iLUC value of roughly 1, meaning every extra acre of corn production diverted to the production of biofuels would cause an acre of tropical rain forests or grassland to be converted. Since 2008, more research into LUC factors has been done and estimates for the iLUC factor are now between 0.15 and 0.30.⁶⁴ iLUC could potentially be mitigated by good governance, management, and certification to protect existing carbon stocks.⁶⁵

The state of California has included iLUC into the state's Low Carbon Fuels Standard (LCFS) and assumes a value of 30 grams per MJ for corn based ethanol.⁶⁶ Other studies present a value of between 7 and 14 grams per MJ.^{67,68} The lack of data and understanding of the complex global system prevents consensus on a single value for iLUC emissions. A study by Plevin *et al.*⁶⁹ presents a range of iLUC values for US based corn to ethanol production between 21 and 142 grams of CO₂-equivalent per MJ ethanol with the median range between 55 and 59 grams of CO₂-equivalent per MJ ethanol. California's LCFS assumes a value of 30 grams MJ⁻¹,⁶⁶ which will be updated to 14 grams MJ⁻¹,⁶⁷ while Nassar *et al.* assume a value of 7 grams MJ⁻¹⁶⁸ (see Table 15).

Table 16 and Fig. 11 show that when iLUC values are included in the calculation (30, 14 and 7 grams CO₂ equivalent per MJ ethanol were assumed), they can influence the final reduction potential of PEF compared to petrochemical PET. Without iLUC included, PEF has a reduction of 54% for GHG emissions

^{|||||} iLUC refers to the process where acreage currently used for the production of food crops is changed to the production of feedstocks for biobased products (fuels and plastics), while the demand for the former land use (*i.e.* food crops) remains. The displaced production of food crops will move to other locations around the world where undesirable land use change may occur (*e.g.* Brazil).^{70,71}

^{****} CH₄ and N₂O are considered the two most important GHGs when calculating the global warming potential (GWP) of a biobased product. GWP is expressed as CO₂-equivalents, meaning the effects of CH₄ and N₂O are expressed relatively to the effect of CO₂. CH₄ has a factor of 24 and N₂O has 298, while CO₂ has a factor of 1.⁷²

^{†††††} Carbon debt refers to carbon previously stored in plants and soils and then released to the atmosphere.^{60,73} It also accounts for the displacement of future carbon sequestration of plants and soils.

Table 15 Different iLUC values in the literature

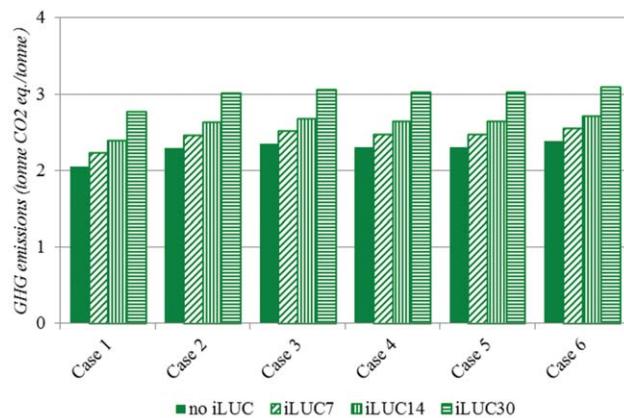
Source	iLUC value	Unit
Plevin <i>et al.</i> , 2010 (ref. 69)	55–59	Grams CO ₂ equivalent per MJ ethanol
Low Carbon Fuels Standard (LCFS) (ref. 66)	30	Grams CO ₂ equivalent per MJ ethanol
Purdue, 2010 (ref. 67)	7–14	Grams CO ₂ equivalent per MJ ethanol
Nassar <i>et al.</i> , 2010 (ref. 68)	7	Grams CO ₂ equivalent per MJ ethanol

compared to PET (Table 16). With an iLUC value of 30 grams per Megajoule for corn based ethanol, this reduction drops down to 38%. However, it is important to note that the research into iLUC factors is still under development and an increased understanding of the many mechanisms involved with iLUC will decrease the uncertainty regarding the iLUC values.

