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FURCHEM and CatBio roadmap

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Contents

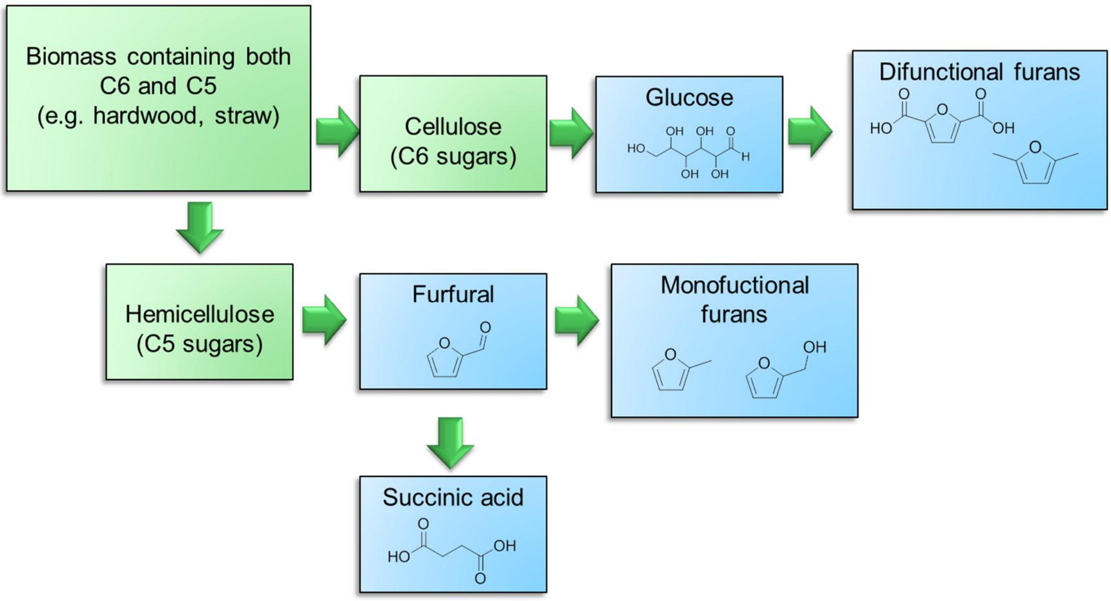
1. Background

Production of furan based platform chemicals is a potential route to bring added value to carbohydrate-rich biomass streams.

75 % of plant biomass consists of carbohydrates, which makes carbohydrates the biggest biomass fraction. CatBio and FURCHEM projects investigate potential routes from carbohydrate biomass to value-added furan based chemicals.

CatBio project - From C5 sugars through furfural to platform chemicals and fuel components.

Reactions of C5 carbohydrate sugars to furfural and further reactions of furfural to platform chemicals as well as biofuel components are reactions worth studying due to potential use of value-added end products. CatBio project investigates profoundly furfural oxygenation to **succinic acid** and other value-added by-products as well as furfural hydrogenation to **2-methylfuran.** Motivation of the project is to find alternative efficient and selective bio-based production routes to current fossil resource based alternatives. Interest of succinic acid rises from its use as a platform chemical for many specialty and commodity chemicals as well as its use in additives. Worldwide production of succinic acid annually is 50 kt in 2013. 2-Methylfuran with excellent characteristics has potential as a bio-based fuel component to be blended in traffic fuels as well as to replace current commercial oxygenates in fuel industry. Annually 50 Mt of current fuel oxygenates are used in gasoline. In the future, the share of bio-based fuel components in traffic fuels is expected to increase significantly.



Scheme 1. Monofuctional furans are obtained from C5 carbohydrates, whereas difuctional furans are obtained from C6 carbohydrates. The scheme shows an example of a value chain starting from biomass containing both C5 and C6 sugars. In addition, route to succinic acid from furfural is illustrated.

FURCHEM project - Furanic compounds as an atom-efficient route to bio-based aromatics.

Carbohydrate streams are not optimum for processes targeting traditional BTX (benzene, toluene, xylenes) aromates, because the atom-economy of the required transitions is inherently poor, irrespective of how much development work will be conducted (Figure 1). Over 53 % of the molecular weight of carbohydrates is oxygen, as carbohydrates often follow the chemical formula $C_nH_{2n}O_n$. When making BTX from carbohydrates, all oxygen must be removed and over 50 % of the carbohydrate mass is lost already at this step. However, to obtain functional BTX derived aromatic compounds, after complete de-oxygenation the BTX must be re-oxygenated for desired functionality, requiring again additional process steps. Oxygen containing BTX derivatives include some of the most common aromatics. FURCHEM project explores the possibility of using furans as replacement chemicals for BTX aromates. This roadmap will describe the application potential of various furanic compounds. In FURCHEM project, replacement of terephthalic acid (market size ca. 50 Mt/a, market price ca. 1100 €/ton) with **furan dicarboxylic acid** (FDCA) is investigated in most detail, including technology development.

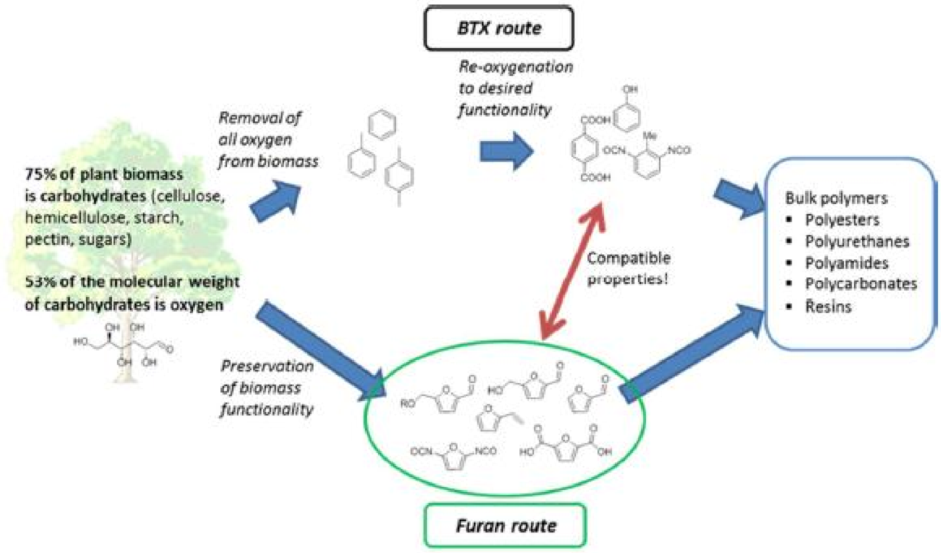


Figure 1**.** Functional furanic compounds can be prepared from carbohydrate biomass with good atom efficiency – potential to replace petroleum based aromatic compounds.

Furan biorefinery.

The production of well-defined furan compounds usually requires carbohydrate streams rich in either C5 sugars or C6 sugars – mixtures of C5 and C6 sugars are not optimal feedstocks. C5 sugars generally provide provide monofunctional furans whereas C6 sugars provide difuctional furans. A schematic value chain concept including furan chemical production from fractionated biomass is shown in Scheme 1. Succinic acid production route from furfural is also included in the scheme, as it is studied in CatBio project.

2. State-of-the-art in bio-based furans

2.1. Biomass raw materials for furan compounds in Finland

Over 15 Mt of non-food carbohydrates are produced in Finland annually. However, most of these are already utilized in applications, especially within forest industry. Potential raw material streams rich in either C6 or C5 sugars are listed in this chapter.

To produce furans, biomass rich in carbohydrates is needed. This chapter describes the carbohydrate rich raw materials available in Finland. In addition, raw materials rich in uronic acids are also looked into, as uronic acids are potential feedstocks in some interesting value chains. Since the amount of uronic acid available in Finland was not very high, the uronic acid containing biomass streams were looked into also in Europe.

The carbohydrate streams available from forest industry in Finland are listed in Table 1, whereas the carbohydrate streams available from agriculture in Finland are listed in Table 2. Side streams containing readily available (i.e. non-lignocellulosic) sugars in Finland are listed in Table 3. Uronic acid containing streams in Finland and Europe are listed in Table 4.

In all of the tables, the potential feedstock streams are listed in order based on the amount of carbohydrates available from the stream. The tables tabulate the actual stream volume, the volume of carbohydrates in the stream, the percentage of C6 sugars in the stream (rest being mainly C5 sugars), feedstock price if available, and current uses of the stream. It must be noted that the values collected into these tables originate from many sources. Therefore, the numerical values should not be taken as exact, but rather to describe the order of magnitude of the available stream.

Table 1. Carbohydrate rich forest industry related streams in Finland.

Feedstock	**Stream volume**	**Carbohydrates**	**C6 content**	**Feedstock price**	**Current use**
Stemwood	42 Mt/a (wet)	15 Mt/a (total) 12 Mt/a (softwood) 3 Mt/a (hardwood)	90% in softwood 70% in hardwood	30 € / m^3 -> ca. 60 € /t (wet pulpwood, no transportation)	pulp, paper & board, timber, energy
Chemical pulp	7 Mt/a[1]	6.5 Mt/a (total) 3.9 Mt/a (softwood) 2.6 Mt/a (hardwood)	90% in softwood 75% in hardwood	900 €/t	paper & board
Sawmill chips and sawdust	5.8 Mt/a (wet)	2 Mt/a	90% in softwood 70% in hardwood	Sawdust: 40 - 110 €/t (dry)	pulp, particle board, energy (less uses available for sawdust)
Harvest residues	5.5 Mt/a (wet)	1.9 Mt/a (total) 600 kt/a (available)		70 - 190 €/t (dry)	unused / energy
Bark	4 Mt/a (wet)	1 Mt/a		50 - 130 €/t (dry)	energy
Kraft black liquor	7 Mt/a (dry)	200 - 700 kt/a	Hardwood: lot of C5	Depends on effects to the process	energy at mill site
Recovered wood	750 kt/a (wet)	360 - 480 kt/a	> 70%	40-160 €/t (dry)	energy, recycling
Recovered paper	610 kt/a[2]	380 kt/a	80%	High	paper & board
Recovered fuel	500 kt/a	150 -200 kt/a	> 70%	Relatively high (high demand in Finland)	energy / gasification
Needles, leaves	1.4 Mt/a (wet)	120 kt/a		Low (without transportation)	unused / energy. Challenging quality, not realistic feedstock?
TMP process waters	45 - 135 Mt/a	90 kt/a	90% in softwood (mainly spruce)	Negative	No use. Would require concentration and purification.
Debarking effluent	9.4 Mt/a	9 - 60 kt/a		Negative	No use. Challenging quality, would require concentration and purification.
Deinking sludge	130 kt/a	57 kt/a	> 70%	Negative	Land construction, energy, landfill. Challenging quality.
Fiber sludge	35 kt/a	15 kt/a	> 70%	Negative	Land construction, energy, landfill.
Prehydrolysis sugars	Currently steam technology in use for dissolving pulp, does not produce extractable stream. Hardwood: lot of C5.				

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[1] Salo R. Chemical pulp production by grade (2015). At: http://www.forestindustries.fi/statistics/15-Pulp%20and%20Paper%20Industry

[2] Salo R. Recovered paper use by the Finnish industry (2015). At: http://www.forestindustries.fi/statistics/15-Pulp% and Paper Industry

Table 2. Carbohydrate rich agriculture side streams in Finland.

Feedstock	**Stream volume**	**Carbohydrates**	**C6 content**	**Feedstock price**	**Current use**
Straw	1.9 Mt/a (dry)[3]	1.1 Mt/a	65 %	50 €/t. Includes 100 km transportation range.	A large extent of straw (e.g. 50%) needs to be left to fields
Reed canary grass (ruoko-helpi)	1.1 Mt/a (max)[3] 100 kt/a (actual)	800 kt/a (max) 70 kt/a (actual)	70 %	15-60€/t (150€/t without subsidies) Includes 100km transportation range.	Max potential requires all set-aside (kesanto) fields.
Sugar beet pulp	18 kt/a (dry)	16 kt/a			Animal feed. Stream size limited by Finland's sugar quota.

Table 3. Side streams containing readily available sugars in Finland.

Feedstock	**Carbohydrates**	**C6 content**	**Current use**
Separated urban biowaste	30 kt/a	Close to 100%. Sugars & starch.	
Barley sludge / b-amylase production	12 kt/a	100%. Starch.	
Bread and pastry	6 kt/a	100%. Starch.	Partially used in St1 Plants in Hamina and Vantaa.
Milk product waste / whey	4.5 kt/a	100%. Lactose.	Animal feed.
Potato processing industry	3- 11 kt/a	100%. Starch.	Animal feed.

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[3] von Weymarn N (ed.) Bioetanolia maatalouden sivuvirroista. VTT Tiedotteita 2412 (2007). http://www.vtt.fi/inf/pdf/tiedotteet/2007/T2412.pdf

Table 4. Uronic acid containing streams in Finland and Europe.

Feedstock	**Stream volume**	**Pectin**	**Uronic acids**	**Feedstock price**	**Current use**
Sugar beet pulp					
Finland	18 kt/a (dry)	4 kt/a	2.8 kt/a	150-250 €/t (pellets)	Animal feed. Stream size limited by sugar quota.
Europe	5 Mt/a (dry)[4]	1.1 Mt/a	780 kt/a		
Citrus peel					
Europe	200 kt/a	100 kt/a	70 kt/a	Feed 100-200 €/t	Animal feed. Pectin produced worldwide 40 kt/a.
TMP process waters					
Finland	45 -135 Mt/a		6 - 9 kt/a	Negative.	No use. Would require concentration and purification.

The production of well-defined furan compounds usually requires carbohydrate streams rich in either C5 sugars or C6 sugars – mixtures of C5 and C6 sugars are not optimal feedstocks. The column “C6 content” in the Tables 1-3 gives indication on the “C6 vs. C5 purity” of the stream before further fractionation.

Based on information in Tables 1-4, the potential Finnish raw material streams rich either in C6 or C5 sugars were identified. These streams are presented in the boxes below. Some of the streams in the boxes have been further fractionated from the ones presented in Tables 1-4. e.g. straw from Table 2 (1.1 Mt/a carbohydrates) has been further fractionated into cellulose (700 kt/a) and hemicellulose (400 kt/a) in the boxes below. The annual volumes given in the boxes are calculated for the amount of carbohydrates in the streams (not the total feedstock volumes).

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[4] CIBE International Confederation of European Beet Growers website. http://www.cibe-europe.eu/Home.aspx

Potential raw materials rich in C6 sugars in Finland include:

Cellulose

- Cellulose in stemwood 9 Mt/a
- Cellulose in straw 700 kt/a
- Cellulose in reed canary grass 40 kt/a (450 kt/a potential)
- Cellulose in other sources (recovered wood, recovered paper)

Other streams

- Sugars in softwood stemwood (90 % C6) 12 Mt/a
- Sugars in softwood sawmill chips & sawdust (90 % C6) 2 Mt/a
- Sugars in softwood hemicellulose (69 % C6) 5 Mt/a
- Sugars in recovered paper (80 % C6) 380 kt/a
- Sugars in TMP process waters (90 % C6) 90 kt/a
- Sugars in starch / sugar containing sidestreams 60 kt/a

(e.g. urban biowaste, bakery waste, potato industry waste)

Potential raw materials rich in C5 sugars in Finland include:

Combined with cellulose fractionation process

- Hardwood hemicellulose 700 kt/a (90 % C5)
- Straw hemicellulose 400 kt/a (ca. 90 % C5)
- Reed canary grass hemicellulose 30 kt/a (>80 % C5), potential 300 kt/a

Other streams

- Sugars in hardwood black liquor (100-300 kt/a rough estimate)
- Hardwood prehydrolysis sugars in pulp mill (currently not done)

2.2. Overview of furan chemistry and furan compounds

Furans are compounds with both aromatic and dienic characteristics. The production of furan chemicals from biomass has been studied over 100 years. The application potential of various furan compounds was estimated.

2.2.1. Furan chemistry

Furan compounds have both dienic and aromatic characteristics (Figure 2). The relative strengths of the dienic and aromatic characteristics depend on the substituents attached onto the furan ring. Directly attached carbonyl or carboxyl groups tend to stabilize the furan ring so that the diene character is suppressed – e.g. furan(dicarboxylic acid) is a rather stable compound. (Properties and chemical structures of several typical furan compounds are listed in next chapter.)

On the other hand, many furan compounds can be used as a diene in Diels-Alder reactions. Diels-Alder link between furan and maleimide provides a link that is thermoreversible at feasible temperatures (Scheme 2). This property has been recently utilized a lot in research towards thermoresponsive, e.g. self-healing materials. Furans that have been used in Diels-Alder reactions include furfuryl alcohol derivatives, bis(hydroxymethyl)furan, and many others.

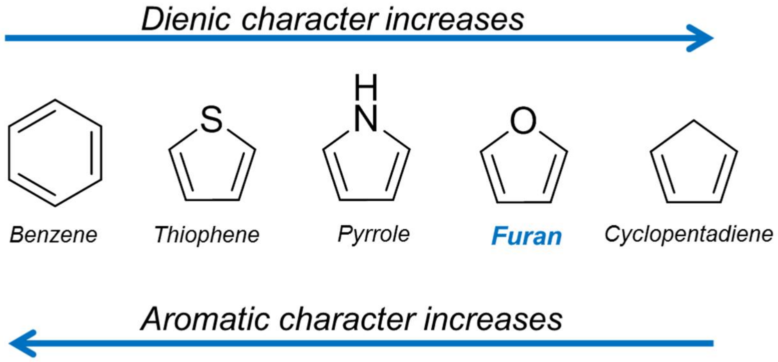
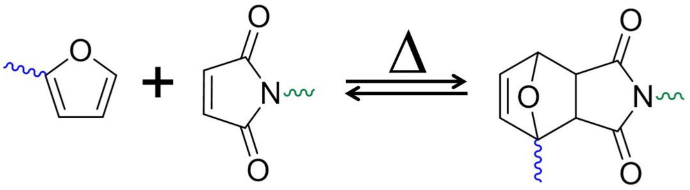


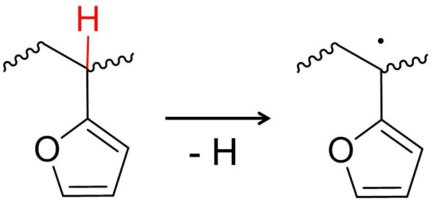
Figure 2**.** The dienic and aromatic character of furan compared to other similar compounds.5



Scheme 2. Furan and maleimide compounds can form thermoreversible links through Diels-Alder reaction. The link can be generated at temperatures around 60-65 ºC, and the link is opened at temperatures higher than ca. 100-110 ºC.

Another feature of furan compounds, especially furanic polymer materials, is that the hydrogens atoms in carbons directly attached to furan ring tend to be unstable (

Scheme **3**). This can reduce the temperature stability of such furanic polymers that contain this type of hydrogens, e.g. during processing. However, the extent of this vulnerability has not been studied to great extent.



Scheme 3. Vulnerable hydrogen atom next to a furan ring.

2.2.2. Furan compounds

Interesting furan compounds that can be derived from C5 sugars and C6 sugars are presented in Table 5 and Table 6, respectively. More information regarding furans (especially for polymer applications) can be found in extensive reviews by Gandini et al.[5,6]

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[5] Gandini A, Belgacem MN. Furans in polymer chemistry. *Prog.Polym.Sci.* 22 (1997) 1203-1379.

[6] Gandini A. Furans as offspring of sugars and polysaccharides and progenitors of a family of remarkable polymers: a review of recent progress. *Polym. Chem.* 1 (2010) 245-251.

Table 5. Furan compounds derived from C5 sugars.