5.4. Shift towards lignocellulosic biomass

Recently, research in the field of biobased products has shifted towards the use of non-food commodities, also known as lignocellulosic biomass, which contain about two-thirds polysaccharides and one-third lignin. The advantages of lignocellulosic biomass are that the yields per hectare are higher, as compared to corn; the GHG emissions per tonne are lower; they do not compete with food crops, as long as no agricultural land is used for its cultivation; and lastly, iLUC effects are non-existent or negligible when marginal or degraded lands are used for its cultivation.⁷⁴

However, the difficulty in using lignocellulosics lies in the fact that the fractionation into useable products requires large amounts of energy and of chemicals, which is primarily caused by lignin removal. Given the early stage of development of the conversion of lignocellulosics into useable sugar product stream and consequently to Furanics, it would be premature at this stage to present energy and GHG emission results on Furanics from such feedstocks. The use of lignocellulosics for Furanics is researched within the CATFUR project, a research corporation between Avantium Technologies B.V., the Energy Research

**Fig. 11** The influence of indirect land use change.

Centre of the Netherlands (ECN) and the Copernicus Institute at Utrecht University (UU).⁷⁵

5.5. The use of biobased byproducts for process energy

The major byproduct that is formed during the Furanics conversion is humins. As a consequence of their complex chemical structure, humins cannot be upgraded further to sellable products and instead they are used for on-site power production in the CHP. The combustion of humins provides enough power and steam to make the core of the process (*i.e.*, the conversion of fructose to HMF and HMF ethers) self-sufficient. This on-site production of process energy significantly reduces overall NREU and GHG emissions of PEF. The process energy for PET production (total process chain) is typically provided through the combustion of natural gas, low value streams from crude oil refining and from naphtha. There is no technical reason why the process energy for PET could not be provided by biomass, thus reducing NREU and GHG emissions of PET as well. The reason why biomass is not used for process energy in PET production is mainly related to costs and local unavailability. Onsite availability of low value biobased byproducts reduces the costs for transport and logistics as compared to the supply of bioenergy to a petrochemical complex. The collaborative relationship between manufacturers of biobased products

Table 16 Influence of iLUC values on GHG reductions for cradle-to-grave^a

	Case					
	1	2	3	4	5	6
GHG emissions PEF without considering iLUC/tonnes CO ₂ eq. per tonne PEF	54%	48%	47%	48%	48%	46%
GHG emissions PEF—ILUC30/tonne CO ₂ eq. per tonne PEF	38%	32%	31%	32%	32%	30%
GHG emissions PEF—ILUC14/tonne CO ₂ eq. per tonne PEF	46%	41%	40%	41%	41%	39%
GHG emissions PEF—ILUC7/tonne CO ₂ eq. per tonne PEF	50%	45%	44%	44%	44%	43%

^a Note: the values of 30, 14 and 7 grams of CO₂ per MJ ethanol were converted back to yield an iLUC value for the fructose, which is then applied to the PEF production process. Example: 30 grams CO₂ per MJ ethanol × 25 MJ kg⁻¹ ethanol = 750 grams CO₂ per kg ethanol. 750 grams CO₂ per kg ethanol/2.2 kg dextrose per kg ethanol = 340 grams CO₂ per kg dextrose. 340 grams CO₂ per kg dextrose × 2 kg dextrose per kg PEF = 680 grams CO₂ per kg PEF. 14 grams CO₂ per MJ ethanol = 320 gram CO₂ per kg PEF. 7 grams CO₂ per MJ ethanol = 160 grams CO₂ per kg PEF.

and the agricultural sector could provide an additional cost advantage, *e.g.* through long-term contracts. Furthermore, the use of bioenergy would only become an option at large scale if the price of natural gas and that of biobased feedstocks converged to similar levels. However, this remains highly unlikely for the short and midterm.

6. Conclusions

Even though the PEF production process from fructose and HFCS is still under development, the energy and GHG emission results presented here show that the process is likely to offer reductions between 43% (case 6) and 51% (case 1) for NREU and 46% (case 6) to 54% (case 1) for GHG emissions. If the effect of iLUC is included, the reductions for GHG emissions drop from 46% (case 6; no iLUC) to 30% for the worst performing case (case 6; iLUC30) and from 54% (case 1; no iLUC) to 38% (case 1; iLUC30) for the best performing case.