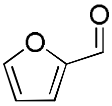
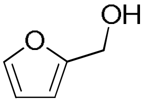
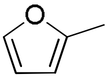
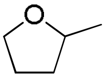
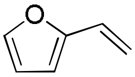
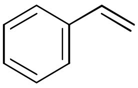
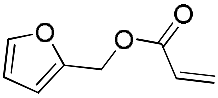
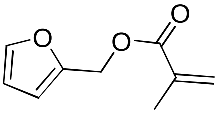
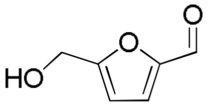
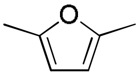
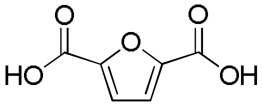
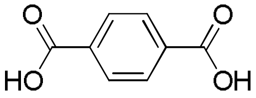
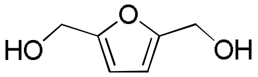
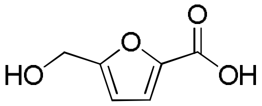
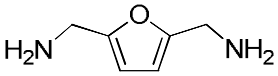
Furan compound	Production route	Current/Potential uses
Furfural 	Produced e.g. in China and South Africa from xylose (e.g. crop residues). 300 – 800 kt/a.	Commercial. Intermediate compound. Mainly used to produce furfuryl alcohol. Some commercial use also as a component in crosslinked polymeric resin.
Furfuryl alcohol 	Produced by hydrogenation of furfural. Production studied in CatBio.	Commercial product with market price at 1000-1500 €/t. Can be polymerized into a crosslinked resin under acidic conditions. Used also as a specialty solvent.
2-Methylfuran (MF) 	Can be produced by hydrogenation of furfuryl alcohol or directly from furfural by hydrodeoxygenation. Production studied in CatBio.	Potential fuel component with high RON. *See chapter 2.3.2.* Also some use as an intermediate in the synthesis of pharmaceuticals, pesticides and perfumes.
2-Methyltetrahydrofuran (MTHF) 	Can be produced from furfuryl alcohol either through tetrahydrofurfuryl alcohol or 2-methylfuran.	Potential fuel component and solvent.*See chapter 2.3.2.*
2-vinylfuran 		Styrene analogue, so in principle it would be interesting to prepare furanic analogues of polystyrene. Unfortunately, 2-vinylfuran is not easily applicable in radical polymerization, and there are also stability issues in 2-vinylfuran polymers. *See chapter 2.7.4.*  *Styrene*
2-furfuryl (meth)acrylate  	Can be produced by esterification between furfuryl alcohol and (meth)acrylic acid chloride	These furan compounds are easily applicable in radical polymerizations. Recently there has been increasing interest in these monomers in the preparation of thermoreversible materials via Diels-Alder reactions. *See chapter 2.7.5.*

Table 6. Furan compounds derived from C6 sugars.

Furan chemical	Production route	Current/Potential uses
Hydroxymethylfurfural (HMF) 	Dehydration of C6 sugars. Difficulties in synthesis and storage – resinifies when formed or when left standing.	Not commercial. Intermediate compound. Lot of recent research interest. Potentially can be used to prepare difuctional furanic compounds.[7]
2,5-Dimethylfuran (DMF) 	Produced by hydrogenolysis of HMF.	Production from HMF not commercial. Potential fuel component – DMF is a component with relatively high energy density. *See chapter 2.3.2.* Relatively widely studied production route.
2,5-Furandicarboxylic acid (FDCA) 	Dehydration and oxidation of C6 sugars. Lot of recent interest in the synthesis route from HMF. **FURCHEM investigates an alternative synthesis route via aldaric acid.** Stable compound (COOH groups reduce dienic character.)	Not commercial. Avantium produces in 40 t/a pilot scale. Could replace e.g. terephthalic acid (market size 50 kt/a, price 1100 €/ton). Could be potentially applied to produce e.g. **polyesters and polyamides**. *See chapters 2.5 and 2.6.*  *Terephthalic acid.*
2,5-Bis(hydroxymethyl)furan (BHMF) 	Can be produced e.g. from HMF through reduction.	Can potentially be used e.g. as a diol in the production of **polyesters and polyurethanes**. Has not been very widely studied – only 34 patents and 55 scientific publications with some relation to polymers were found. Diene character of this monomer has been utilized recently in Diels-Alder reactions to prepare thermoresponsive materials. *See chapter 2.7.2.*
2,5-Hydroxymethylfuroic acid 	Can be produced from HMF with selective oxidation.	Hardly any studies, no recent papers. In principle could be polymerized to **polyester.** *See chapter 2.7.3.*
	Thermodynamically unstable.	Cannot be produced and applied – i.e. the most rigid version of furanic polyamides/aramides, with amide bond directly in furan ring, cannot be obtained.
2,5-Bis(aminomethyl)furan 	Quite unstable against resinification (salt form more stable). No recent studies – the extent of stability issues not clear.	Not much studied. Could be potentially applied in **furanic polyamides /aramides.** Polymerized with FDCA to study furanic aramides in 1990's. Difficulties in obtaining pure diamine resulted in low yield and low molecular weight.
	In case isocyanate groups are directly attached to furan ring, the product is very unstable (must be stored in cold and inert conditions).	Polyurethanes from this monomer are unstable, the monomer is too reactive.

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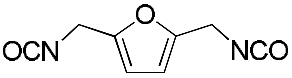
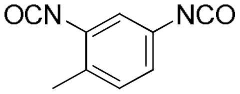
[7] van Putten, R.-J., van der Waal, J. C., de Jong, E., Rasrendra, C. B., Heeres, H. J., de Vries, J. G. 2013. Hydroxymethylfurfural, a versatile platform chemical made from renewable resources. Chem. Rev. 113, 1499-1597.

	This furanic di-isocyanate is rather stable. Can be produced from the diamine (2,5-Bis(aminomethyl)furan) with triphosgene. However, production of the diamine intermediate is quite tricky, which can be a bottleneck.	Can be potentially used in **polyurethane** production. Not a direct analogue to e.g. TDI (common commercial di-isocyanate applied in polyurethanes), because –NCO groups are not directly attached to furan ring. Polyurethanes with furanic di-isocyanate have not been studied much, a couple of examples by Gandini et al. in 1989-1995.  *2,4-TDI*

2.3. Furans as fuel components

Furanic compounds 2,5-Dimethylfuran, 2-Methylfuran and 2-Methyltetrahydrofuran are being considered as bio-based fuel additives. The current major fuel additives are ethanol, MTBE and ETBE. Their combined consumption in fuels is currently ca. 100 Mt/a.[8,9]

Components used in fuels to improve properties, also called oxygenates, have been used widely in spark-ignition engines. The name “oxygenate” comes from the chemical formula, oxygenates contain oxygen. Use of oxygenates has already started in 1970`s. The purpose of oxygenates back then was to enhance the volume and octane rating of gasoline. Late 1970`s the removal of lead from gasoline was made compulsory and due to that octane rating in gasoline decreased. At that time use of oxygenates was used to further enhance the octane rating. More recently use of oxygenates as emission controlling components has been also one of the main purposes of oxygenates. Applying oxygenates improves combustion and thereby reduces CO and hydrocarbon emissions. However, NO_x emissions are increased with the use of oxygenates.[9] Another disadvantage of using oxygenates is that the use of oxygenates decreases the energy content of the fuel, hence increasing the fuel consumption.[10] Nowadays use of oxygenates in gasoline is mandated by current legislation.[11] Use of ethanol is based on biomandate on reducing greenhouse gases. Opposite to many other fuel oxygenates, use of ethanol does not improve combustion.[12]

Oxygenated fuel components commercially used in gasoline include ethanol, methyl tertiary-butyl ether (MTBE), ethyl tertiary-butyl ether (ETBE), tertiary amyl-ethyl-ether (TAEE) and tertiary-amyl-methyl-ether (TAME). Other oxygenates, for example higher alcohols (1-butanol) are also allowed as fuel components but previously mentioned ethanol, MTBE and ETBE cover the most used components. Maximum limit of oxygenates is reported in European Parliament directive 2009/30/EC. For ethanol the maximum limit is 10.0 v/v% and for MTBE/ETBE 22.0 v/v% in gasoline.[11] Typical amount of MTBE/ETBE varies between countries. In Finland use of MTBE average is 12 v/v%, whereas in UK the amount is 1-2 v/v% (the lowest in Europe).[13]

In United States of America the Federal requirements allow the use of substantially similar fuel additives to be added to gasoline. This requirement is presented in Clean Air Act of 1977, section 206. The oxygen amount by weight in 1991 has been 2.7 wt%.[14] More recently European standard SFS-EN 228 (2009) concerning requirements and test methods of unleaded petrol specifies the oxygen content of unleaded gasoline to 3.7 % (m/m).[15]

Furanic compounds are seen as potential fuel components. Furanic compounds have excellent characteristics for use in blend fuels, e.g. high octane number, comparable energy density, and lower emissions. From furanic compounds, 2-methyltetrahydrofuran (MTHF) can be considered as substantially similar compound to other commercial oxygenates as it is ether and aliphatic compound. Maximum 14.5 wt% of MTHF can be added to gasoline to still fulfill the oxygen content limit. 2-Methylfuran (MF) and 2,5-dimethylfuran (DMF) on the other hand are aromatics and are not considered as substantially similar compounds.[14] Potential of MF and DMF has however been noticed and research of component use as blend fuels is ongoing.

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[8] Renewable Fuels Association, World fuel Ethanol Production, http://www.ethanolrfa.org/resources/industry/statistics/, accessed December 2015.

[9] GOMEZ, J., BRASIL, T., CHAN, N. An overview of the use of oxygenates in gasoline, 1998:1-31.

[10] AAKKO-SAKSA, P., KOPONEN, P., KIHLMAN, J., REINIKAINEN, M., SKYTTÄ, E., RANTANEN-KOLEHMAINEN, L., ENGMAN, A. Biogasoline options for conventional spark-ignition cars, 2011.

[11] EUROPEAN PARLIAMENT AND COUNCIL, Directive 2009/30/EC, 2009.

[12] EUROPEAN PARLIAMENT AND COUNCIL, Directive 2009/28/EY, 2009.

[13] ANON. Methyl tertiary-butyl ether, http://www.essentialchemicalindustry.org/chemicals/methyltbe.html. Updated 2013.

[14] YANOWITZ, J., CHRISTENSEN, E., MCCORMICK, R.L. *Utilization of renewable oxygenates as gasoline blending components.* Colorado: National Renewable Energy Laboratory (U.S.) Center for Transportation Technologies and Systems; 2011:58.

[15] ANON. European standard SFS-EN 228, 2009.

Certain characteristics of fuel components have to be fulfilled to be suitable for blend fuel component use. Some of the most important aspects to be considered are emissions (CO, NO_x, non-methane organic gas), vapor pressure, corrosiveness, permission levels of impurities, and water tolerance. Also safety, toxicity, and environmental issues need to be considered before further investigations. The component characteristics must fulfill the requirements of fuels used in spark-ignition engines.[11,14]

2.3.1. Current commercial compounds

Current commercial bio-based products (at least partially) applied as fuel components or fuels include ethanol, tertiary amyl-ethyl-ether, tertiary amyl-methyl-ether, methyl-tertiary-butyl-ether, and ethyl-tertiary-butyl-ether. In this chapter the production methods, advantages and disadvantages as well as their use in fuel will be discussed. The properties of these components are presented in detail in Table 7 (on page 22).

Bioethanol. One of the current commercial fuel products is bioethanol. Bioethanol has been already used for a longer time in spark-ignition engines. The use of bioethanol in diesel engines has also been under research lately and introduced in heavy duty vehicles; ST1 in Finland is currently testing an ethanol-diesel RED95 in delivery and garbage trucks as well as in few buses.[16,17] Bioethanol has advantages, like renewability and high octane number. Disadvantages of the component are low energy density and high vapor pressure. Production of bioethanol also requires a lot of energy.[16]

Ethanol can be used as fuel itself or it can be blended to gasoline. In America and Brazil blending of ethanol to gasoline is used to make the process more environmentally friendly. Amount of blended ethanol to gasoline is 10 v/v% in America and Europe.[11,18] In Brazil the Government has allowed higher blending ratios, in 2011 the amount was reduced to 20 v/v%, but in 2015 the allowed amount of ethanol in gasoline is increased again to 25 v/v%.[19,20]

Production of ethanol proceeds through fermentation of sugar by yeasts. The sugar can be produced from biomass with hydrolysis. Most usual raw materials used to produce sugar for ethanol production are sugarcane and corn grain.[18] Glucose fermentation to ethanol and carbon dioxide is presented in Equation 1.

$$C_6O_6H_{12} \rightarrow 2C_2H_5OH + 2CO_2 \qquad (1)$$

Drawback of this process is that half of the sugar mass used for ethanol production will be released as CO_2. On the other hand sugar energy is not lost, almost all energy goes to ethanol in this process. Process conditions of carbohydrate fermentation are mild, temperature is between 30 – 38 °C, pH 4 – 5, and residence time varies between 28 and 48 hours. From one metric ton of sugarcane, 160 – 190 liters of ethanol is produced.[18,21] Theoretical yield of ethanol from sucrose is 62 %, but in real life plant operation the theoretical yield decreases to 53 %.[22]

Production cost of ethanol is depending on the raw material used for the production. With sugar cane, over half (53 %) of the production costs is coming from raw material costs, with corn grains the costs are a

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[16] Wang C, Xu H, Daniel R, et al. Combustion characteristics and emissions of 2-methylfuran compared to 2,5-dimethylfuran, gasoline and ethanol in a DISI engine. *Fuel.* 2013;103:200-211.

[17] ANON. RED95 etanolidiesel, http://www.st1.fi/tuotteet/etanolidiesel, Updated 2015.

[18] HUBER, G.W., IBORRA, S., CORMA, A. Synthesis of transportation fuels from biomass: Chemistry catalysts, and engineering *Chemical Reviews*, 2006;106:4044-4098.

[19] BARROS S. Biofuels annual. [BR12013], 2012:1-28.

[20] VOEGELE E. Brazil to increase ethanol blend level to 25 percent. *Ethanol Producer Magazine*, 2013.

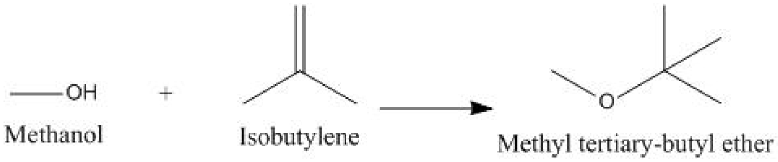
[21] KLASS DL. *Biomass for renewable energy, fuels and chemicals,* San Diego: Academic Press, 1998:651.

[22] ANON. The economic feasibility of ethanol production from sugar in the United States, 2006:1-78.

little lower. Production costs are lower with corn grains also while side products of this process can be further sold.[18,23]

Amounts of ethanol produced are relatively large, America and Brazil produced in total 14 Mt/a in 2001.[18,23] Since 2001 the amount of produced ethanol has risen enormously as the ethanol amount used as gasoline blend fuel in 2010 was almost 45 Mt/a.[14]

Methyl tertiary-butyl ether (MTBE) is a fuel component produced from methanol and isobutylene. From MTBE raw materials methanol can be bio-based, but isobutylene is based on fossil raw materials. In case methanol is bio-based, the percentage of biofuel in MTBE is 36 %.[24] Catalysts used in MTBE production are acidic catalysts (cation ion-exchange resins) and the process temperature is approximately 66-100 °C.[13,25] Pressure in the production is 8 atm and in this process excess of methanol is used. In Scheme 4 production of methyl tertiary-butyl ether is presented.



Scheme 4. Production of Methyl tertiary-butyl ether.

MTBE can be used in gasoline as an oxygenate to increase octane rating. The production volumes of MTBE are large, 15.2 Mt was produced in 2013 globally. In Europe the amount was 2.6 Mt.

Use of MTBE has raised concerns especially in America due to its high solubility in water. If MTBE ends up in the ground soil it is easily transferred to ground water where it addresses many problems to humans.[26] Use of MTBE has been banned in some countries (many states in USA, Denmark) and in many countries the amount used has decreased (France). Ethanol has been used as a replacement for MTBE in gasoline in USA.[13]

Ethyl tertiary-butyl ether (ETBE) is a fuel component produced from ethanol and isobutylene. From ETBE production raw materials, ethanol can be produced from renewable raw materials and isobutylene is produced from fossil materials. In case ethanol is bio-based, the percentage of biofuel in ETBE is 47 %.[24] Catalysts used in the process are acidic catalysts.[25] In Scheme 5 production of ethyl tertiary-butyl ether is presented.

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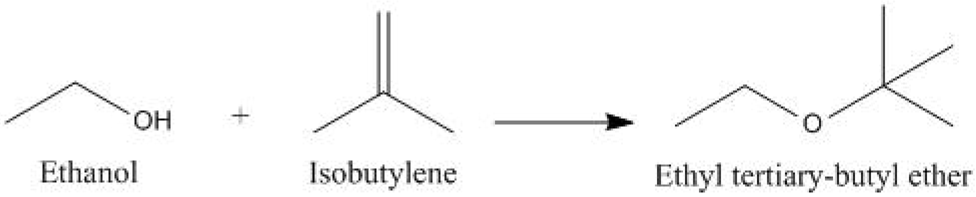
[23] WYMAN CE. Ethanol fuel. In: CLEVELAND CJ, ed. *Encyclopaedia of energy,* New York: Elsevier, 2004:541-555.

[24] EUR LEX. Directive 2003/30/EC of the european parliament and of the council of 8 may 2003 on the promotion of the use of biofuels or other renewable fuels for transport , http://eur-lex.europa.eu/legal-content/en/ALL/;ELX_SESSIONID=R1yTJ2WWyT1hGYR-nvY77typk3ptJ4bj7m5v1lmDKHv9wzvR6J57Q!-727278793?uri=CELEX:32003L0030.

[25] HAMID, H., ASHRAF ALI, M. *Handbook of MTBE and other gasoline oxygenates.* USA: CRC Press, 2004.

[26] KARINEN R. *Etherification of some C8-alkanes to fuel ethers,* 2002.



Scheme 5. Production of Ethyl tertiary-butyl ether.

ETBE can be used as an oxygenate component blended to gasoline, up to 15 v/v% of ETBE can be blended to increase octane rating of gasoline. Advantages of ETBE include lower volatility than ethanol, indicated as lower vapor pressure in Table 7 (on page 26).[18] Another advantage using Bio-ETBE compared to ethanol in gasoline blending is the higher energy density; ETBE contains triple amount of energy compared to ethanol.[27] Also emissions are decreasing with the use of commercial oxygenates. Figure 3 presents the effect of MTBE, ETBE and ethanol on emissions.

Drawbacks of using ETBE can be found in groundwater contamination as with MTBE.[18] However, when properties of ETBE are compared to MTBE, the solubility of components to water differ significantly. Solubility of ETBE to water is 1.1 w%, while with MTBE it is 4.3 w%. Lower water solubility of ETBE makes it more desirable oxygenate than MTBE in gasoline blending.[27]

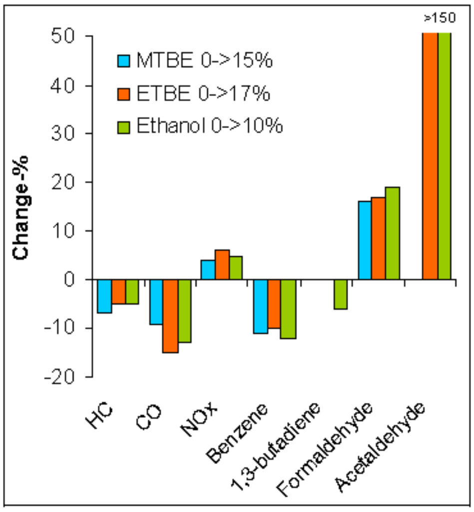


Figure 3. Effect of MTBE, ETBE and ethanol on emissions.[10]

Tertiary amyl-ethyl-ether (TAEE) is a fuel component produced from isoamylenes and ethanol. Two isoamylene isomers can be used for TAEE production: 2-methyl-1-butene and 2-methyl-2-butene. TAEE production proceeds through an etherification reaction of ethanol with isoamylene. Production is performed in a catalytic distillation column with heterogeneous catalysts. Production process of TAEE is presented in Scheme 6.