Based on the global PET bottle market (approximately 15 Mt per year⁴ or approx. 1/3 of the global PET production), complete substitution of PEF for PET would result in savings of 520 PJ for NREU and 35 Mt of CO₂ eq. respectively for the best performing case (case 1) and 440 PJ and 20 Mt of CO₂ eq. for the worst performing case (case 6, iLUC30). To put these absolute savings in perspective, they can be compared to the primary energy supply and GHG emissions of the Netherlands^{†††††⁷⁵}

(entire country covering emissions from all sectors of the economy): the savings related to the global replacement of petrochemical PET by biobased PEF would allow us to avoid 12 to 16% of the Netherlands's total NREU and 11 to 20% of its GHG emissions. The savings increase accordingly when substantial replacement of PEF for PET takes places in the fibre production, which accounts for approx. 2/3 of the global PET production.

Compared to other biobased plastics currently under development, PEF production is clearly superior, as shown in Fig. 10 (PEF 2.1 tonne CO₂ eq. per tonne and PEF+ 1.4 tonne CO₂ eq. per tonne vs. PHA 3.5 tonne CO₂ eq. per tonne, PLA 3.1 tonne CO₂ eq. per tonne and PE 2.8 tonne CO₂ eq. per tonne). However, the assessment is based on modeled process data. The technology must hence be proven in demonstration plants, followed by an update of the environmental assessment, if necessary. Moreover, due to the possible adverse effects of land use changes, the transition towards biobased products produced from lignocellulosic biomass should be fostered and assessments similar to the one presented in this paper should be conducted for lignocellulosic feedstocks.

Acknowledgements

This study has been supported by the Innovation vouchers program of the Dutch Government (Furanix Technologies: G101578 and Avantium Chemicals: G101580). The authors would like to express their gratitude to Ed de Jong, Ana de Sousa Dias and Jan Kees van der Waal at Avantium Chemicals B.V. for their valuable insights into the biobased furan pathway production of bioplastics. The authors would also like to thank

††††† In 2008, the primary energy supply in the Netherlands was 3.34 EJ and GHG emissions were 183 Mt of CO₂ eq.⁷⁶

two colleagues at our department: Birka Wicke for contributing her insights into the iLUC discussion and Değer Saygin for his insights into energy and emission accounting at the country level.

References

- 1 L. Shen, E. Worrell and M. K. Patel, *Biofuels, Bioprod. Biorefin.*, 2010, **4**, 25–40.
- 2 K. Balser, L. Hoppe, T. Eicher, M. Wandel, H. J. Astheimer, H. Steinmeier, *et al.*, Cellulose Esters, in *Ullman's Encyclopedia of Industrial Chemistry 2007*, Wiley-VCH Verlag GmbH & Co, KGaA, Weinheim, 7th edn, 2004.
- 3 L. Shen, *PhD thesis*, Utrecht University, Utrecht, the Netherlands, 2011.
- 4 Plastics Europe Market Research Group (PEMRG), *Business Data and Charts 2009/2010—Status April 2011*, Plastics Europe, 2011.
- 5 IEA—International Energy Agency, *Energy Balances for Non-OECD Countries—2010 Edn*, OECD/IEA, Paris, France, 2010.
- 6 T. Werpy, J. Holladay and J. White, *Top Value Added Chemicals from Biomass*, PNNL-14808, Pac. Northwest Nat. Lab., Richland, WA, 2004, <http://www1.eere.energy.gov/biomass/pdfs/35523.pdf>.
- 7 J. J. Bozell and G. R. Petersen, Technology development for the production of biobased products from biorefinery carbohydrates—The US department of energy's “Top 10” Revisited, *Green Chem.*, 2010, **12**, 539–554.
- 8 P. Vinke, H. E. van Dam and H. van Bekkum, Platinum catalyzed oxidation of 5-hydroxymethylfurfural, *Stud. Surf. Sci. Catal.*, 1990, **55**, 147–158.
- 9 J. Lewkowski, Synthesis, chemistry and applications of 5-hydroxymethylfurfural and its derivatives, *ARKIVOC*, 2001, **i**, 17–54.
- 10 X. Tong, Y. Ma and Y. Li, Biomass into chemicals: conversion of sugars to furan derivatives by catalytic processes, *Appl. Catal. A*, 2010, **385**(1–2), 1–13.
- 11 K. J. Zeitsch, *The Chemistry and Technology of Furfural and its many By-products*, Sugar Series 13, Elsevier, Amsterdam, 1st edn, 2000.
- 12 M. Kröger, U. Prüße and K. D. Vorlop, A new approach for the production of 2,5-furandicarboxylic acid by *in situ* oxidation of 5-hydroxymethylfurfural starting from fructose, *Top. Catal.*, 2000, **13**, 237–242.
- 13 B. Kamm, P. R. Gruber and M. Kamm, *Biorefineries—Industrial Processes and Products*, Wiley-VCH, Verlag GmbH & Co. KGaA, Weinheim, 2006.
- 14 G. J. M. Gruter and E. de Jong, Furanics: novel fuel options from carbohydrates, *Biofuel Technol.*, 2009, **1**, 11–17.
- 15 A. Gaset, L. Rigal, G. Paillassa, J. P. Salomé, and G. Flèche, *US Pat.*, 4590283, 1986.
- 16 K. M. Rapp, *US Pat.*, 4740605, 1988.
- 17 A. A. Rosatella, S. P. Simeonov, R. F. M. Frade and C. A. M. Afonso, 5-Hydroxymethylfurfural (HMF) as a building block platform: biological properties, synthesis and synthetic applications, *Green Chem.*, 2011, **13**, 754–793.
- 18 G. W. Huber, S. Iborra and A. Corma, Synthesis of transportation fuels from biomass: chemistry, catalysts and engineering, *Chem. Rev.*, 2006, **106**, 4044–4098.
- 19 G. J. M. Gruter and F. Dautzenberg, *EU Pat.* 1834950A1, 2007.
- 20 G. J. M. Gruter and F. Dautzenberg, *EU Pat.* 1834951A1, 2007.
- 21 M. J. Antal, W. S. L. Mok and G. N. Richards, Mechanism of formation of 5-(hydroxymethyl)-2-furaldehyde from D-fructose and sucrose, *Carbohydr. Res.*, 1990, **199**, 91–109.
- 22 J. Horvat, B. Klaic, B. Metelko and V. Sunjic, Mechanism of levulinic acid formation, *Tetrahedron Lett.*, 1985, **26**(17), 2111–2114.
- 23 E. de Jong and J. C. van der Waal, Avantium Chemicals B.V., Amsterdam, The Netherlands, personal communication.
- 24 Y. Román-Leshkov, J. N. Chheda and J. A. Dumesic, Phase modifiers promote efficient production of hydromethylfurfural from fructose, *Science*, 2006, **312**, 1933–1937.
- 25 Biofine Renewables, LLC, 2011, <http://mainebioproducts.com/default.asp?page=default&topic=Technology>.
- 26 Segetis, 2011, <http://www.segetis.com/>.
- 27 J. P. Lange, K. Prince, P. M. Ayoub, J. Louis, L. Petrus, L. Clarke and H. Gosselin, Valeric biofuels: a platform of cellulosic transportation fuels, *Angew. Chem., Int. Ed.*, 2010, **49**(26), 4479–4483.
- 28 NIST, 2011, <http://trc.nist.gov/tde.html>.