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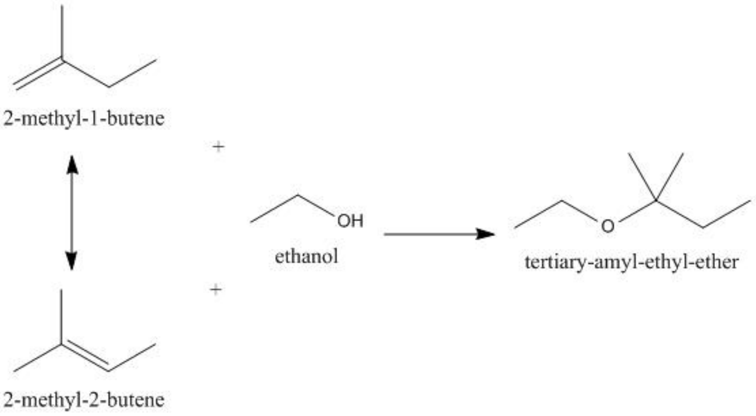
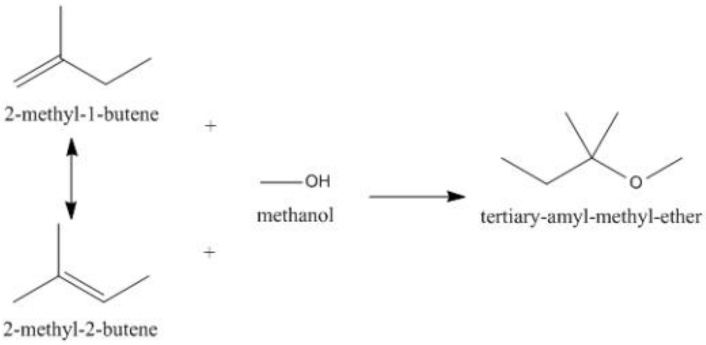
[27] ANON. Bio-ETBE: The right road to high quality 21st century motor fuels, 2008.



Scheme 6. Production of TAEE.

Advantages of TAEE are relatively similar to other oxygenates commercially used. Emissions of gasoline are decreased with the use of oxygenates and the vapor pressure of TAEE is lower than gasoline. TAEE is more desirable oxygenate than MTBE due to its lower water solubility. With lower water solubility the groundwater pollution risk is reduced.[28]

Tertiary-amyl-methyl-ether (TAME) is a fuel component produced from methanol and isoamylenes (2-methyl-1-butene / 2-methyl-2-butene). The production occurs through an etherification process with isoamylenes and methanol. Isoamylenes used in etherification can isomerize over the catalyst used in the process. Possible catalysts used are acid-functionalized ion-exchange resins; for example Amberlyst-15.[29] Production process of TAME is presented in Scheme 7.



Scheme 7. Production of TAME.

The use of TAME as oxygenate in gasoline has the same advantages as other oxygenates. Compared to TAEE, TAME is still more applied fuel component.[30] An advantage of TAME compared to a much applied fuel component MTBE is the lower water solubility and lower vapor pressure. To fulfill certain oxygen level for gasoline, an accurate amount of TAME has to be blended. To achieve 2.0 w% oxygen content in gasoline, 13 v/v% of TAME should be blended.[9]

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[28] González-Rugerio CA, Keller T, Pilarczyk J, Sałacki W, Górak A. TAEE synthesis from isoamylenes and ethanol by catalytic distillation: Pilot plant experiments and model validation, *Fuel Process Technol.* 2012;102:1-10.

[29] SYED, F.H., EGLESTON, C., DATTA, R. Tert-amyl methyl ether (TAME). thermodynamic analysis of reaction equilibria in the liquid phase. *Journal of Chemical & Engineering Data*, 2000;45:319-323.

[30] ANON. Ethers for blending with gasoline. http://www.iea-amf.org/content/fuel_information/ethanol/ethers.

Production volume of TAME in USA in 1998 has been 44.6 kt/a.[9] Global demand in 2009 for all the fuel ethers has been reported to be 16.5 Mt/a. The combined amount of TAEE and TAME is reported to be 8 % of this amount, so the demand for these components has been 1.32 Mt/a.[31]

Fuel ether demand. Demand of fuel ethers has been increasing constantly but the proportion of certain components has been decreasing and proportion of others increasing. Figure 4 presents the demand of fuel ethers in Europe in years 2003 - 2009. From the figure it can be seen that the use of MTBE is decreasing and it is being replaced with ETBE. The production volume of ETBE is increasing and in 2013 it was 3 Mt worldwide.[13] Demand of all fuel ethers has been increasing constantly.[30] Demand of TAEE and TAME are relatively small compared to MTBE and ETBE. However, the demand of these components has risen also constantly.

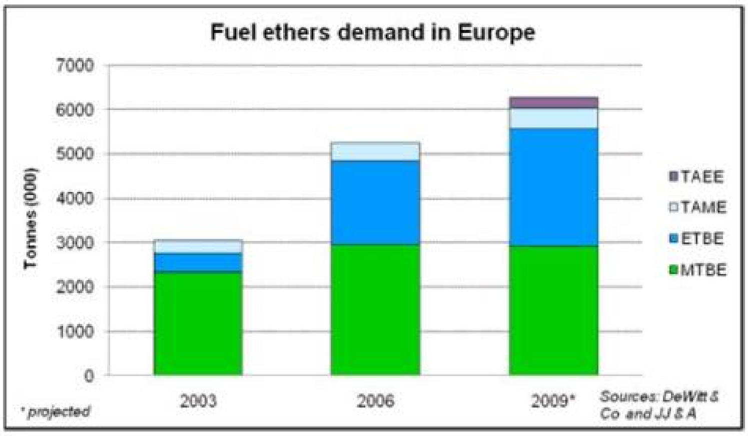

Figure 4. Demand of fuel ethers in Europe in years 2003-2009.

2.3.2. Furanic compounds

Furanic compounds produced from renewable sources could provide an excellent alternative for current commercial compounds. Furanic compounds with excellent properties possible to use as fuel components are 2,5-Dimethylfuran, 2-Methylfuran, and 2-Methyltetrahydrofuran. However, these furanic compounds have differences for example in emissions, energy density, octane number, and flash point. In following chapter 2,5-Dimethylfuran, 2-Methylfuran and 2-Methyltetrahydrofuran are presented and compared and the properties of these components are presented in Table 7.

2,5-Dimethylfuran (DMF) has been proven to be an excellent fuel component. Many studies have confirmed that DMF has similar combustion characteristics as typical gasoline components.[16,32] This is excellent as it means that massive changes to existing techniques are not required.[32]

Production of DMF consists of multiple steps. The production is started from C6 sugars of cellulose. C6 sugars, for example fructose, are converted to 5-hydroxymethylfurfural (HMF) with dehydration. After dehydration two oxygen atoms of HMF are removed with hydrogenolysis to form DMF. Reaction scheme of DMF production from C6 sugars is presented in Scheme 8.

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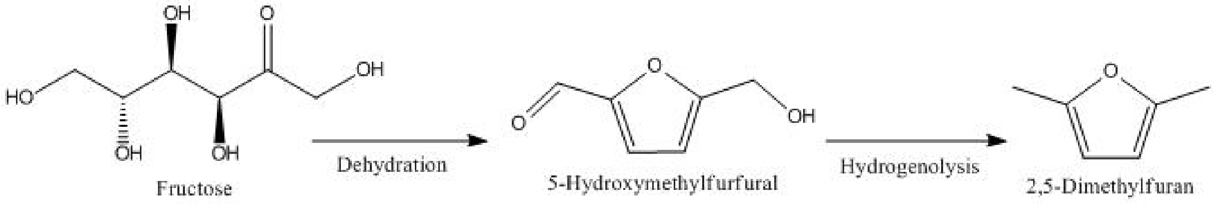
[31] ANON. Ethers for blending with gasoline. http://www.iea-amf.org/content/fuel_information/ethanol/ethers. Updated 2015.

[32] TIAN, G., XU, H., DANIEL, R.,. DMF - A new biofuel candidate. In: DOS SANTOS BERNARDES, M. A., ed. *Biofuel production - recent developments and prospects.* InTech, 2011:487-520.



Scheme 8. DMF production from C6 sugars.

Advantages of DMF can be found in amount of emissions as they are in the same category as emissions of typical gasoline components. Compared to average properties of gasoline (e.g. according to EN228), higher energy density and better cold-start performance make DMF even more desirable fuel component.[16,32] All these good characteristics make DMF easily adoptable to existing spark-ignition engines.[16] DMF could be applied as an octane booster in gasoline but its use as an alternative fuel as such in gasoline engines has also been researched.[32] In 2007 a group of researchers developed an efficient and low energy demanding way to produce DMF.[33]

2-Methylfuran (MF) can be produced from furfural. Furfural is produced from C5 sugars in hemicellulose with dehydration, where three water molecules are released during reaction. Reaction conditions in furfural production are the following: temperature 170–185 °C, retention time 3 hours, and acid catalysts are used. Also autocatalytic reaction is possible in elevated temperatures.[34] Considerably high yield of furfural (60 %) can be obtained when xylose sugar is used as a raw material.[35]

Worldwide, 300 kt of furfural is produced annually.[34] At the moment the use of furfural as a precursor for fuels is too expensive, but new ways of producing it simultaneously in biorefineries is investigated as a more inexpensive option. Another factor instead of price influencing on furfural production is its tendency to polymerize.[18]

Production of MF from furfural can occur through two reaction routes. MF can be produced through an intermediate furfuryl alcohol with hydrogenation or directly from furfural with hydrodeoxygenation. Reaction scheme of MF production from furfural is presented in Scheme 9.

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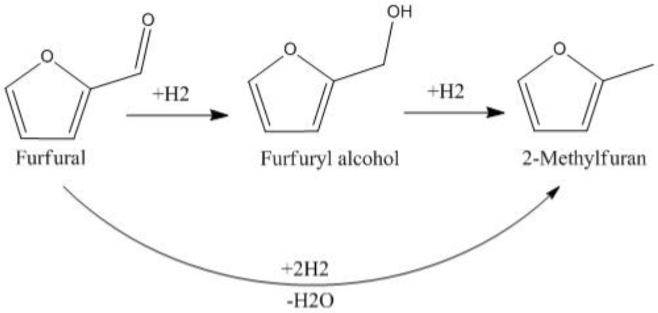
[33] ROMAN-LESHKOV, R., BARRETT, C.J., LIU, Z.Y. and DUMESIC, J.A. Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates. *Nature*, 2007;447:982-985.

[34] MONTANE, D., SALVADO, J., TORRAS, C., FARRIOL, X. High temperature dilute-acid hydrolysis of olive stones for furfural production. *Biomass Bioenergy,* 2002;22:295-304.

[35] Antal Jr. MJ, Leesomboon T, Mok WS, Richards GN. Mechanism of formation of 2-furaldehyde from d-xylose. *Carbohydr Res*, 1991;217:71-85.

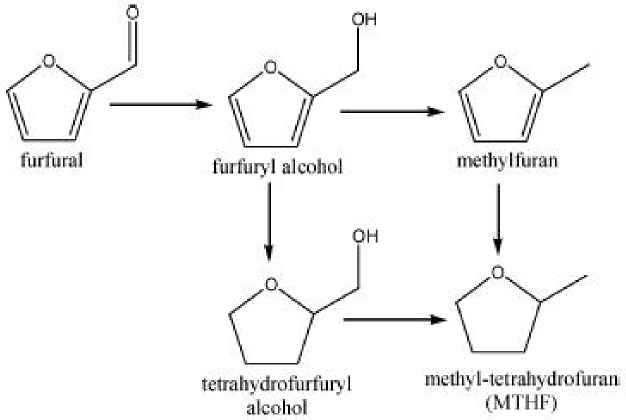


Scheme 9. 2-methylfuran production from furfural.

2-methylfuran has been proven to be an efficient fuel component. As well as DMF, also MF has a comparable energy density to typical gasoline components. Other advantage of MF is that it also produces 3 % higher indicated thermal efficiency than typical gasoline and DMF. Advantages of this higher thermal efficiency are faster burning rate and better knock suppression ability. Also the fuel consumption rate of MF is lower compared to ethanol; it can be even 30 % lower when indicated volumetrically.[16] Other advantages compared to DMF and ethanol are: lower flash point (MF -22 °C, DMF 16 °C), higher density, higher heat of vaporization, and closer boiling point with gasoline (63 °C).[16]

Oxygenates are used to reduce emissions of incompletely burned products. Emissions of MF are not thoroughly investigated yet but it is expected to have notably lower emissions as gasoline. Few studies made of MF emissions have discovered hydrocarbon emissions of MF can be even 61 % lower than with gasoline. On the other hand the NOx emissions were noticed to be relatively high.[16]

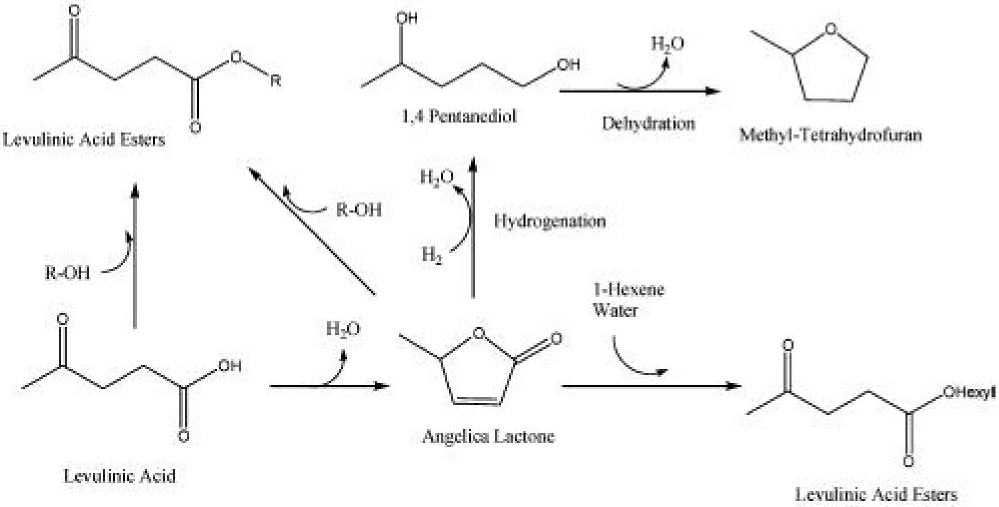
2-Methyltetrahydrofuran (MTHF) is a component produced from furfural with two possible reaction routes. MTHF can be produced from furfural through intermediates furfuryl alcohol and tetrahydrofurfuryl alcohol (THFA) or then through furfuryl alcohol and 2-methylfuran with hydrogenation.[18] MTHF production from furfural is presented in Scheme 10.



Scheme 10. Furfural hydrogenation and hydrogenation products.[18]

In addition to furfural hydrogenation routes, MTHF can be produced also from levulinic acid with dehydration/hydrogenation reaction. MTHF can be blended to gasoline (up to 70 %). The use of MTHF in gasoline increases the oxygen content, while MTHF oxygen content is 20 wt%. USDOE has already proven this component as an oxygen increasing component in P Series fuels.18 MTHF production from levulinic acid is presented in Scheme 11.

Currently MTHF has been used as an alternative solvent for tetrahydrofuran (THF) due to its comparable properties. Catalysts studied for the production of MTHF include homogeneous ruthenium catalysts, copper catalysts, and noble-metal catalysts. High conversions of MF and levulinic acid have been detected in multiple studies concerning MTHF production. MTHF yield of 91 % has been achieved using levulinic acid intermediate (γ-valerolactone (GVL)) as raw material. Over 90 % yields of MTHF can be achieved also with furfural hydrogenation to MTHF.[36]



Scheme 11. MTHF production from levulinic acid.[18]

2.3.3. Comparison of current commercial and furanic compounds

Current commercial fuel products such as ethanol, ETBE, and MTBE have differing chemical and physical properties compared to furanic compounds such as DMF, MF and MTHF (Table 7).

Another factor possibly influencing on use of furanic components as fuel components is the toxicity of chemicals. In Table 8 symptoms, oral LD50 values, and carcinogenicity of commercial and furanic components are presented. From the table it can be seen, that oral LD50 values of MF and DMF are greatly larger than for the other components. MF is also toxic if inhaled, so special working methods should be used with this component.

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[36] YAN, K., WU, G., LAFLEUR, T., JARVIS, C. Production, properties and catalytic hydrogenation of furfural to fuel additives and value-added chemicals. *Renewable and Sustainable Energy Reviews*, 2014;38:663-676.

Table 7. Chemical and physical properties of bio-based gasoline components and gasoline.[14,26,30,37,38,39]

	Gasoline	Ethanol	ETBE	MTBE	TAEE	TAME	DMF	MF	MTHF
Formula		C2H6O	C6H14O	C5H12O	C7H16O	C6H14O	C6H8O	C5H6O	C5H10O
Lower heating value (MJ/kg)	41-44	26.8	36.3	35.1	-	36.4	33.8	31.2	32.8
Higher heating value (MJ/L)	30-33	21.4	39.2	38.0	-	39.3	30.1	27.6	28.2
Latent heat of vaporization (kJ/kg)	352	919.6	33.0 kJ/mol		-	-	330.5	358.4	375.3
Lower flammability limit (%)	1.4	3.3	1.4	1.5	-	1.1 expl.	-	1.9	1.5
Upper flammability limit (%)	7.6	18.95	10.1	8.5	-	7.1 expl.	-	14	8.9
Vapor pressure at 20 °C (kPa)	50-100	5.8	0.3	0.6	7	9	5	1.5	13.6
Autoignition temperature (°C)	257	363	310	435	0.75	430	286	450	270
Boiling point (°C)	27-225	78	70-73	55.2	101	86	94	64,7	78
Melting point (°C)	-40	-114	-94	-109	-	-80	-63	-61	-136
RON	88-98	109	118	117	105	112	119	103	86
MON	80-88	90	101	101	95	98		86	73
Specific gravity (20°C)	0.69-0.79	0.79	0.75	0.74	0.70	0.77	0.89	0.91	0.86
Solubility in water (%v/v)	negligible	miscible	1.2%	4.3%	0.5%	2.0%	0.3%	0.3%	12.1%

Table 8. Symptoms, oral LD50 values and carcinogenicity of commercial and furanic compounds.

	Symptoms	Oral LD50/rat (mg/kg)	Carcinogenicity
Gasoline	Skin irritation / dizziness	14000	Possible carcinogen
Ethanol	Mild eye irritation	7060	Carcinogen
MTBE	Skin irritation	4000	Not confirmed by IARC
ETBE	Drowsiness / dizziness if inhaled	2003	Not confirmed by IARC
TAEE	-	-	-
TAME	Drowsiness/dizziness	1602	Not confirmed by IARC
DMF	Harmful if swallowed	300	Not confirmed by IARC
MF	Toxic if inhaled	167	Not confirmed by IARC
MTHF	Mild eye irritation	4500	Not confirmed by IARC

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[37] AMERICAN PETROLEUM INSTITUTE. Alcohols and ethers, A technical assessment for their application as fuels and fuel components, *API Publication 4261*, 2001.

[38] ANON. Tert-amyl methyl ether. http://pubchem.ncbi.nlm.nih.gov/compound/tert-Amyl_methyl_ether#section=Top, Updated 2015.

[39] ANON. GREET, the greenhouse gases, regulated emissions, and energy use in transportation model, GREET 1.8d.1, 2010.

2.3.4. Market state-of-art

Market state-of-art of current commercial fuel components are relatively well known and presented publically. Little information of production volumes and prices of furanic compounds can be found. It is obvious that with current fuel components the price range is somewhat lower than with furanic compounds. Production volumes and prices of components are presented in Table 9.

Table 9. Production volumes and process of commercial and furanic fuel products.

Fuel component	Production	Amount used as blend fuel	Price (€/l)	Reference
Ethanol	70 Mt/a	45 Mt/a	0.40-0.60	[14,40,41]
MTBE	15 Mt/a	-	0.10-0.40	[13,42,43]
ETBE	3 Mt/a	-	0.76-2.17	[13,44,45]
TAEE	-	-		
TAME	-	-		
2,5-Dimethylfuran	-	-	0.50-1.91	[46,47]
2-Methylfuran	-	-	1.17-4.74	[48,49]
2-Methytetrahydrofuran	14 Mt/a	-	0.30-0.43	[50]

2.3.5. Catalysts in the production of furan fuel components

Catalysts in conversion of furanic compounds vary greatly. In furfural hydrogenation commercially used catalyst is copper chromite ($Cu_2Cr_2O_5$) which has been successfully applied in furfural hydrogenation to furfuryl

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[40] ANON. World fuel ethanol production. http://ethanolrfa.org/pages/World-Fuel-Ethanol-Production, Updated 2013.