- 29 R. Hoefnagels, E. Smeets and A. P. C. Faaij, Greenhouse gas footprints of different biofuel production systems, *Renewable Sustainable Energy Rev.*, 2010, **14**, 1661–1694.
- 30 M. K. Patel, M. Crank, V. Dornburg, B. Hermann, L. Roes, B. Hüsing, L. van Overbeek, F. Terragni and E. Recchia, *Medium and Long-term Opportunities and Risks of the Biotechnological Production of Bulk Chemicals from Renewable Resources—The BREW Project*, Utrecht University, The Netherlands, September 2006, <http://www.chem.uu.nl/brew/>.
- 31 L. Hobbs, in *Starch: Chemistry and Technology*, Elsevier, Amsterdam, 3rd edn, 2009, ch. 21, pp. 797–832.
- 32 E. T. H. Vink, S. Davies and J. J. Kolstad, The eco-profile for current Ingeo® polylactide production, *Ind. Biotechnol.*, 2010, **6**(4), 212–224.
- 33 E. C. Ramirez, D. B. Johnston, A. J. McAloon, W. Yee and V. Singh, Engineering process and cost model for a conventional corn wet milling facility, *Ind. Crops Prod.*, 2008, **27**, 91–97.
- 34 *Corn Sweetener Refining With Ion Exchange Resins*, The Purolite Company, 2007, http://www.purolite.com/customized/uploads/pdfs/purolite_corn_sweetener_guide_011807.pdf.
- 35 A. Chauvel and G. Lefebvre, *Petrochemical Processes, volume 2: Major Oxygenated, Chlorinated and Nitrated Derivatives*, Institute Français Du Pétrole Publications, Éditions Technip, 1989, ch. 13, pp. 291–293.
- 36 C. Muñoz de Diego, W. P. Schammel, M. A. Dam and G. J. M. Gruter, *WO Pat.*, 043660A2, 2011.
- 37 C. Muñoz de Diego, M. A. Dam and G. J. M. Gruter, *WO Pat.*, 043661A1, 2011
- 38 *CCaLC Carbon Footprinting Tool (V2.0), Carbon Calculations over the Life Cycle of Industrial Activities*, University of Manchester, version 2.0, 2010, <http://www.ccalc.org.uk/>.
- 39 M. K. Patel and G. Chen, *Chem. Rev.*, DOI: 10.1021/cr200162d.
- 40 I. Boustead, *Ecoprofile of Natural Gas*, PlasticsEurope, 2005, <http://www.plasticseurope.org/plastics-sustainability/eco-profiles.aspx>.
- 41 *Ecoprofile of Polyethylene Terephthalate (PET) (Bottle Grade)*, PlasticsEurope, May 2011, <http://www.plasticseurope.org/plastics-sustainability/eco-profiles.aspx>.
- 42 I. C. Macedo, J. E. A. Seabra and J. E. A. R. Silva, Green house gases emissions in the production and use of ethanol from sugarcane in Brazil: the 2005/2006 averages and a prediction for 2020, *Biomass Bioenergy*, 2008, **32**, 582–595.
- 43 *Handbook of Chemistry and Physics*, W. M. Haynes and D. R. Lide, 91st edn, 2011.
- 44 I. Boustead, *Ecoprofile of Polyethylene Terephthalate (PET) (Amorphous Grade)*, PlasticsEurope, March 2005, <http://www.plasticseurope.org/plastics-sustainability/eco-profiles.aspx>.
- 45 J. Reap, et al. A survey of unresolved problems in life cycle assessment, part 1: goal and scope and inventory analysis, *Int. J. Life Cycle Assess.*, 2008, **13**, 290–300.
- 46 L. Shen, E. Worrell and M. K. Patel, Environmental impact assessment of man-made cellulose fibres, *Resour., Conserv. Recycl.*, 2010, **55**, 260–274.
- 47 E. de Jong, *Presented at the 7th Conference on Renewable Resources and Biorefineries*, Bruges, Belgium, June 2011.
- 48 P. Pawelzik and M. K. Patel, Utrecht University, Utrecht, The Netherlands, unpublished work.
- 49 ISO, *ISO14040: Environmental Management—Life Cycle Assessment—Principles and Framework*, 2006.
- 50 ISO, *ISO14044: Environmental Management—Life Cycle Assessment—Requirements and Guidelines*, 2006.
- 51 I. Boustead, *Ecoprofile of High Density Polyethylene (HDPE)*, PlasticsEurope, March 2005.
- 52 S. Kim and B. E. Dale, Life cycle assessment of biopolymers (polyhydroxyalkanoates) derived from no-tilled corn, *Int. J. Life Cycle Assess.*, 2005, **10**(3), 200–210.
- 53 The Coca Cola Company, *Introducing Plant Bottle*, 2011, <http://www.thecoca-colacompany.com/citizenship/plantbottle.html>.
- 54 Avantium Announces Start-up of YXY Polyester Pilot Plant, Avantium Chemicals B.V., 2011, <http://www.yxy.com/Avantium-announces-start-up-of-YXY-polyester-pilot-plant/>.