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alcohol already for five decades. Recently, concern of CuCr catalyst has risen due to its toxicity. New environmental restrictions prevent deactivated copper chromite from being used in landfill sites.[51] Furfural hydrogenation to other products than furfuryl alcohol is also possible, although with CuCr the selectivity of other products is minor. Multiple metal alternatives deposited on various supports have been studied but the problem seems to be the rapid deactivation of active and selective catalysts. Some studied catalysts, reaction conditions, and the product achieved in liquid phase furfural hydrogenation are presented in Table 10. As seen from the table most of the research is concerning furfural hydrogenation to furfuryl alcohol. Catalyst research on possible fuel components MF and MTHF has been low compared to furfuryl alcohol.

Despite of the lower research activity on MF production from furfural hydrogenation, some research on substitutive catalyst has been performed. It is known that production of 2-methylfuran from furfural proceeds through furfuryl alcohol. When producing 2-methylfuran high temperatures are required. At lower temperatures the main product is furfuryl alcohol. The production temperature has to be optimized; too high temperatures would increase energy cost and polymerization of furfural, which results in catalyst coking.

One good metal for blend fuel component MF production is copper. Yan *et al.* [65] studied Cu-Fe noble metal free catalyst for MF production. In this study catalyst was in form of $CuO-CuFe_2O_4$. With this catalyst 51 % yield of MF was achieved with 99 % conversion of furfural. Copper catalysts are an excellent option while they are inexpensive, simple, and possible to scale up. It has been claimed that Cu^0 and Cu^+ species work as active centers of Cu catalysts. Cu catalysts have been observed to deactivate quite rapidly but the regeneration is possible. In this study reaction temperature was 220 °C, hydrogen pressure 90 bar, solvent used was octane and reaction time 14 h. In temperatures under 180 °C the main product was furfuryl alcohol. In another study by Yan *et al.* [52] 51 % yield of 2-methylfuran with 99 % conversion of furfural was achieved. In the reaction temperature was 200 °C, hydrogen pressure 60 bar, reaction time 14 h and solvent used was octane. In this process same 2-methylfuran yield is achieved with lower pressure and temperature.

Also nickel deposited on supports is able to convert furfural to 2-methylfuran. To work selectively nickel needs to be used together with e.g. iron. Sitthisa *et al.*[53] studied activity of $Ni-Fe/SiO_2$ catalyst in furfural hydrogenation. It was observed that addition of Fe suppresses decarbonylation reaction and promotes the hydrogenolysis reaction to 2-methylfuran in high temperatures. Fe molecules are oxyphilic and they interact well with carbonyl O-atoms. It was discovered that addition of 2 wt% Fe achieved the highest yields, increase of Fe deposition over this amount the yield of MF starts to decrease. In this process 39 % yield of 2-methylfuran and 96 % conversion of furfural were achieved. Reaction temperature was 250 °C, pressure 1 bar, and H_2/furfural ratio 25. This high temperature and low pressure the process was conducted in vapor-phase.

Supports mostly used in furfural hydrogenation are silica, titania or other oxides (Table 10). Carbonaceous materials could be potential but not yet widely researched supports. Advantages of carbonaceous support materials include inertness, good mechanical and thermal stability, and high surface area. Potential carbonaceous support materials that could be used as upports include graphene, carbon nanofibers, carbon nanotubes, activated carbon, activated carbon cloths, and carbon coated structured materials. More research on catalysts on carbonaceous support for furfural hydrogenation to blend fuel components, MF and MTHF, should be performed.

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Table 10. Catalysts, reaction conditions and achieved products of liquid phase furfural hydrogenation.

Catalyst	Solvent	Pressure (bar)	Temperature (°C)	Time (h)	Conversion (%)	Product / selectivity (%)	Ref.
Cu/Fe_2O_3	2-propanol	15 Ptot	180	7.5	37	Furfuryl alcohol (75%)	[54]
Ni/Fe_2O_3	2-propanol	15 Ptot	180	7.5	46	Furfuryl alcohol (73%)	[54]
$Ni\text{-}Sn/TiO_2$	1-propanol	30 P_{H2}	110	1.25	99	Furfuryl alcohol (99%)	[55]
$Ni\text{-}Pd/SiO_2$	water	80 P_{H2}	40	2	99	Tetrahydrofurfuryl alcohol (96%)	[56]
$Ni(Cu_{3/2}PMo_{12}O_{40})$	ethanol	20 P_{H2}	80	1	98	Furfuryl alcohol (98%)	[57]
Pd/Fe_2O_3	2-propanol	15 Ptot	180	7.5	68	Furfuryl alcohol (61%)	[54]
$Pt\text{-}Sn/SiO_2$	1-propanol	10 P_{H2}	100	8	90	Furfuryl alcohol (98%)	[58]
$Pt/TiO_2\text{-}V_2O_5/SiO_2$		1 Ptot	150		87	Furfuryl alcohol (91%)	[59]
Cu-Zn-Cr-Zr oxide	1-propanol	20 P_{H2}	170	3,5	99	Furfuryl alcohol (96%)	[60]
Co-Mo-B alloy	ethanol	10 P_{H2}	100	3	99	Furfuryl alcohol (100%)	[61]
$Ir\text{-}ReO_x/SiO_2$	water	8 P_{H2}	30	6	99	Furfuryl alcohol (99%)	[62]
RuO_2	methanol	40 P_{H2}	120	1	99	Tetrahydrofurfuryl alcohol (76%)	[63]
Ru/C	cyclohexane	25 P_{H2}	132	6.5	32	Tetrahydrofurfuryl alcohol (50%)	[64]
Cu-Fe	octane	90 P_{H2}	220	14	99	2-Methylfuran (51%)	[65]

2.4. Succinic acid

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[64] ORDOMSKY VV, SCHOUTEN JC, VAN DER SCHAAF J, NIJHUIS TA. Biphasic single-reactor process for dehydration of xylose and hydrogenation of produced furfural. *Applied Catalysis A: General*. 2013;451(0):6-13.

[65] YAN, K., CHEN, A. Selective hydrogenation of furfural and levulinic acid to biofuels on the ecofriendly cu-fe catalyst. *Fuel*. 2014;114:101-108.

Succinic acid (Figure 5), a large volume commodity chemical, is regarded as one of the most important compounds derived from sugar platform, as published in a report by US department of Energy.[66] It is considered as a replacement for a large number of intermediates that are currently derived from non-renewable resources. A variety of industrially relevant compounds, such as γ-butyrolactone (GBL), 1,4-butanediol (BDO), and tetrahydrofuran (THF) have a high probability to be derived from succinic acid. There are a number of technologies available for the production of this acid, utilizing renewable and non-renewable resources. Nowadays, a number of leading market players are interested in producing this compound through biotechnological process, which is considered to be more environmental friendly in comparison to conventional fossil based resources. These circumstances create an intense competition within the bio-based succinic acid sector. Some of the enduring development projects are listed in Table 10.

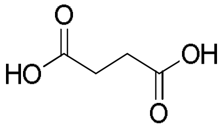

Figure 5. Chemical structure of succinic acid.

In addition to recent developments in the biotechnological route, a US based renewable chemical firm (Novomer) is interested in developing a process which is claimed to be cheaper than current biotechnological and petrochemical routes. This route is based on the combination of carbon monoxide (CO) and ethylene oxide (EO) to produce an intermediate called beta-propiolactone. The latter can then be converted into different chemicals such as acrylic acid, acrylate esters, 1.4-butanediol, and succinic acid.[67] However, the technology is still on the lab scale and there is no evidence that the process is viable for industrial production. In 2013, the global production of fossil based succinic acid was 32 kt/a, while biobased succinic acid exceeded its value and reached 51 kt/a.[68] The market is expected to reach ca. 600 kt/a, generating a revenue of ca. $990 million by 2020.[69] The market price of bio-succinic acid fluctuates between 2800-3000 $/t, while for petrochemical-based succinic acid, it is between 2400-2600 $/t depending on the supplier, grade, and quantity.[68] However, it is expected that with this fastest growing market, biosuccinic acid will easily compete with its counterpart fossil based succinic acid with a price much lower than petroleum based succinic acid.[68,70]

A number of joint ventures and partnerships between downstream companies is developing. Reverdia and Succinity are the major actors in Europe, while in the rest of the world BioAmber and Myriant play an important role in producing bio-succinic acid. The main producers of petroleum based succinic acid are DSM, Gadiv petrochemical industries, Mitsubishi Chemical, Kawasaki Kasel Chemical, Nippon Shokubai, and several producers from China and India.[68]

Furthermore, the recent biotechnological route of producing succinic acid by Succinity claimed to achieve 75 % saving in carbon footprint than the fossil based succinic acid production process,[71] while BioAmber reported to have 100 % reduction in greenhouse gases by emitting -0.18 kg CO_2 e/kg of succinic acid on a

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[66] T. Werpy and G. Petersen, "Top value added chemicals from biomass. Volume, 1: Results of screening for potential candidates from sugars and synthesis gas," Washington, DC, 2004.

[67] "CO business overview," [Online]. Available: http://www.novomer.com/co-business-overview. [Accessed April 2015].

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[69] "Bio Succinic Acid Market Analysis And Segment Forecasts To 2020," March 2014. [Online]. Available: http://www.grandviewresearch.com/industry-analysis/bio-succinic-acid-market. [Accessed April 2015].

[70] E4tech, "From the sugar platform to biofuels and biochemicals," 2015.

[71] "Our product: Succinity," [Online]. Available: http://www.succinity.com/biobased-succinic-acid/our-product-succinity. [Accessed April 2015].

field-to-gate basis.[72] The energy consumption for producing petroleum based succinic acid is approximately 97.7 MJ/kg of succinic acid, while the bio-based route followed by BioAmber claimed to have an energy requirement of 34.7 MJ/kg of succinic acid.[72] However, a comprehensive study of life cycle assessment (LCA) has proven that a low pH route with a direct crystallization to biosuccinic acid has the least impact on environment in terms of energy and greenhouse gas emissions.[73] This route is used by Reverdia.

2.4.1. Petrochemical route to succinic acid

The non-renewable commercial technology of producing succinic acid is quite mature and based on catalytic hydrogenation of maleic anhydride to succinic anhydride, followed by hydration of the latter. Some manufacturers utilize an alternative route, through hydration of maleic anhydride to maleic acid and subsequent hydrogenation to succinic acid.[74] The end product is obtained after crystallization and drying of concentrated succinic acid solutions. Hence, maleic anhydride is the main source for making succinic acid in chemical industry. After crude oil refining, benzene and C4 hydrocarbons (butane/butene) are typically utilized as feedstock for producing maleic anhydride.[75] However, the benzene route is an outdated one, even if share is ca. 15-30 % of the global capacity, due to environmental restrictions and process economics.

Currently, maleic anhydride is mainly produced from butane as a raw material.[76,77] Regardless of the raw material selection, the oxidation technology is quite similar, employing heterogeneous catalysis in fixed, fluid, and circulating bed reactors. Fluidized bed reactors have an advantage of providing much better heat transfer than fixed beds, maximizing yield and selectivity. The main process steps include feed preparation, oxidation reaction, separation, purification of the product, and energy recovery from the exhaust gases (Scheme 12).[78] The lower yield of this process generates unreacted butane, which is then incinerated in the exhaust gases producing carbon dioxide and other gases.[73,75]

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[72] "LIfe cycle Analysis (LCA)," April 2015. [Online]. Available: https://archive.is/WgAeM. [Accessed April 2015].

[73] B. Cok, I. Tsiropoulos, A. L. Roes and M. K. Patel, "Succinic acid production derived from carbohydrates: An energy and greenhouse gas assessment of a platform chemical toward a bio-based economy," Biofuels, Bioproduct and Biorefining, vol. 8, no. 1, pp. 16-29, 2014.

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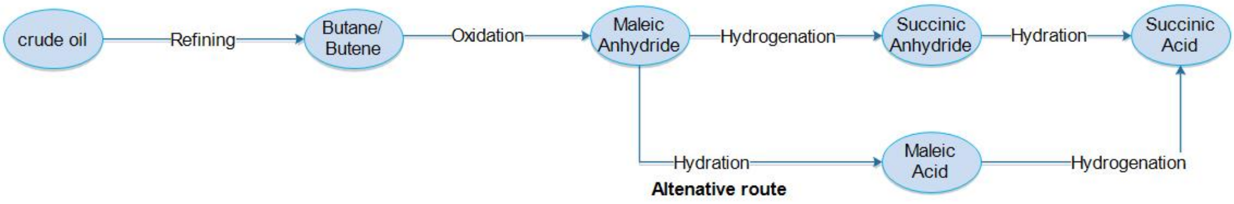
Table 10. Global production capacities of bio-succinic acid.[68,79,80,81,82]

Company	Raw material	Product	Location of plant	Capacity (kt/a)	Operational date
BioAmber	Glucose (Corn)	SA, BDO	Sarnia, Ontario, Canada	30	2015
	Sugars (Cane, Biomass, Tapioca)	SA, BDO	Rayong, Thailand	65	2015
	Sugars	SA, BDO	North America	70	2017
	Sugars	SA	Pomacle, France	3	2010
Myriant	Sorghum	SA	Lake Providence, Louisiana	77	2013
	-	SA	Leuna, Germany	5	2012
	-	SA	Nanjing, China	110	-
Reverdia	-	SA	Cassano Spinola, Italy	10	2012
Succinity (BASF-Purac)	Sugars/Biomass	SA	Barcelona, Spain	25	2013
	-	SA	-	50	-
			Total	445	



Scheme 12. Petrochemical route to succinic acid.

2.4.2. Biotechnological route to succinic acid

The biotechnological route to succinic acid is fundamentally based on aerobic or anaerobic fermentation, using natural (A. succiniciproducens) or genetically engineered microorganisms (Escherrichia coli), which act as a biocatalyst. These microorganisms have the capability to convert renewable feedstock, which mainly comprises of hexoses (C6 sugar) and pentoses (C5 sugar) to bio-succinic acid and to some byproducts

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[79] "Bioamber partners with PTTMCC Biochem for PBS production in Thailand," September 2011. [Online]. Available: http://www.bio-amber.com/bioamber/en/news/2011/bioamber-partners-with-pttmcc-biochem-for-pbs-production-in-thailand/455. [Accessed April 2015].

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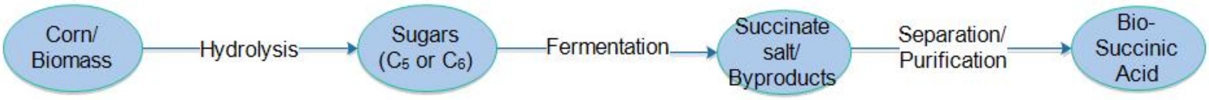
(acetic, formic, lactic and pyruvic acids). Fermentation itself can be carried out at low pH to neutral pH conditions. Although the yields of these processes are quite good, they suffer from high downstream processing costs, which contribute to 50 % of the overall production costs. Another drawback is inhibition of microorganism through accumulation of the end product. Common processing steps are shown in Scheme 13.[83]



Scheme 13. Biotechnological route to succinic acid.

2.4.3. Potential route from furfural to succinic acid

Lignocellulosic biomass originating from wood is an abundant non-food alternative feedstock for chemical and petrochemical industry. However, the conversion processes of lignocellulose to fuels and chemicals are at the moment often ineffective and unprofitable. Catalytic processes can provide the most selective routes from biomass to the desired products. Furfural is an important compound which is obtained from acid-catalyzed dehydration of C5 sugars. This furan derivative has been regarded as a key component to link carbohydrates based chemistry and petrochemistry. A range of chemical intermediates and products can be produced from this compound. One such component is succinic acid.

Succinic acid can be used in a variety of commercial applications, which include food and beverage industry, as precursors to pharmaceuticals ingredients, as additives, solvents, and polymers, and as an intermediate for the production of high value commodity chemicals (Scheme 14). The most important commodity chemical which can be synthesized by catalytic hydrogenation of bio-succinic acid is BDO. This important derivative is mainly used in the production of tetrahydrofurane (THF), γ-butyrolactone (GBL), in manufacturing of engineering plastics and as a hot melt adhesive. In 2013, the global market volume of BDO was 2.0 Mt/a, which is expected to increase to 2.7 Mt/a in 2020.[84] The price of BDO fluctuates between 1600 $/ton to 3400 $/ton depending on the region.[85] The current demand for bio-succinic acid for the production of BDO is approximately 80 kt/a, which is expected to reach 315 kt/a in 2020.[68]

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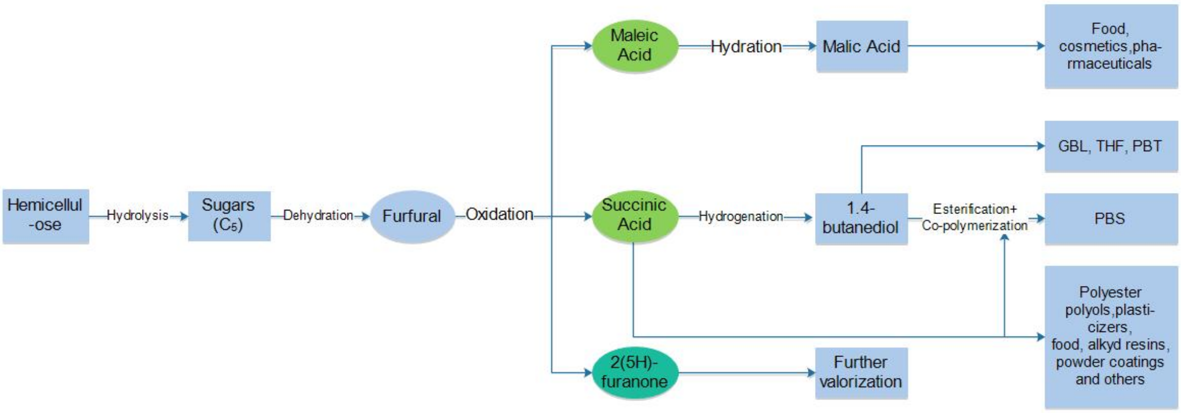
[83] J. Yi, S. Choi, M. -S. Han, J. W. Lee and S. Y. Lee, "Production of succinic acid from renewable resources," in *Bioprocessing Technologies in Biorefinery for Sustainable Production of Fuels, Chemicals and Polymers*, 1st ed., S. -. Yang, H. A. El-Enshasy and N. Thongchul, Eds., Hoboken, New Jersey: John Wiley and Sons, Inc, 2013, pp. 317-330.

[84] "Global 1,4-Butanediol Market Expected to Reach USD 6,947.1 Million by 2020," March 2014. [Online]. Available: http://www.grandviewresearch.com/press-release/global-1-4-butanediol-market. [Accessed April 2015].

[85] "1,4-Butanediol, Chemical market insight and foresight -on a single page.," November 2013. [Online]. Available: http://www.orbichem.com/userfiles/CNF%20Samples/bdo_13_11.pdf. [Accessed April 2015].



Scheme 14. Product value chain of succinic acid.

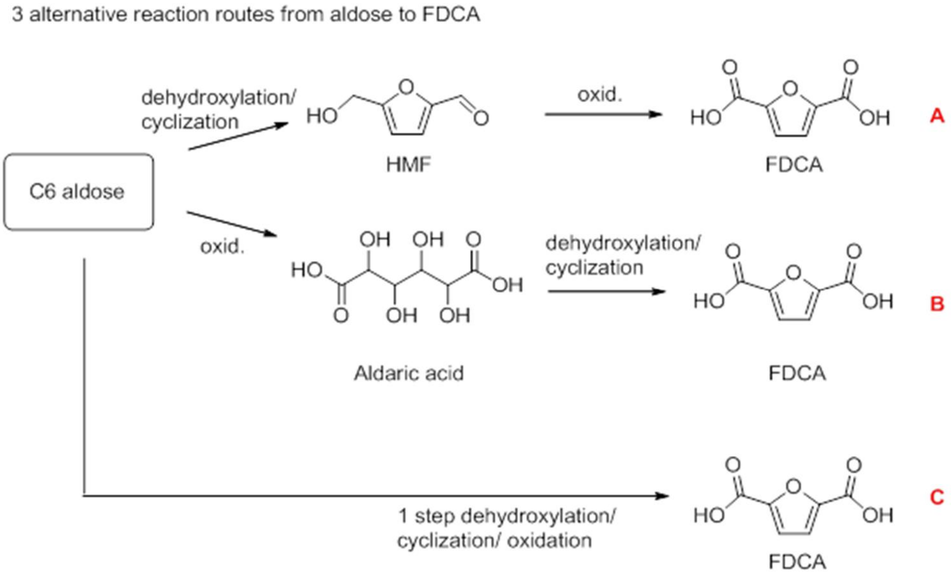
The second largest application of bio-succinic acid is polybutylene succinate (PBS). This important biodegradable polymer, which is a product of esterification and co-polymerization of BDO and bio-succinic acid has a huge potential to replace conventional petroleum based plastics in packaging films, bags, and boxes. This derivative can also be combined and blended with other compounds like polypropylene (PP), polystyrene (PS), bioplastics, fibers, and fillers, and can be used in number of applications. Currently, the targeted market of this derivative and its composites is small, but expected to nurture in the future as the demand for biodegradable plastics increases.[80] The demand of bio-succinic acid for the synthesis of PBS is expected to reach approximately 80 kt in 2020.[68]

Polyurethanes are another emerging market of bio-succinic acid, which has a huge potential to replace adipic acid in polyester polyols. The resultant bio-succinic acid based polyol has enhanced properties, such as abrasion and better chemical resistance in polyurethane based systems. In 2020, the required demand for bio-succinic acid for synthesis of polyester polyol used in polyurethanes has been estimated at 50 kt/a.[68]

2.5. Production of furan dicarboxylic acid (FDCA)

There are mainly two reaction routes for making FDCA from C6 sugars (Scheme15, routes A and B). The most commonly studied reaction route A uses hydroxymethyl furfural (HMF) or a derivative of HMF as an intermediate. In this route the aldose, preferably fructose is converted to HMF. Then in the second step HMF is further oxidised to FDCA. There is a second alternative (route B), where the sugar is first oxidised to aldaric acid, and the aldaric acid is then converted to FDCA. **The route B is currently under study at FURCHEM project.** Route C is very little studied but an interesting alternative.

The state-of-the-art of the route A is discussed in the following chapter 2.5.1. The state-of-the-art of the first step in route B is discussed in chapter 2.5.2. The state-of-the-art of the second step in route B is discussed in chapter 2.5.3.



Scheme 15. Three reaction routes from C6 aldose sugars to FDCA. The route A is the most commonly studied, whereas the route B is currently under study at FURCHEM project.

2.5.1. Reaction routes to FDCA via HMF and HMF derivatives

There are hundreds of literature references for the production of HMF and its derivatives from aldoses. Only in 2014 there were 90 references for the production methods for HMF (Figure 6). There has been a clear rise in the number of publications between 2002-2014. Therefore, these methods are not listed here in detail. However, there is a comprehensive review article from 2013 which describes in great detail the various methods for producing HMF and derivatives from aldoses.[86]

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[86] van Putten, R.-J., van der Waal, J. C., de Jong, E., Rasrendra, C. B., Heeres, H. J., de Vries, J. G. 2013. Hydroxymethylfurfural, a versatile platform chemical made from renewable resources. Chem. Rev. 113, 1499-1597.

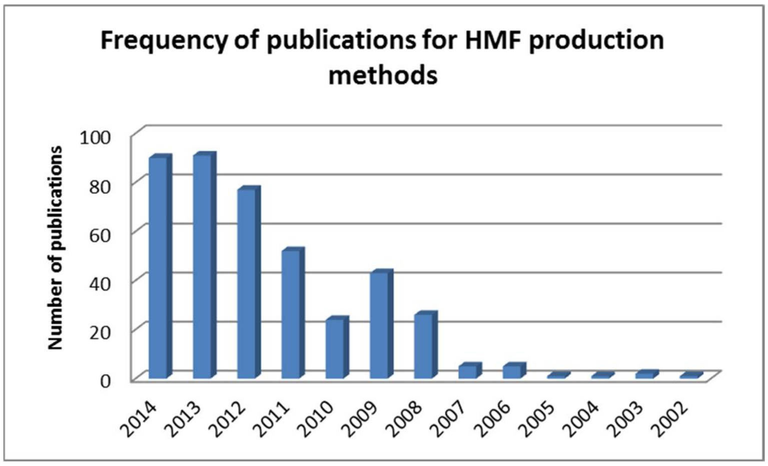


Figure 6. Frequency of literature reports for the production of HMF from aldoses (years 2002-2014).

Also for the oxidation of HMF to FDCA, there are over 150 literature reports for this reaction, and these are not described here in detail (Figure 7). Also for this transformation there has been a clear increase in the number of publications in the recent years. Many of these processes are using catalytic oxidations (Figure 8). The catalysts are often noble metals (Au, Pt, Pd) or then Co or Mn. Also some examples with for example Rh or Cu catalysts exist. The most common oxygen source is oxygen or air in these transformations. Also chemical oxidants have been used, with or without catalyst. The chemical oxidants can be for example $KMnO_4$, H_2O_2 or HNO_3.

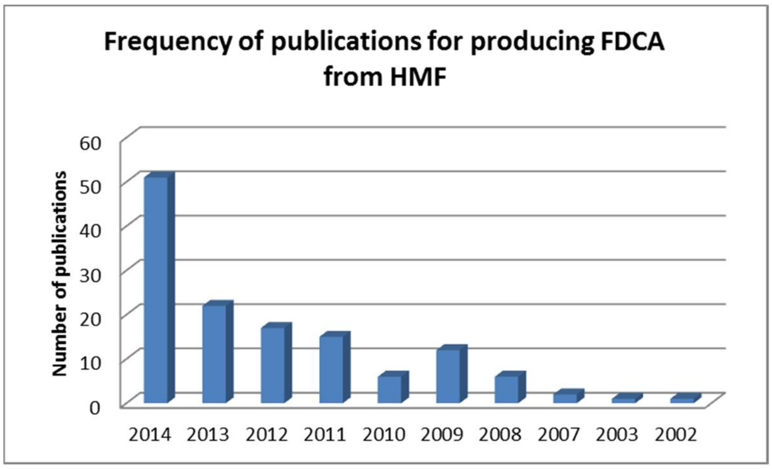


Figure 7. Frequency of literature reports for the production of FDCA from HMF (years 2002-2014).

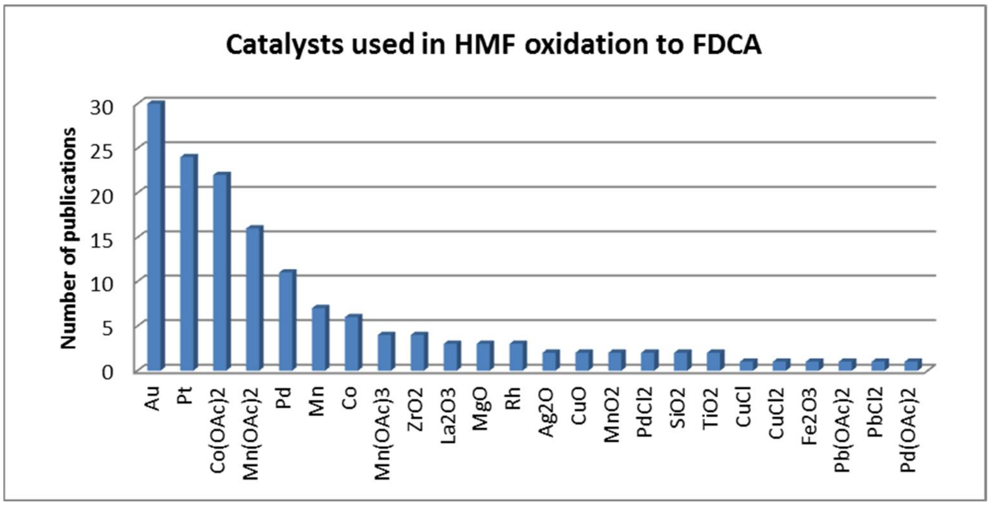
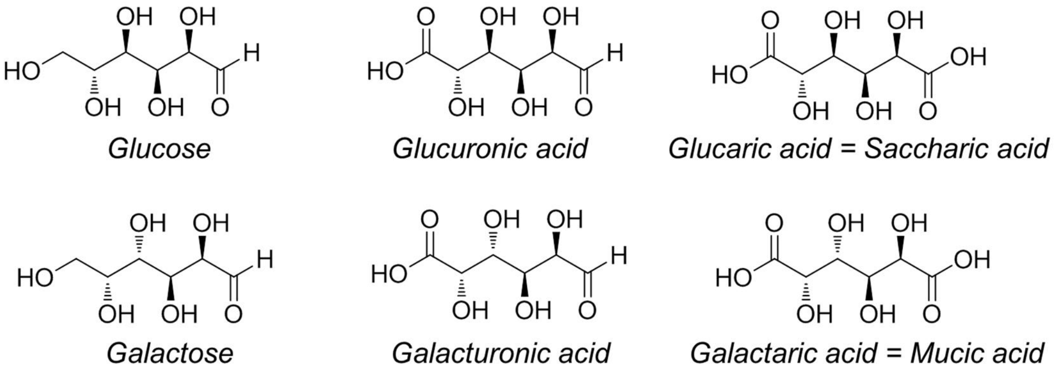


Figure 8. Catalysts used in the oxidation of HMF to FDCA.

The Dutch company Avantium is very visible in the field of furan chemicals. Avantium has a pilot scale plant operating in the Netherlands producing FDCA. The technology of Avantium is based on the HMF reaction route. Avantium uses fructose syrup as the feedstock for the process where HMF methyl ether is the reaction intermediate on the way to FDCA. In the process also levulinic acid esters are formed. The oxidation of HMF methyl ether to FDCA is done with homogeneous cobalt/ manganese catalysis, and the oxidation process is similar to the oxidation of xylene to terephthalic acid.

2.5.2. Oxidation routes to aldaric acids

The reaction route B to FDCA (Scheme 15 on page 30) utilizes aldaric acids as an intermediate product. Aldaric acids can be produced by oxidation of aldoses or uronic acids. Both aldoses and uronic acids are widely present in the nature as discussed in chapter 2.1. In this chapter we will focus on the oxidation reactions of C6-sugars and derivatives. The nomenclature of the oxidised sugar derivatives follows the aldose nomenclature. Glucose can be oxidised to glucuronic acid and further to glucaric acid, which is also called saccharic acid. Galactose can be oxidised to galacturonic acid and further to galactaric acid, which is also called mucic acid (Figure 9).



Glucose

Glucuronic acid

Glucaric acid = Saccharic acid

Galactose

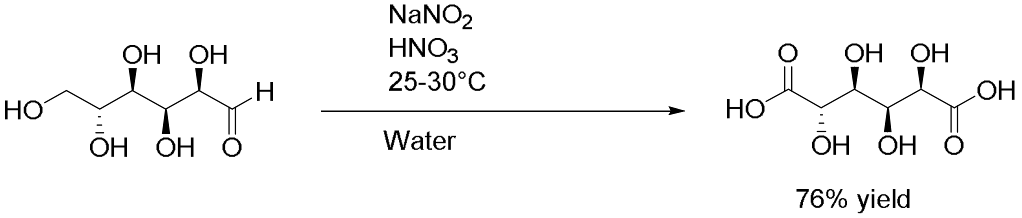
Galacturonic acid

Galactaric acid = Mucic acid

Figure 9. Nomenclature of certain C6 sugars and sugar acids.

Oxidation of aldoses to aldaric acids. There are several methods reported in the literature for the oxidation of aldoses, in particular glucose and galactose, to the corresponding aldaric acids. Traditionally, the oxidation is performed in nitric acid (HNO_3), which acts both as a solvent and as an oxidizing agent in the reaction. The nitric acid methods often yield 40-45% yields of the aldaric acid[87]. Recently, several alternative methods have been developed, and the methods with highest yields are listed below.

Kiely and Hash [88] have reported an improved method for the nitric acid oxidation for D-glucose which yields upto 76.7% yield of the di-sodium D-glucarate salt. The method is presented in Scheme 16. Rivertop Renewables, a company located in Montana, US, aims for the utilization of this method. The company states their production capacity is at 4.5 kt/a in 2015.[89]



Scheme 16. Nitric acid oxidation of glucose according to method by Kiely and Hash.[88]

Merbouh et al. [90] have reported a halogen aided TEMPO oxidation of glucose and galactose which yields glucaric acid and its salts with 70-95% yields and galactaric acid and its salts with 70-80% yields. The method is presented in Scheme 17.

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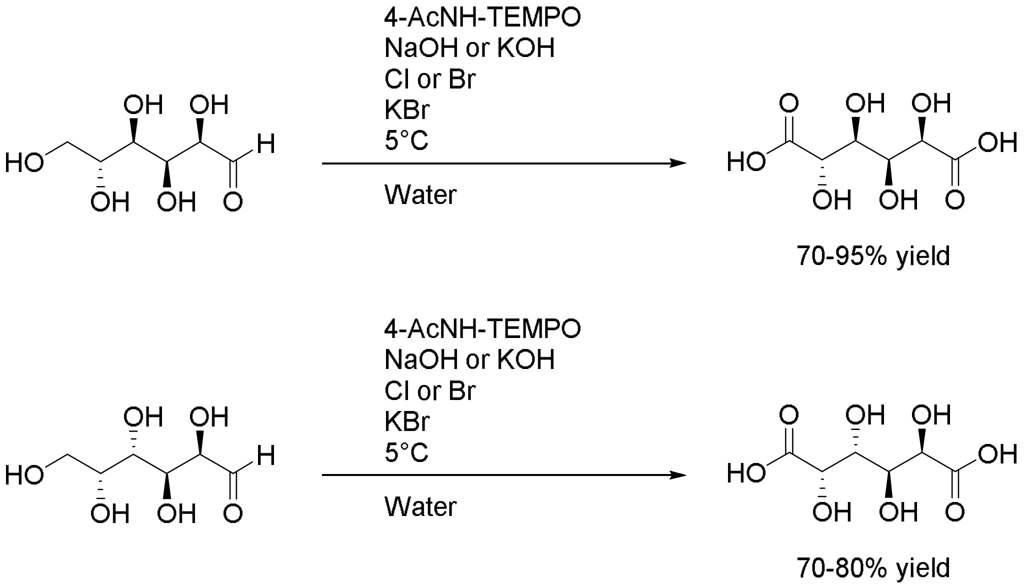
[87] Smith, T. N., Hash, K., Davey, C.-L., Mills, H., Williams, H., Kiely, D. E. 2012. Modifications in the nitric acid oxidation of D-glucose, Carbohydrate Research, 350, 6-13.

[88] Kiely, D. E., Hash, K. R. 2008, Method of oxidization using nitric acid, US 2008/ 0033205 A1.

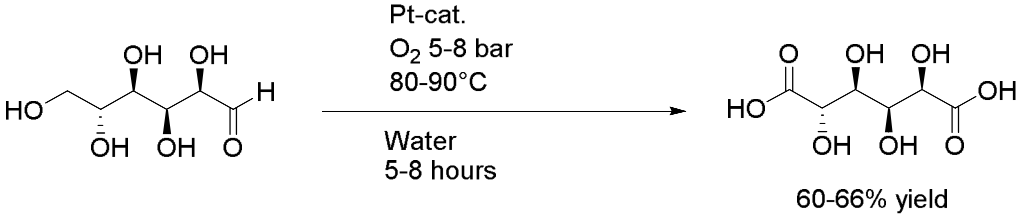
[89] Rivertop Renewables website, http://www.rivertop.com/ Accessed: May 2015.

[90] Merbouh, N., Bobbit, J. M., Brückner, C. 2011. 4-AcNH-TEMPO-catalyzed oxidation of aldoses to aldaric acids using chlorine or bromine as terminal oxidants. Journal of Carbohydrate Chemistry, 21 (1-2), 65-77.



Scheme 17. TEMPO oxidation of aldoses according to method by Merbouh et al. [90]

Boussie et al. [91] have reported a catalytic process for the oxidation of glucose to glucaric acid, which uses Pt-catalyst on a solid carrier and oxygen or air as oxidant. This method yields glucaric acid with 60-66% yields. The method is presented in Scheme 8. The company Rennovia aims for the utilization of this method. They aim to use glucaric acid as an intermediate to bio-based adipic acid.[92]



Scheme 18. Catalytic oxidation of glucose according to method by Boussie et al. (company Rennovia)[91]

Oxidation of uronic acids to aldaric acids. There are a handful of methods reported in the literature for the oxidation of uronic acids to aldaric acids. The oxidation can be performed both by biotechnology or by chemical or chemo-catalytic means. Below are listed some promising methods for the oxidation.

By metabolic engineering, the fungal strains of *Hypocrea jecorina* and *Aspergillus niger* have been induced to produce meso-galactarate (mucate) from galacturonic acid. The process yields muconic acid with 80-90% yields (work conducted at VTT).[93] The enzymatic oxidation of glucuronic acid to D-glucaric acid with

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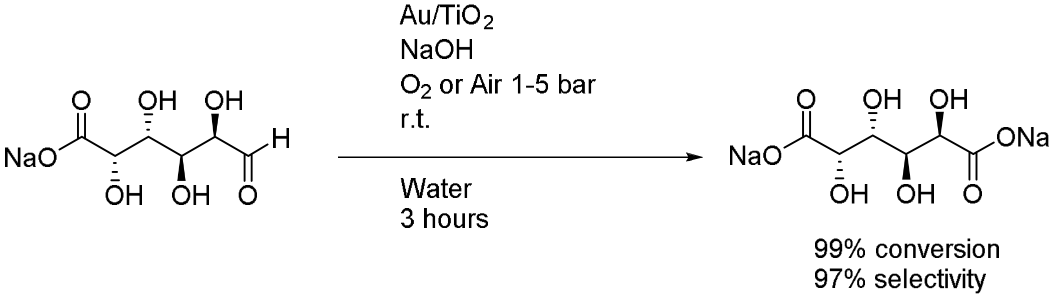
[91] Boussie, T. R., Dias, E. L., Fresco, Z. M., Murphy, V. J., Shoemaker, J., Archer, R., Jiang, H. 2010. Production of adipic acid and derivatives from carbohydrate-containing materials. WO 2010/ 144862 A2.

[92] Rennovia website, http://www.rennovia.com/ Accessed: May 2015.

[93] a) Mojzita, D., Wiebe, M., Hilditch, S., Boer, H., Penttilä, M., Richard, P., 2010. Metabolic engineering of fungal strains for conversion of D-galacturonate to meso-galactarate. Appl. Environ. Microb. 76, 169-175. b) Boer, H., Hildich, S., Richard, P., Penttilä, M. 2012. Conversion of hexuronic acid to hexaric acid. US 2012/0045804 A1.

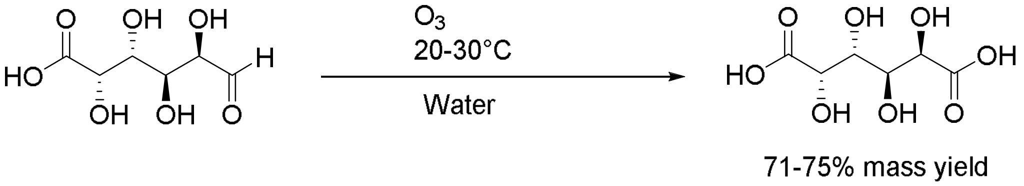
engineered uronate dehydrogenases or oxidases has been reported by Kambourakis and co-workers. The yields of the oxidised products were not disclosed.[94]

Gold catalysed oxidation of sodium galacturonate to disodium galactarate has been reported by van der Klis and co-workers. The heterogeneous Au/TiO$_2$ catalyst is highly active in this oxidation in the presence of a base, and the catalyst is also stable for at least three consecutive cycles. Oxygen is used as the oxidant. The method yields disodium galactarate with upto 99 % conversion and 97 % selectivity in 3 hours at room temperature.[95] The method is presented in Scheme 9.



Scheme 19. Catalytic oxidation of sodium galacturonate according to method by van der Klis et al.[95]

Also ozone has been used for the oxidation of uronic acids. Bonhoure and co-workers have patented a method for the production of mucic acid from galacturonic acid by using ozone as the oxidant in aqueous solutions. They report a mass yield of 71 - 75 % from the process.[96] The method is presented in Scheme 20.