- 55 L. Shen, J. Haufe and M. K. Patel, *Product Overview and Market Projection of Emerging Bio-based Plastics—PRO-BIP 2009 Final Report*, Utrecht University, the Netherlands, November 2009, <http://www.projects.science.uu.nl/nws/publica/Publicaties%202009/PROBIP2009%20Final%20June%202009.pdf>.
- 56 Dupont, *Sorona® Renewably Sourced Fiber*, 2011, http://www2.dupont.com/Sorona_Consumer/en_US.
- 57 A. D. Patel, et al., Techno-economic analysis of 5-nonenone production from levulinic acid, *Chem. Eng. J.*, 2010, **160**, 311–321.
- 58 L. Shen, E. Worrell and M. K. Patel, Open-loop recycling: an LCA case study of PET bottle-to-fibre recycling, *Resour., Conserv. Recycl.*, 2010, **55**, 34–52.
- 59 I. Mersiowsky, DEKRA Certification GmbH, Stuttgart, Germany, personal communication.
- 60 T. Searchinger, R. Heimlich, R. A. Houghton, F. Dong, A. Elobeid, J. Fabiosa, S. Tokgoz, D. Hayes and T. H. Yu, Use of U.S. croplands for biofuels increases greenhouse gases through emissions from land-use change, *Science*, 2008, **319**, 1238–1240.
- 61 E. Worrell, R. J. J. van Heijningen, J. F. M. de Castro, J. H. O. Hazewinkel, J. G. de Beer, A. P. C. Faaij and K. Vringer, New gross energy-requirements figures for materials production, *Energy*, 1994, **19**(6), 627–640.
- 62 D. S. Ojima, D. W. Valentine, A. R. Mosier, W. J. Parton and D. S. Schimel, Effect of land use change on methane oxidation in temperate forest and grassland soils, *Chemosphere*, 1993, **26**(1–4), 675–685.
- 63 P. Thustos, T. W. Willison, J. C. Baker, D. V. Murphy, D. Pavlikova, K. W. T. Goulding and D. S. Powlson, Short-term effects of nitrogen on methane oxidation in soils, *Biol. Fertil. Soils*, 1998, **28**, 64–70.
- 64 IPCC, *Special Report on Renewable Energy Sources and Climate Change Mitigation*, United Nations, 2011, ch. 2, <http://srren.ipcc-wg3.de/report>.
- 65 B. Wicke, P. Verweij, H. van Meijl, D. P. van Vuuren and A. P. C. Faaij, Indirect land use change: Review of existing models and Strategies for Mitigation, *Biofuels*, 2012, **3**(1), 87–100.
- 66 LCFS, http://www.energy.ca.gov/low_carbon_fuel_standard/.
- 67 W. E. Tyner, F. Taheripour, Q. Zhuang, D. Birur and U. Baldos, *Land Use Changes and Consequent CO₂ Emissions due to US Corn Ethanol Production: a Comprehensive Analysis—Final Report (revised)*, Department of Agricultural Economics, Purdue University, 2010, <http://www.transportation.anl.gov/pdfs/MC/625.PDF>.
- 68 A. M. Nassar, L. B. Antoniazzi, M. R. Moreira, L. Chiodi and L. Harfuch, *An Allocation Methodology to Assess GHG Emissions Associated with Land Use Change—Final Report*, Institute For International Trade Negotiations, 2010, <http://www.iconebrasil.org.br/arquivos/noticia/2107.pdf>.
- 69 R. J. Plevin, M. O'Hare, A. D. Jones, M. S. Torn and H. K. Gibbs, Greenhouse gas emissions from biofuels' indirect land use change are uncertain but may be much greater than previously estimated, *Environ. Sci. Technol.*, 2010, **44**, 8015–8021.
- 70 F. Cherubini, GHG balances of bioenergy systems—overview of key steps in the production chain and methodological concerns, *Renewable Energy*, 2010, **35**, 1565–1573.
- 71 U. W. Fritzsche, *The “ILUC Factor” as a Means to Hedge Risks of GHG Emissions from Indirect Land Use Change—Working Paper*, Energy & Climate Division, Öko-Institut, Darmstadt Office, 2010, <http://www.oeko.de/oekodoc/1030/2010-082-en.pdf>.
- 72 IPCC, *Climate Change 2007: The Physical Science Basis*, Cambridge University Press, Cambridge, UK and New York, USA, 2007.
- 73 V. Piemonte and F. Gironi, Land-use change emissions: how green are the bioplastics? *Environmental Progress & Sustainable Energy*, 2010, **30**(4), 685–691.
- 74 B. Wicke, PhD thesis, Utrecht University, Utrecht, The Netherlands, 2011.
- 75 The CATFUR Project, 2009–2011, <http://www.catfur.nl>.
- 76 IEA—International Energy Agency, *Energy Balances for OECD Countries—210 Edn*, Paris, France, OECD/IEA, 2010.