Scheme 20. Ozone oxidation of galacturonic acid according to method by Bonhoure et al.[96]

2.5.3. Reaction routes from aldaric acids to FDCA

The second step of the reaction route B to FDCA (Scheme 15 on page 350) proceeds from aldaric acids to FDCA. Aldaric acids, unlike HMF, are stable and crystalline compounds, and therefore they are easy to store and handle.

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[94] Kambourakis, S., Griffin, B. M., Martin, K. V. 2014. Compositions and methods for producing chemicals and derivatives thereof. US2014/0206047 A1.

[95] a) van der Klis, F., Frissen, A. E., van Haveren, J., van Es, D. S. 2013. Waste not, want not: mild and selective catalytic oxidation of uronic acids. Chem. Sus. Chem. 6, 1640-1645. b) van Es, D. S., van Haveren, J., Wilhelmus, H., Raaijmakers, C., van der Klis, F., van Engelen, G. P. F. M., Frissen, A. E. 2012. Catalytic oxidation of uronic acids to aldaric acids. US 2015/0065749 A1.

[96] Bonhoure, J.-P., Abboud, H., Aussenac, T. R., Coste, C. U., Hoang, L., Ralainirina, R., Rannou, A. C. 2013. New method for synthesising mucic acid using ozone, nouvelle method de synthese de l' acide mucique par l' ozone. WO 2013/144483 A1.

There are only ca. 10 literature references for the production of FDCA (or esters of FDCA) from aldaric acids, the oldest reference dating back to 1876.[97] Only one of these references is a patent.[98] As in the patent method, the most common way uses mineral acids (HBr, HCl, H_2SO_4, HNO_3) for the dehydroxylation of the aldaric acid to FDCA. These acids are used in large excess. For example in the patented method by Gaset and co-workers 1.49 kg of HBr is used for converting 70 g of galactaric acid to FDCA with 60 % yield. This reaction takes 9 - 10 hours.

Very similar methods are reported also by other authors, where excess of either H_2SO_4 or HBr is used to produce FDCA, typically the yields vary around 50 %.[99]

Alternatively, an excess of benzene sulfonic acid or *p*-toluene sulfonic acid can be used for the dehydroxylation of aldaric acids to obtain around 50 % yield of FDCA.[100] When a sub-stoichiometric amount of these acids are used, the yields are typically between 6 – 40 % for FDCA.[101]

The route from aldaric acids to FDCA was considered interesting and largely unexplored, and **the route was chosen as a topic of technology development in FURCHEM project**.

2.6. FDCA applications

FDCA could potentially be applied as replacement of terephtalic acid (TPA). Current worldwide TPA consumption is ca. 50 Mt/a. The most important application of TPA is polyesters, mainly poly(ethylene terephthalate) (PET). TPA is also applied to some extent in the production of polyamides. FDCA has also potential to replace isophthalic acid or bisphenol A (polycarbonates) in applications. It can be noted, that the properties of the FDCA replacements e.g. in polymers are not directly the same as the original polymers, but new and also advantageous properties may appear. In a recent EU project BioConSepT, management consultancy company Weastra estimated the projected market for FDCA in 2020 to approximately 500 kt/a with the value of approximately 500 M$/a.[102] Of this number, 65% is expected to be PET replacement (PEF), 16 % polyamides, and 8 % polycarbonate replacements, and 7 % plasticizers.

Patents related to FDCA in connection to polymers were surveyed. 91 relevant patents were found. Vast majority of the patents were published after 2007 (72 patents). 83 patents were related to polyesters (polymerization or applications). 8 patents were related to polyamides, and 5 patents were related to plasticizers. The 91 relevant patents are listed in Appendix 1, Table 1.

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[97] Fittig, Rudolph, Heinzelman. 1876. Mittheilungen aus dem Chemischen Institute der Universität Strassburg. H. Chem. Ber. 9. 1189-1199.

[98] Gaset, A. 1996. Preparation of furan-2,5-dicarboxylic acid. Fr Demande 2723945.

[99] a) Kuhn, R., Dury, K. 1951. Ringschlüsse mit α, α'-Dioxymuconsäure-estern. Liebigs Ann. Chem. 571, 44-68. b) Muramatsu, H. 1992. Syntheses of acetylenes containing trifluoromethyl substituted heterocyclic ring. Kenkyu Hokoku- Asahi Garasu Zaidan, 60, 167-174. c) Haworth, W. N., Jones, W. G. M., Wiggins, L. F. 1945. The conversion of Sucrose into Furan Compounds. J. Chem. Soc. (1), 1-4.

[100] a) Bratulescu, G. 2000. Cyclization of the D-saccharic acid to 2,5-furandicarboxylic acid under the effects of microwaves. Revue Roumaine de Chimie, 45 (9), 883-885. b) Lewkowski, J. 2001. Convenient synthesis of furan-2,5-dicarboxylic acid and its derivatives. Polish Journal of Chemistry, 75(12), 1943-1946.

[101] a) Bratulescu, G. 2000. Novel technique for one-step synthesis of 2,5-bis(alkoxycarbonyl)furans. Journal de la Societe Algerienne de Chimie. 10(1), 135-137. b) Taguchi, Yoichi. 2008. One-step synthesis of dibutyl furandicarboxylates from galactaric acid. Chem. Lett., 37(1), 50-51.

[102] http://www.bioconsept.eu/wp-content/uploads/BioConSepT_Market-potential-for-selected-platform-chemicals_report1.pdf. Report dated in 2012.

2.6.1. Terephtalic acid (TPA), isophtalic acid and furan(dicarboxylic acid) (FDCA) properties and markets

Terephtalic acid (TPA) is a colorless to white crystalline solid nearly insoluble in water and alcohols (Figure 10). TPA was first synthesised in 1847. Nowadays TPA is made by air oxidation of para-xylene. The main application of TPA is in various polymers, especially poly(ethylene terephthalate) (PET). In order to be applicable in the polymerization of polyesters, TPA is purified (purified therephthalic acid PTA). Common impurities in TPA are 4-carboxybenzaldehyde and various monoacids.

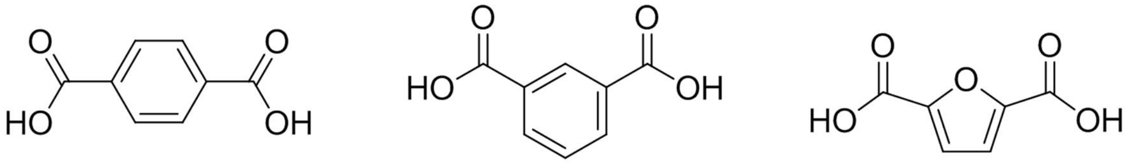

Figure 10. Chemical structures of therephtalic acid (TPA), isophtalic acid (IPA) and furan(dicarboxylic acid) (FDCA).

The global consumption of TPA was approximately 47 Mt in 2012, with a market value of about $60 billion and is forecasted to grow 6 % per year, reaching about 65 Mt/a in 2018.[103] Asia-pacific region is expected to account for the majority of the demand in 2020, as shown in Figure 11. China's demand for purified terephthalic acid (PTA) has grown at a fast pace in the past decade.

BP (British Petroleum) is the world's largest producer of PTA. On the other hand, China's PTA capacity stood at 33 Mt/a in 2012, which means that China has more than half of the world's PTA production capacity.[104] Nowadays China is also importing PTA. The price of PTA stood at 1185 US$/t in January 2013.[105]

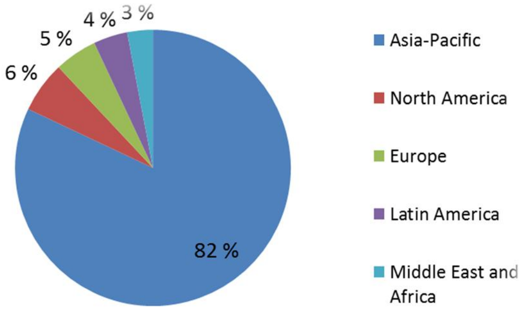

Figure 11. Demand of PTA by region in 2020.

Worldwide around 65 % of the PTA goes to polyester fibre manufacturing, 27 % to PET bottle resin and the remaining 8 % to film and other plastic end uses (Figure 12). Other minor uses of PTA include coatings and composite materials, and hotmelt adhesives.

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[103] Smith K, Sriram P, Pujari A. Dimethyl terephthalate (DMT) and terephthalic acid (TPA). (695.4020) IHS Chemical Economics Handbook. (ihs.com/chemical) September 2013.

[104] http://www.platts.com/news-feature/2013/petrochemicals/asia-paraxylene/index

[105] http://www.fibre2fashion.com/textile-market-watch/purified-terephthalic-acid-pta-price-trends.asp

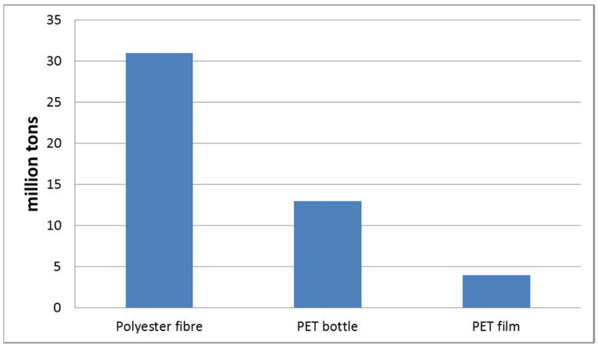

Figure 12. Worldwide use of PTA in different applications (2012).

Bio-based terephtalic acid can be considered an alternative route, alongside FDCA, to obtain bio-based aromatic materials. Bio-based TPA production has been under active research in recent years. Gevo, Inc. (www.gevo.com) has developed a technology to produce para-xylene directly from isobutanol. i-BuOH is produced from C5/C6 sugars through a fermentation process using proprietary microorganisms developed by Gevo. In May 2014 it was announced that Gevo is selling i-BuOH based para-xylene to Toray for futher processing into bio-polyester.[106]

Virent (www.virent.com) is developing a technology for commercialization called BioForming® that uses C5/C6 carbohydrates and converts them into a BTX stream rich in para-xylene. The development of Virent's BioForming® technology platform is supported through strategic investors including Cargill, Shell and Honda.

Muconic acid, limonene as well as methyl coumalate have been used as intermediates for the bio-based TPA production without going through the biobased para-xylene intermediate. Companies/universities active in this area are Amyric (muconic acid), Sabic (limonene) and Iowa state university (methyl coumalate).

Genomatica inc. has developed a direct fermentation process to produce TPA from carbohydrates derived from treated biomass as a carbon source using a genetically modified bacteria.

Biochemtex, which is part of M&G (www.mg-chemicals.com, producer of PET) have developed a propriatery process and enabeling technologies to convert lignin to biobased BTX, resulting in a biobased para-xylene called MOGHI. The MOGHI process, to which M&G holds exclusive licenses is still in the early stages. M&G is developing capabilities to produce both biobased para-xylene and biobased MEG. These two biobased chemicals can then be incorporated into M&G's existing, traditional PET production processes, which could ultimately yield 100 % biobased PET.

Isophthalic acid. The current market size of isopthalic acid (IPA) has been estimated to be ca. 600 kt/a, and there are recent reports on overcapacity.[107] IPA is applied e.g. as a comonomer in PET production, in polyester resins, alkyd resins, and as a monomer to produce aramides. Due to low market price and overcapacity issues, the Weastra BioConSepT report did not consider IPA to have as attractive replacement potential as TPA.[109] However, when considering the physical properties of the polymers, some recent reports have shown that FDCA polyesters can have properties that are closer to IPA polyesters than TPA polyesters.

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[106] www.nasdaq.com

[107] Chemical Economics Handbook, Isophthalic Acid, 2012. https://www.ihs.com/products/isophthalic-acid-chemical-economics-handbook.html Accessed May 2015.

E.g. Burgess et al. discuss that both poly(ethylene furanoate) and poly (ethylene isophthalate) have significantly better O_2 barrier properties than poly(ethylene terephthalate).[108]

Furan dicarboxylic acid (FDCA) is currently only produced by a few companies on a demand basis. The estimated production volume is 3.5 – 5 t/a. The current estimated price for FDCA is 2 300 000 $/ton. The main producers of FDCA are V & V Pharma Industries (Indian company established 2000), Carbone Scientific (currently located in London, UK) and Chemsky (Chemsky was founded in 2010 in Shanghai).[109] Some other Chinese suppliers of FDCA can also be found on Alibaba. The Dutch company Avantium has declared an economically feasible way of producing FDCA with a price tag around 1000 $/ton from 2016. The company is operating a pilot plant with a total capacity of 40 t/a and there is a plan to start the first industrial FDCA production in 2016 with a capacity of 30 – 50 kt/a. The company plans commercialization starting 2018, on a base of license production with a capacity of 300 - 500 kt/a.

2.6.2. Polyesters from TPA vs. FDCA

Poly(ethylene terephthalate) (PET) is the most important application of terephtalic acid. The structure of PET is shown in Figure 13. The market size of PET is ca. 50-60 Mt/a. It is a clear, strong and lightweight plastic. It is typically called "polyester" when used for fibers or fabrics, and "PET" or "PET Resin" when used for bottles, jars, containers and packaging applications. Ca. 60 % of PET is applied in fibers, and ca. 30 % in bottles, and 10 % in other applications.

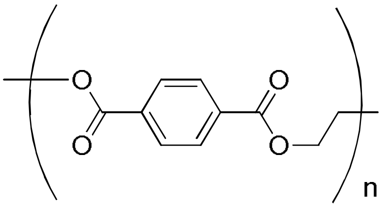

Figure 13. Chemical structure of poly(ethylene terephthalate) (PET).

The polyester fibre market has been predicted to continue growth at the expense of other synthetic and natural fibres. The global polyester fibre demand was in 2012 around 38 Mt/a. More than 90 % of the polyester fibre capacity resides in Asia. Since peaking in the mid-1990`s, the polyester fibre production in North America and Europe has declined.[110]

As polyester textile production in North America and Europe was lost, these regions experienced rapid growth in PET packaging markets. However, the North American PET packaging resin market has seen a stagnation in recent years, largely attributed to an ongoing decline in soda, juice and sweetened beverage consumption. Global PET capacity currently outpace the demand. The estimated demand for PET packaging resins was around 20 Mt/a in 2014. Recycled resins are increasingly competing with virgin PET resins due to good growth in collection. Most of the collected recycled material is used in the fibre industry. There has also been a strong growth in the use of recycled PET packaging resin for food and bevarege packaging in the west. The current U.S. recycling rate for PET is 31 %. Europe has a PET recycling rate of 52 %.[111]

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[108] Burgess et al. Oxygen sorption and transport in amorphous poly(ethylene furanoate) Polymer 55 (2014) 4748-4756. DOI:10.1016/j.polymer.2014.07.041

[109] WP 8.1. Determination of market potential for selected platform chemicals, Waestre

[110] http://www.foodbev.com/news/polyester-fibre-now-commands-almost-50-o#.U70EYVXyV9A

[111] www.petresin.org

Neo Group (Lithuania) is the biggest producer of PET resin in Europe with 300 kt/a (12 % of the European production).[112] Globally, Indorama is the market leader of PET resin with a combined capacity of 3.75 Mt/a.

Bio-based PET. As PET resin is widely used in the food and bevarege packaging, there is a drive toward bio-based production. The ethyleneglycol (EG) part of PET is already produced through a bio-based way, based on bioethanol. Coca Cola company launched in 2010 the Plant bottle, a PET bottle with bio-based EG and oil-based PTA. The Plant bottle can be successfully recycled along with all other PET bottles. There is active reseach ongoing to obtain also bio-based PTA (see chapter 2.6.1).

Poly(ethylene furanoate) (PEF). Polymerization routes to PEF and other FDCA polyesters were shortly looked into around 1970's,[5] after which very few publications on FDCA polyesters appeared until Canon published a FDCA polyesterification patent in 2007,[113] followed by a set of patents (altogether 13 patents on FDCA polyesters in 2007-2012, see Appendix 1, Table 1). The first Avantium (Furanix) PEF polymerization patent was published in 2010,[114] and in 2009 Gandini et al.[115] published a paper on PEF polymerization. Since then the topic has aroused increasing interest both in scientific journals and patent literature. The structure of PEF is shown in Figure 14.

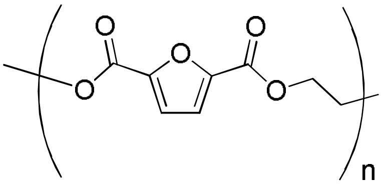

Figure 14. Chemical structure of polyethylene furanoate (PEF).

Comparison of physical properties of PEF and PET is shown in Table 12. Especially noteworthy is the ca. 10 times higher O_2 barrier of PEF, and on the other hand the lower elongation values of PEF.

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[112] www.CPME-pet.org

[113] WO07052847, 2007. Polymer compound and method of synthesizing the same.

[114] WO10077133, 2010. Process for preparing a polymer having a 2,5-furandicarboxylate moiety within the polymer backbone and such (co)polymers.

[115] Gandini A et al. The furan counterpart of poly(ethylene terephthalate): An alternative material based on renewable resources. *J.Polym.Sci.Part A*, 49 (2009) 295-298.

Table 11. Comparison of physical properties of PEF and PET, measured in various studies.

	density (g/ml)[116]	T_g (°C)[116,117]	T_m (°C)[116,117,118,119]	T_d (°C)[116]	**O_2 permeability (barrer)[116]**	Modulus (MPa)[118,120]	Max. Stress (MPa)[118,120]	Elongation (%)[118,120]
PEF	1,43	85 86	211 235 239(eq.) 247(eq.)	389	**0,0107**	2500 (amorphous) 2100	35 (amorphous) 67	3 (amorphous) 4
PET	1,33	76 74	247 265	413	**0,114**	2000 (amorphous)	45 (amorphous)	250 (amorphous) 90 (semi-crystalline)

Barrier properties of PEF. Avantium website[117] shortly advertises:

PEF oxygen barrier is 10 times better than PET
PEF carbon dioxide barrier is 4 times better than PET
PEF water barrier is 2 times better than PET

Burgess et al.[116] have a set of recent papers regarding barrier properties of PEF. The group is from Atlanta, US, and their work has been done in collaboration with the Coca-Cola Company. The first paper [116] describes reasons behind the ca. 10 times higher O_2 barrier of PEF when compared to PET (The O_2 permeability comparison in Table 11 is from this paper). According to this paper, the difference arises from the polarity and nonsymmetrical axis of ring rotation in the furan ring of PEF: this hinders ring-flipping in PEF, reducing polymer chain mobility, which affects O_2 diffusion (Figure 15). Follow-up paper [121] from the same group continues the oxygen transport discussion by e.g. comparing the O_2 permeability of PEF to various aromatic polyesters. They note that poly(ethylene isophtalate) has also rather low O_2 permeability (0.015 barrer), but this value is still higher than the value measured for PEF (0.011 barrer). They also note that even though PEF has rather good O_2 barrier, the PEF O_2 permeability values are still at least five times higher than the values measured typically for commercial O_2 barrier polymers (Nylon-MXD6, dry EVOH).

Two other follow-up papers from Burgess et al.[122,123] deal with water sorption properties of PEF. Different techniques were applied to study water sorption in amorphous films, which were exposed to water and water vapour. They find out that when compared to PET, PEF exhibits 1.8 x higher water sorption capacity (solubility). On the other hand, PEF exhibits 5 x reduced water diffusion coefficients. When these effects are mathematically combined, the group calculated reduction in water permeability of 2.8 for PEF compared to

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[116] Burgess et al. Chain Mobility, Thermal, and Mechanical Properties of Poly(ethylene furanoate) Compared to Poly(ethylene terephthalate). Macromolecules 47 (2014) 1383-1391. DOI:10.1021/ma5000199

[117] Avantium website: http://avantium.com/yxy/products-applications/fdca/PEF-bottles.html

[118] Knoop et al. High molecular weight poly(ethylene-2,5-furanoate); critical aspects in synthesis and mechanical property determination. J.Polym.Sci.Part A 51 (2013) 4191-4199. DOI:10.1002/pola.26833

[119] Codou et al. Non-isothermal Crystallization Kinetics of Biobased Poly(ethylene 2,5-furandicarboxylate) Synthesized via the Direct Esterification Process. Macr.Chem.Phys. 215 (2014) 2065-2074. DOI:10.1002/macp.201400316

[120] Jiang et al. A series of furan-aromatic polyesters synthesized via direct esterification method based on renewable resources. J. Polym. Sci. Part A 50 (2012) 1026-1036. DOI:10.1002/pola.25859

[121] Burgess et al. Oxygen sorption and transport in amorphous poly(ethylene furanoate) Polymer 55 (2014) 4748-4756. DOI:10.1016/j.polymer.2014.07.041

[122]: Burgess, Mikkilineni et al. Water sorption in poly(ethylene furanoate) compared to poly(ethylene terephthalate). Part 1: Equilibrium sorption. Polymer 55 (2014) 6861-6869. DOI:10.1016/j.polymer.2014.10.047

[123] Burges, Mikkilineni et al. Water sorption in poly(ethylene furanoate) compared to poly(ethylene terephthalate). Part 2: Kinetic sorption. Polymer 55 (2014) 6870-6882. DOI:10.1016/j.polymer.2014.10.065

PET, which is consistent with the reduction of 2 x for PEF vs. PET reported at the Avantium website.[117] However, actual permeation experiments were not conducted in these papers, and the authors state that such measurements cannot be found in the current literature.

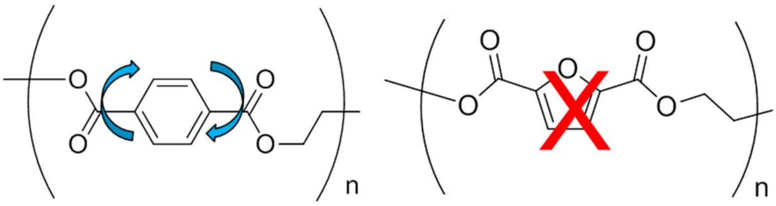

Figure 15. Aromatic rings in PET chains are symmetrical, allowing ring-flipping. In contrast, furan rings in PEF chains are non-symmetrical (and also more polar), which hinders ring-flipping and reduces O_2 permeability, according to Burgess et al.[116]

***Thermal and mechanical properties of PEF**.* A recent paper by Knoop et al.[118] gives information on the mechanical properties of high molecular weight PEF (M_n= 83 000 g/mol). The authors apply both melt and solid state polymerizations in this study to produce PEF under relatively mild conditions. They state that despite the fact that FDCA is one of the most stable known monocyclic furan derivatives, the thermal stability is somewhat lower than that of terephtalic acid. Hence, polymerization conditions need to be adapted to accommodate for this to avoid discoloration. Authors report “very low level of discoloration, but slightly yellow” polymers in this study. In contrast to PET, PEF displays brittle fracture behavior which is clear from the lack of yielding during stress-strain tests (see elongation values in Table 11, which are mainly taken from this study). The authors comment: “Whereas the low elongation at break can be limiting for bottle applications it can be useful for high tenacity fiber applications.” They also note that similar issues were encountered in the case of polylactic acid, and for poly(lactic acid) these issues have been increasingly resolved by proper processing conditions and the development of impact modifiers.

***PEF commercialization situation**.* Avantium together with the Coca cola company, Danone and ALPLA are currently working on PEF bottle. The PEF bottle is made of FDCA and bio-based EG. The consortium has planned to launch the first PEF bottles on the market in 2017. PEF has better barrier properties (oxygen, water, carbon dioxide) and thermal stability than the conventional PET material. PEF can be recycled and incorporated into the PET recycle streams at up to 5 % PEF with no affect on the recycled PET performance.[124]

In case the FDCA price 1000 $/ton predicted by Avantium is realized, the market of FDCA in PEF application is expected to reach around 300 kt/a by 2020. The estimated potential of replacing PTA in PET with FDCA is 0.6 % of the PTA used in PET by 2020 according to Waestra market analysis.[125]

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[124] http://polymerinnovationblog.com/polyethylene-furanoate-pef-100-biobased-polymer-to-compete-with-pet/

[125] http://www.bioconsept.eu/wp-content/uploads/BioConSepT_Market-potential-for-selected-platform-chemicals_report1.pdf

Poly(butylene terephthalate) (PBT) was introduced on the market in the late 1960`s. PBT is a crystalline thermoplastic polymer that is mainly used as an insulator in the electrical and electronics industries as well as the automotive industry. The chemical structure of PBT is shown in Figure 16. The global PBT market breakdown by application can be seen in Figure 1717. According to GIA, the global market for PBT is projected to reach 1.3 Mt/a in 2017.[126] There are over 50 companies engaged in the manufacture of PBT plastics, the major suppliers being SABIC, Ticona, Dupont, BASF, Lanxess, Celanese, Teijin, and Toray.

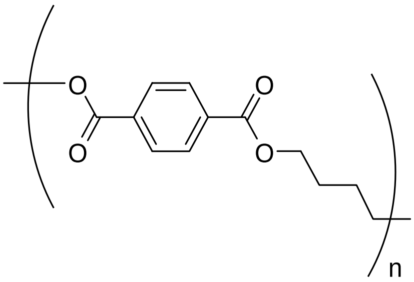

Figure 16. Chemical structure of PBT.

PBT faces inter-material competition from other engineering thermoplastics. Polyacetal can be used instead of PBT in small parts. In the automotive industry, nylon 6 and nylon 6,6 are the main competitors, particularly for under-hood components. In electronics and electrical applications, PBT competes with PET. Polycarbonate/PBT blends compete with alternative bumper designs utilizing compounded polypropylene. Additionally, PBT faces new competition from polytrimethylene terephthalate (PTT), which exhibits performance and processing characteristics similar to high-performance PBT.[127]

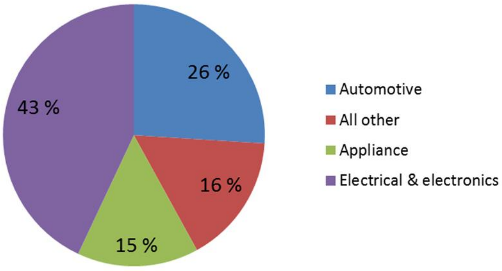

Figure 17. The global PBT market breakdown by application.

Poly(butylene furanoate) (PBF). The market potential for PBF to replace PBT is considered minor since most of the material is used in industries where the bio-based image is not pushed that hard. It would in the future be possible to make 100 % bio-based PBF utilizing bio-based 1,4-butadiol and FDCA as monomers. According to Waestra's business model, until 2020 there will be no use of FDCA in the production of PBF despite of its potential.[128]

Biodegradable polyesters based on TPA. Poly(butylene adipate-co-terephthalate) (PBAT) is a biodegradable, but not bio-based polymer (Figure 18), produced commercially by BASF under the trade name

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[126] http://www.prweb.com/releases/polybutylene_PBT/terephthalate_PTMT/prweb8285963.htm.

[127] http://guichon-valves.com/pbt/

[128] http://www.bioconsept.eu/wp-content/uploads/BioConSepT_Market-potential-for-selected-platform-chemicals_report1.pdf

Ecoflex. Although being fully fossil based at the moment, there are developments to produce all the monomers (i.e. butandiol, apidic acid and terephatalic acid) from biomass. PBAT is expected to be increasingly bio-based reaching bio-contents of 50 % by 2020 according to Nova institute GmbH.[129] Suppliers in China and also other nations have also begun to produce PBAT. BASF advertises that PBAT is the ideal blend component for bioplastics, certified compostable, elastic and tear-resistant, processable on conventional blown film plants, printable and weldable, and suitable for food contact.[130] According to a press release in 2011, BASF will increase its production capacitiy to 74 kt/a from 14 kt/a. [131]

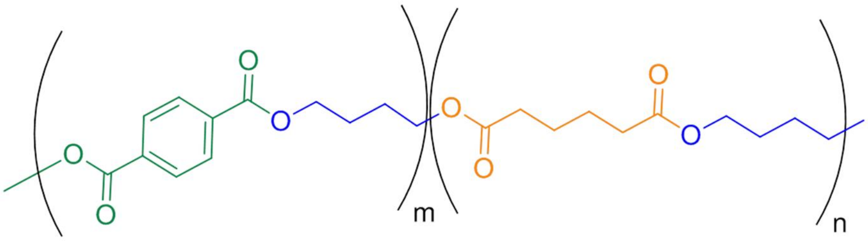

Figure 18. Chemical structure of poly(butylene adipate-co-terephthalate). Terephtalic acid moiety in green, adipic acid moiety in orange, 1,4-butanediol moieties in blue.

Biodegradable polyesters based on FDCA. No scientific papers were found describing the biodegradable aliphatic-aromatic polyester, analogous to PBAT structure presented in Figure, but with FDCA instead of TPA. However, Italian bioplastics company Novamont has seven recent patent applications (2009-2012) describing such structures. (See Appendix 1, Table 1.)

2.6.3. Polyamides from TPA vs. FDCA

Polyamides can be divided into three groups – 1) aliphatic polyamides (e.g. nylon), 2) semi-aromatic polyphthalamides, and 3) fully aromatic aramides. FDCA could replace the aromatic unit in the current commercial polyphthalamides and aramides.

Polyphthalamides (PPA) based on TPA are heat resistant semi-aromatic polymers used mainly in the transportation and electrical industries (e.g. LEDs, cable/wire protection). PPA is also used e.g. as toothbrush bristles. TPA in the polyamide sturcture raises the melting point, glass transition temperature and improves chemical resistance, when compared to aliphatic polyamides. The most common type of PPA in the market is based on PA6T (Figure 19). The North American and Western European markets witnessed a volume sales of 70 kt in 2012 and are forecasted to post a CAGR of 8.9 percent from 2012 to 2019. This market is expected to reach volume sales of 130 kt in 2019. In Figure 20 these volumes per end user application are shown for 2012 as well as the forecasted volumes in 2019.

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[129] http://www.bio-based.eu/market_study/media/files/13-07-24PRMarketStudynova.pdf

[130] http://www.plasticsportal.net/wa/plasticsEU~en_GB/portal/show/content/products/biodegradable_plastics/ecoflex).

[131] http://worldaccount.basf.com/wa/plasticsAP~en_GB/portal/show/common/plasticsportal_news/2011/11_139)

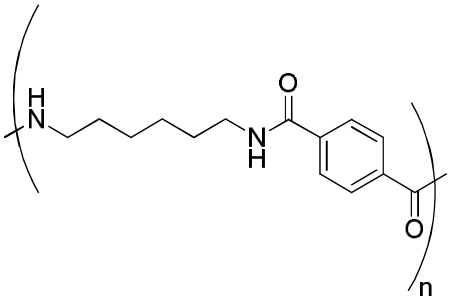

Figure 19. Chemical structure of PA6T.

PPA is a high growth market and its volume share in the high temperature thermoplastics is expected to increase. However, growth in the automotive segment is expected to be lower than other application areas (i.e. electrical and electronic segments) as the penetration into automotive applications is already high.

In 2012, the market was valued to 450 M$/a and is expected to post a CAGR of 8.5 percent from 2012 to reach a value of 800 M$/a in 2019 (North America and Western Europe). The main PPA resin manufacturers include DSM, Arkema, DuPont, EMS Grivory, Evonik and Solvay (www.frost.com).

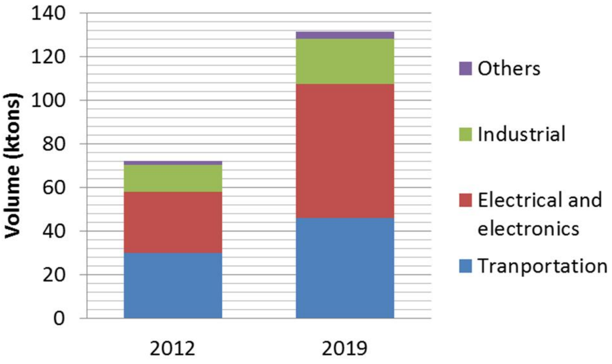

Figure 20. Volume of PPA in North American and Western European markets. Volume in 2012 and the forecasted volume in 2019 by application.

Aramides based on TPA are polyamides in which the monomer unit is an aromatic dicarboxylic acid combined with an aromatic diamine. The most famous aramid fibers are known under their tradenames Kevlar and Nomex (Figure 21). Aramide fibers are characterized by their rigid polymer chains. They are used e.g. in aerospace and military applications, for ballistic rated body armor fabric and ballistic composites, in bicycle tires, and as an asbestos substitute. Kevlar is a so called para-aramid fibre while Nomex is a meta-aramid fibre. The total world production of para-aramid fibers stood at 26 kt in 1998 and for meta-aramid fibers at 19 kt.[132] Main producers of para-aramid include DuPont, Teijin and Toray and for meta-aramid fibres DuPont and Teijin.

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[132] http://www.chem.uwec.edu/Chem405_s01/malenirf/project.html

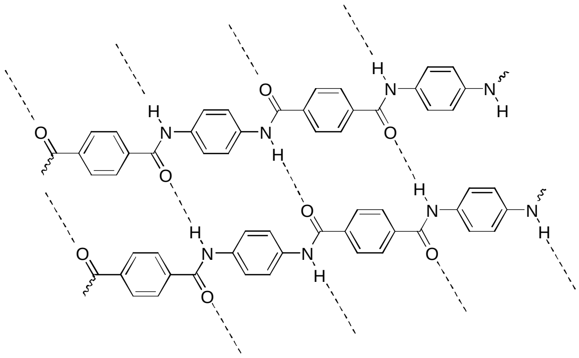

Figure 21. Chemical structure of Kevlar.

Polyamides based on FDCA. Polyamides based on FDCA have been studied since 1950`s. A set of studies were conducted in 1961-1975 regarding the preparation of polyamides from FDCA and aliphatic amines. FDCA in combination with aromatic amines was studied (mainly by Gandini et al.) in 1985 - 1991.5 The polymerization of FDCA with aromatic diamine resulted in lyotropic aramide material with glass transition temperature at 325 ºC and degradation temperature at 385 ºC. Despite these studies, high quality information on the mechanical and thermal properties of FDCA polyamides remains scarce, and hardly any recent scientific papers are available.

Avantium announced in 2010 that it will in collaboration with Rhodia (Solvay) develop FDCA-based polyamides and together with Teijin develop FDCA-based aramid fibres. Rhodia (Solvay) will test these new polyamides for fibres and engineering applications in various areas such as consumer goods, automotive and electronic material.[133]

Teijin and DuPont have recently (2013) published patent applications on FDCA based aramides (see Appendix 1, Table 1).

Waestra predicts that the FDCA based polyamide potential in 2020 is at 80 kt/a with a value of 80 M$/a. The real potential of FDCA based polyamides until 2020 strongly depends of the FDCA production as well as the price of FDCA.[125]

2.6.4. FDCA polymers as replacements to current polycarbonate materials.

Polycarbonates are important derivates of bisphenol A. The structure of bisphenol A based polycarbonate is shown in Figure 22. There is no directly analogous FDCA based structure for this polymer. However, as both FDCA-based polymers and polycarbonates can provide rigid materials, FDCA polymers have potential to compete for the polycarbonate applications.

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[133] http://avantium.com/news/2010-2/Teijin-Aramid-and-Avantium-enter-partnership-to-explore-green-high-performance-polymers.html

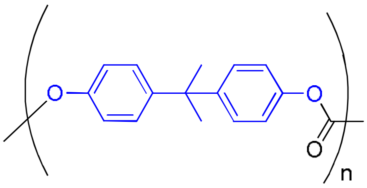

Figure 22. The structure of polycarbonate based on Bisphenol A. The part derived from Bisphenol A is shown as blue in the figure.

Overall the bisphenol A market was worth 13 billion $/a and is expected to reach 19 billion $/a by 2019. In terms of volume, bisphenol A demand in 2012 was around 6.5 Mt in 2012 and is expected to grow at a CAGR of 4.6 % from 2013 to 2019. Polycarbonate led the overall bisphenol A market and accounted for a market share of 72.5 % in 2012. The rebounding automobile and electronic industries in North America and Europe, as well as rapid economic growth in Asia Pacific is expected to remain a major driving force for bisphenol A market.[134]

Bisphenol A exhibits hormone-like properties that raise concern about its suitability in some consumer products and food containers. Bisphenol A has the ability to mimic the effects of natural estrogen, caused by the similarity of phenol groups on both bisphenol A and estradiol, leading bisphenol A to trigger estrogenic pathways in the body. Several governments have investigated its safety, which prompted some retailers to withdraw polycarbonate products. The European Union and Canada have banned bisphenol A use in baby bottles. FDA's current assessment is that bisphenol A is safe at the very low levels that occur in some food. The assessment is based on review of hundreds of studies including the latest finds from new studies initiated by the agency. FDA will continue its review of bisphenol A, and acknowledges the food and packaging industries' efforts, in response to consumer demand, to provide products that are BPA-free.[135]

According to Waestre, FDCA will be developed and tested in new products in the polycarbonate area.[125] According to Waestre's market model the market volume for FDCA in this application will not be higher than 43 kt/a in 2020. The estimated potential of replacing bisphenol A in polycarbonates with FDCA is project to 0.9 % of the biphenol A used in polycarbonates by 2020.

2.7. Other furanic compounds in polymer applications

Currently the commercially most important polymer applications of furans are crosslinked resins, especially the furfuryl alcohol resin that is produced several hundred kt/a. However, in this report the resinous, crosslinked materials were not in the focus. Some of the furan compounds (other than FDCA) that have been studied as monomers to produce well-defined (i.e. not-crosslinked) polymers are described in this chapter.

2.7.1. Thermoresponsive materials from Diels-Alder chemistry

Furan and maleimide compounds can be combined into thermoreversible links through Diels-Alder reaction. The link can be generated at temperatures around 60-65 ºC, and the link is opened at temperatures higher than ca. 100 – 110 ºC. The thermoreversibility allows the production of materials where the linked components can be reverted back to non-linked structures at relatively mild temperatures. Diels-Alder applications of furanic compounds have been reviewed recently.[136] Very typically the furan counterpart in the materials

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[134] http://www.prnewswire.com/news-releases/global-bisphenol-a-market-is-expected-to-reach-usd-188-billion-by-2019-transparency-market-research-231534731.html

[135] http://www.fda.gov/newsevents/publichealthfocus/ucm064437.htm

[136] Gandini A. The furan/maleimide Diels–Alder reaction: A versatile click–unclick tool in macromolecular synthesis. Prog. Polym. Sci. 38 (2013) 1-29. DOI:10.1016/j.progpolymsci.2012.04.002

was prepared by covalently attaching either furfuryl alcohol or furfuryl amine into the structure. Also other types of structures have been utilized, e.g. polymers of 2,5-Bis(hydroxymethyl)furan (BHMF). The thermoreversible bonds can be used in many types of applications. These include:

Reversible network structures. Recyclable thermosets, removable adhesives, thermoplastic elastomers, dissolvable hydrogels etc.

As a few examples: Mcelhanon et al.[137] and Tian et al.[138] prepared epoxy resins containing vulnerable Diels-Alder bonds (based on furfuryl alcohol / furfuryl amine and maleimide) in the epoxy monomer. The aim of these studies was to prepare removable epoxy resin, that could be applied e.g. in the encapsulation of electrical components. Magana et al.[139] prepared thermally reversible crosslinks to polyethylene during extrusion process, again utilizing furan/maleimide linkages. Stoichet et al.[140] prepared hydrogels with the Diels-Alder reaction, utilizing hyaluronic acid functionalized with furfuryl amine in combination with maleimide derivative.

Self-healing structures. In principle, the self-healing structures tend to be also crosslinked networks. In these applications, the networks are so dense that the material breaks down to monomer level upon heating above 110 ºC, and can be re-polymerized to non-faulty structure by cooling the material to ca. 60 ºC. When this heating-cooling cycle is done locally to a crack in the material, the crack can be removed. Since the Diels-Alder bonds are the mechanically weakest bonds in the self-healing material, it can be expected that exactly these bonds will break when a fracture is formed to the material under stress.

Chen and Wudl published in *Science* (2002)[141] their concept of the self-healing network. It was based on 4-armed furfuryl alcohol ester that was crosslinked with a three-armed maleimide derivative. Cracks in the material could be removed (up to 60 % of the original strength) by heat-treatment.

Patents related to termoresponsive polymeric materials, utilizing furans in Diels-Alder chemistry were surveyed. 26 relevant patents were found, and thermoreversibly crosslinked network was the most common topic (12 patents). Other studied topics were e.g. thermoreversible surface functionalization and thermoreversible stabilization (thermoset crosslinking occurs only when crosslinking component is liberated at elevated temperature). The patents are listed in Appendix 1, Table 2.

2.7.2. 5-Bis(hydroxymethyl)furan

2,5-Bis(hydroxymethyl)furan (BHMF) (Figure 23) can be produced e.g. from HMF through reduction. It can potentially be used e.g. as a diol in the production of polyesters and polyurethanes. It has not been very widely studied in polymerizations – only 34 patents and 55 scientific publications with some relation to BHMF polymers were found. The most relevant 12 patents are listed in Appendix 1, Table 3, including all patents referred to in this chapter. A characteristic feature of BHMF is that the furan ring has a diene character (much more than FDCA, which has rather stable furan ring). This has in some recent papers been used as an advantage to prepare thermoresponsible materials using Diels-Alder reactions.

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[137] Mcelhanon et al. Removable foams based on an epoxy resin incorporating reversible Diels–Alder adducts. J.Appl.Polym.Sci. 85 (2002) 1496-1502.

[138] Tian et al. A thermally remendable epoxy resin. J.Mat.Chem. 19 (2009) 1289-1296. DOI:10.1039/B811938D

[139] Magana et al. Thermally reversible crosslinked polyethylene using Diels–Alder reaction in molten state. React. Funct. Polym. 70 (2010) 442-448. DOI: 10.1016/j.reactfunctpolym.2010.04.007

[140] Nimmo et al. Diels−Alder Click Cross-Linked Hyaluronic Acid Hydrogels for Tissue Engineering, Biomacromolecules 12 (2011) 824-830. DOI: 10.1021/bm101446k

[141] Chen et al. A Thermally Re-mendable Cross-Linked Polymeric Material. Science 295 (2002) 1698-1702. DOI: 10.1126/science.1065879

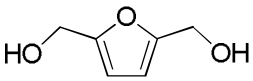

Figure 23. The chemical structure of 2,5-Bis(hydroxymethyl)furan (BHMF).

Polyesters. As a historical example, Moore et al. published in 1978 some details of oligomeric BHMF polyesters with various aliphatic, aromatic, and furanic diacids.[142] Recently, BHMF polyester topic has been reintroduced in few papers. Jiang et al.[143] published in 2014 a set of low molecular weight BHMF polyesters with various aliphatic diacids (diacids ranging from C4 to C12). Yoshie et al.[144,145] published in 2013-2014 two studies, where oligomeric BHMF polyesters were crosslinked through thermoreversible Diels-Alder reaction with maleimides and showed self-healing properties. This chemistry was also patented (by University of Tokyo).[146]

Polyurethanes. Gandini et al.[5,147] published several papers in 1989-1995 on BHMF as a component in polyurethanes, e.g. in combination with commercial isocyanates. Some patents have also appeared on the same topic (e.g. Quaker Oats 1982 & 1984, Univ. Rostock 2000).[148,149,150] Recently, in 2013 Nguyen et al.[151] published a study where polyurethanes containing small amount BHMF were surface fuctionalized through Diels-Alder reaction.

Other applications. In two recent examples, BHMF was further functionalized to diacrylate [152] or diepoxy [153] monomer, and applied in the production of crosslinked structures. In patent literature, several recent examples have applied BHMF as a component in crosslinking resins (e.g.Transfurans Chemicals 2009, Sekisui Chemical 2013, see Appendix 1, Table 3.)

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[142] Moore J.A., Kelly, J.E., Polyesters Derived from Furan and Tetrahydrofuran Nuclei, Macromolecules, 11 (1978) 3, 568-573.

[143] Jiang Y., Woortman A. J. J., Alberda v. E., Petrovi D. M., Loos K., Enzymatic Synthesis of Biobased Polyesters Using 2,5-Bis(hydroxymethyl)furan as the Building Block, Biomacromolecules, (2014).

[144] Zeng C., Seino H., Ren J., Hatanaka K., Yoshie N., Bio-Based Furan Polymers with Self-Healing Ability, Macromolecules, 46 (2013) 1794-1802.

[145] Ikezaki T., Matsuoka R., Hatanaka K., Yoshie N., Biobased poly(2,5-furandimethylene succinate-co-butylene succinate) crosslinked by reversible Diels-Alder reaction, Journal of Polymer Science Part A: Polymer Chemistry, 52 (2014) 216-222.

[146] JP2008303237A, 2008, Polymer compound prepared by crosslinking polyester compound having furan ring in main chain with polyvalent maleimide.

[147] Boufi S., Belgacem M. N., Quillerou J., Gandini A., Urethanes and polyurethanes bearing furan moieties. 4. Synthesis, kinetics and characterization of linear polymers, Macromolecules, 26 (1993) 6706-6717.

[148] US4318999, 1982, Low fire hazard rigid urethane insulation foam, polyol mixtures used in the manufacture thereof, and method for manufacture thereof.

[149] US4426460, 1984, Polyurethanes or isocyanurates from alkoxylated hydroxymethylfuran.

[150] DE19928927A1, 2000, New polyurethanes containing 2,5-disubstituted furan rings, useful for preparing flexible foams with surface-bonded active agents for medicinal applications, especially as breast prostheses.

[151] Nguyen L. T., Devroede J., Plasschaert K., Jonckheere L., Haucourt N., Du Prez F. E., Providing polyurethane foams with functionality: a kinetic comparison of different "click" and coupling reaction pathways, Polym.Chem., 4 (2013) 1546-1556.

[152] Jang N. R., Kim H., Hou C. T., Kim B. S., Novel biobased photo-crosslinked polymer networks prepared from vegetable oil and 2,5-furan diacrylate, Polym.Adv.Technol., 24 (2013) 814-818.

[153] Hu F., La Scala J. J., Sadler J. M., Palmese G. R., Synthesis and Characterization of Thermosetting Furan-Based Epoxy Systems, Macromolecules, 47 (2014) 3332-3342.

2.7.3. 2,5-Hydroxymethylfuroic acid

There are almost no examples utilizing **2,5-Hydroxymethylfuroic acid** (5-hydroxymethyl-2-furan-carboxylic acid) (Figure 24) as a monomer. In principle, it is applicable in polyester production. In scientific literature, Hirai et al.[154] obtained oligomeric black tar in their polyesterification experiments in 1984. Only a couple of polymer patents were found that included this compound, and even in these patents this compound was only mentioned within a long list of furanic compounds.

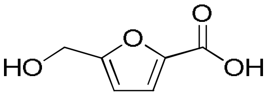

Figure 24. The chemical structure of 5-hydroxymethyl-2-furan-carboxylic acid.

2.7.4. 2-vinylfuran

2-vinylfuran is in principle the furanic analogue for styrene (Figure 25). However, the furan ring is not stable, and may take part in the polymerizations. E.g. in radical polymerizations the furan ring acts as a radical trap, resulting in slow polymerizations and low molecular weights. Best results in radical polymerizations have been reported for emulsion polymerizations. As another problem, the polymer has been observed to be highly susceptible towards oxidative damage.[1] Few polymer related patents exist, but they mainly describe 2-vinylfuran as one example in a list of aromatic vinyl monomers.

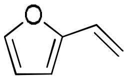

Figure 25. The chemical structure of 2-vinylfuran.

2.7.5. Furfuryl (meth)acrylate

Furfuryl acrylate and methacrylate monomers (Figure 26) are produced through the esterification reaction of furfuryl alcohol with corresponding acid chloride. Their polymerizations were studied already in 1960`s, and it was observed that these monomers can be polymerized with radical mechanism with no significant interference from the furan group. In general, the success of radical polymerization of furanic monomers depends on relative reactivity of the double bond vs. the furan ring. In furfuryl (meth)acrylates this balance favors polymerization (as opposed to 2-vinylfuran described in the previous chapter).

Recently, most of the references related to these monomers have connection to thermoreversible Diels-Alder materials. As a few most recent examples: Peterson et al.[155] prepared furfuryl methacrylate homopolymers, and then crosslinked them with bismaleimides. Bose et al.[156] prepared copolymers of furfuryl meth-

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[154] Hirai H., Oligomers from Hydroxymethylfurancarboxylic Acid, Journal of Macromolecular Science: Part A - Chemistry, 21 (1984) 1165-1179.

[155] Peterson et al. Reaction Kinetics and Thermodynamic Aspects of Thermoreversibly Cross-Linked Polymer Networks, Macromol. Chem. Phys. 16 (2013) 1798-1805. DOI: 10.1002/macp.201300334

[156] Bose et L. A rheological and spectroscopic study on the kinetics of self-healing in a single-component diels–alder copolymer and its underlying chemical reaction. J. Polym. Sci Part A 52 (2014) 1669-1675. DOI: 10.1002/pola.27164

acrylate, maleimide methacrylate and lauryl methacrylate, and studied the self-healing properties of the material. Galbis et al.[157] prepared hydrogels from copolymers of hydroxyethyl methacrylate and furfuryl methacrylate.

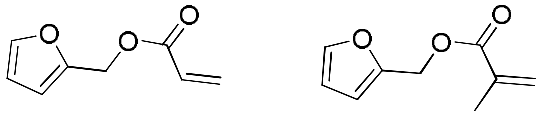

Figure 26. Chemical structures of furfuryl acrylate (left) and furfuryl methacrylate (right).

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[157] Galbis et al. Tandem ATRP/Diels–Alder synthesis of polyHEMA-based hydrogels. Polym. Chem. 5 (2014) 5391-5402. DOI:10.1039/C4PY00580E

3. Value chains to furan compounds – experimental and technoeconomic studies

Three different processes to produce valuable compounds from sugars, utilizing furan chemistry, were selected for experimental studies in CatBio and Furchem projects. **The first process**, CatBio Process 1, utilizes C5 sugars to produce a mixture of valuable compounds through furfural intermediate. The compounds are intended for fuel components, and the main product in the process is 2-methylfuran. **The second process**, CatBio Process 2, utilizes C5 sugars to produce another mixture of valuable compounds through furfural intermediate. The main product of this process is succinic acid. **The third process**, Furchem Process, utilizes C6 sugars to produce furan dicarboxylic acid (FDCA) via aldaric acid intermediate.

In Chapter 2.8, each of these processes is described separately. A general description is given of each process, followed by summary of the experimental results obtained in the projects. The following chapters 2.9 -2.11 describe techno-economic considerations for these processes.

In the techno-economic considerations, following aspects were examined:

1. How much product is obtained from 100 kt of sugar (C5 or C6)?
2. What are the sugar (main raw material) costs of the processes?
3. How do the raw material costs relate to predicted product value?
4. What are the most probable biomass options in Finland that can provide 100 kt of sugar for the processes? (Either C5 or C6 sugar, depending on process.)
5. What are the other products that can be produced alongside, depending on biomass?
6. What is the size of the business (turnover) in the total process, if 100 kt of sugar is consumed?

The main results of the value chain calculations are summarized in Chapter 2.9. Chapter 2.9 also summarizes the assumptions, which the calculations were based on. The answers to questions 1 - 3 are further elaborated in Chapter 2.10 – “Sugar costs vs. predicted product value.” The answers to questions 4 - 5 are further elaborated in Chapter 2.11 – “Biomass source comparisons.”

2.8. Descriptions of selected processes

2.8.1. CatBio Process 1: From C5 sugars to 2-Methylfuran (Fuel components)

General description.

The CatBio process 1 is described in Scheme 21. In this process the production is started from pentose sugars, i.e. sugars containing five carbon atoms. The first step of the CatBio 1 process is the production of platform chemical furfural from pentose sugars with dehydration.[158] This dehydration process is performed in liquid-phase applying usually homogeneous catalysts e.g. sulfuric acid, acetic acid and formic acid.[159]

To produce valuable chemicals from furfural various reactions are possible and one of them is hydrotreatment. With furfural hydrotreatment many valuable products can be produced, for example furfuryl alcohol, tetrahydrofurfuryl alcohol (THFA), 2-methylfuran (MF) and 2-methyltetrahydrofuran. From these components 2-methylfuran has attracted attention with excellent characteristics presented more in detail in Chapter 2.3.2.

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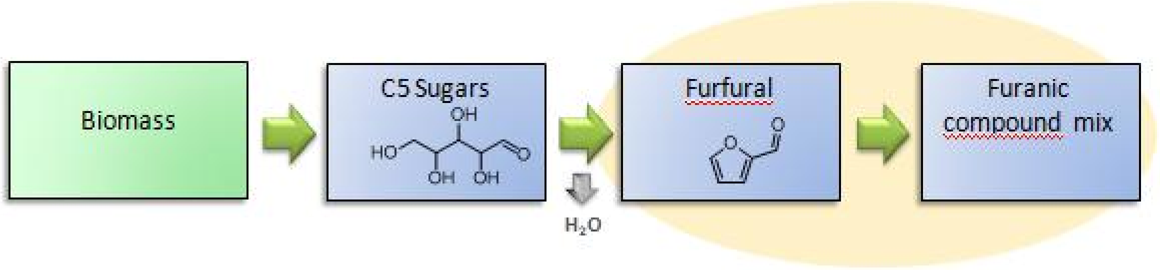
[158] Sairanen E. et al. Fuctionalized Activated Carbon Catalysts in Xylose dehydration, Topics in Catalysis, 56 (2013) 512-521.

[159] Karinen R. et al. Biorefining: Heterogeneously Catalyzed Reactions of Carbohydrates for the Production of Furfural and Hydroxymethylfurfural, ChemSusChem 4 (2011), 8, 1002-1016.

This chemical could be potentially used as a replacement for fully or partially fossil-based MTBE, ETBE, TAEE and TAME in gasoline in the future.

The production of 2-methylfuran can occur in gas- or liquid-phase. With gas-phase the yields of MF obtained can be higher but liquid-phase study offers easier merging to upstream liquid-phase production of furfural as furfural does not have to be vaporized. Also the energy consumption and production of side products has been reported to be lower in liquid-phase studies. Catalyst in this reaction has traditionally been copper chromite (CuCr) but new environmental regulations are preventing the use of this catalyst no longer. New catalyst studies have focused on screening metal options usually on oxide supports (alumina, silica). Temperatures of liquid-phase studies vary from 100 – 230 °C and hydrogen pressure from atmospheric to 90 bar. Production times have usually been from 1 – 14 h.



Scheme 21. The CatBio process 1. The step under experimental research in CatBio project process 1 is highlighted with orange (hydrotreatment step).

Experimental results.

Wide study of the effect of process conditions and comparison of many catalysts was performed for CatBio process 1 to produce 2-methylfuran as desired end product. Optimal process conditions for high MF yield were 230 °C and a cold hydrogen pressure of 40 bar. In this case cold pressure stands for hydrogen pressure before vapor pressure has increased the total pressure. For catalyst comparison following options were tested: Cu/C, Ni/C, CuNi/C, CuFe/C and NiFe/C. Within these catalysts tested the metal content was varied from 2 wt-% to 10 wt-% depending of the catalyst. The highest yield of MF was achieved with 10 wt-% Ni/C in 120 minutes (49 mol-%). In future it is considered possible to increase MF yield from furfural hydrotreatment to 60 mol-% with catalyst and process condition optimization.

In the CatBio process 1, 2-methylfuran was not the only valuable product obtained. In addition to this possible fuel component also furfuryl alcohol, tetrahydrofurfuryl alcohol and 2-methyltetrahydrofuran were produced in larger quantities. All these chemicals have applications and value as separated from the mixture.

Yield assumptions used in the value chain calculations.

In the calculations of following chapters, 70 mol-% yield assumption was used for furfural dehydration from C5 sugars and 60 mol-% yield assumption for the hydrotreatment step. The yield assumption of furfural production from pentoses is an actual maximum at the moment and yield assumption of MF production is considered as the target of the development work in CatBio process.

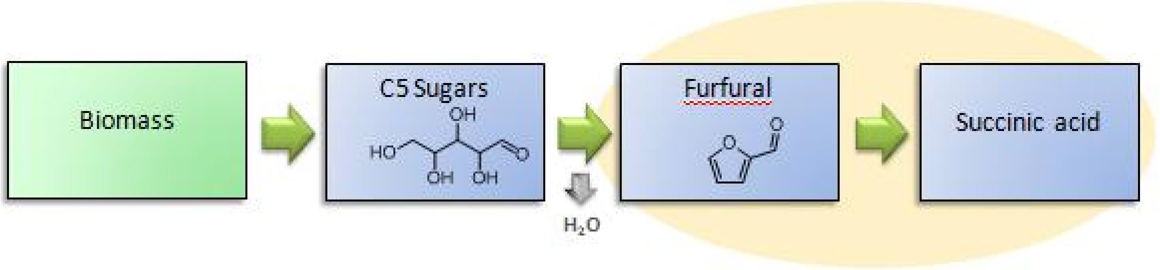
2.8.2. CatBio Process 2: From C5 sugars to succinic acid

General description.

The second process under study in CatBio project is the oxidation of furfural with hydrogenperoxide into value-added chemicals, such as succinic acid (Scheme 22.)[160]. This platform chemical is used as an intermediate for the manufacturing variety of industrially relevant compounds, such as γ-butyrolactone (GBL), 1,4-butanediol (BDO) and tetrahydrofuran (THF)[161]. The most possible derived products and their expected future demands are given in section 2.3. Furthermore, the use of hydrogenperoxide as a green oxidizing agent is more environmentally friendly compared to the conventional oxidizing agents such as nitric acid and molecular oxygen, which forms toxic wastes and requires high safety procedures in case of molecular oxygen.[162] Secondly, the reaction proceeds directly in liquid-phase under moderate conditions at low temperature and atmospheric pressure after distillation of aqueous furfural solution from dehydration process.

The application of heterogeneous acid catalysts for manufacture of value-added chemicals can be one of the significant phases in evolving the idea of integrated forest biorefinery. The change towards new ecologically sustainable practices to chemical processes has inspired the use of recyclable solid acids as alternates for the unrecyclable liquid acid catalyst such as suphuric acid. The heterogeneous acid catalyst can be simply separated from the product solution after the reaction for recycling without loss of activity and are successfully applied in many chemical processes. Furthermore, the heterogeneous acid catalyst does not cause corrosion problems associated with homogeneous acid catalyst. Cation exchangers are class of ion-exchange resins that have hydrogen ions as counter ions with fixed negative functional groups and exhibit comparable catalytic properties as homogeneous acid catalyst. The magnitude of ion exchange capacity depend on the acid strength of the exchange group.

The catalyst used in this study is Smopex-101. It is a fibrous non-porous catalyst with sulphonic acid functional groups on poly-ethylene-graft-styrene. The mean fiber diameter is about 0.01 mm and the average fiber length is 4 mm. The cation exchange capacity by dry weight (mm_{eq}/g) for Smopex-101 varies between 2.1 - 3.6.[163,164].The high surface area provided by this fibrous catalyst with strong acidic surface functional groups SO_3H greatly diminishes the internal mass transfer limitations, normally present in porous catalyst, which provide high catalytic efficiency and are very suitable for biomass derived large molecules (furfural). The catalyst can be utilized in both, batch and continuous processes. Moreover, they are easy to reuse and recover and the use of these heterogeneous catalysts contributes to principles of sustainability and green chemistry.



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[160] A. Takagaki, S. Nishimura, and K. Ebitani, “Catalytic Transformations of Biomass-Derived Materials into Value-Added Chemicals,” *Catal. Surv. from Asia*, vol. 16, no. 3, pp. 164–182, 2012.

[161] J. G. Zeikus, M. K. Jain, and P. Elankovan, “Biotechnology of succinic acid production and markets for derived industrial products,” *Appl. Microbiol. Biotechnol.*, vol. 51, no. 5, pp. 545–552, 1999.

[162] R. Noyori, “Pursuing practical elegance in chemical synthesis,” *Chem. Commun.*, no. 14, p. 1807, 2005.

[163] J. Lilja, J. Aumo, T. Salmi, D. Y. Murzin, P. Mäki-Arvela, M. Sundell, K. Ekman, R. Peltonen, and H. Vainio, “Kinetics of esterification of propanoic acid with methanol over a fibrous polymer-supported sulphonic acid catalyst,” *Appl. Catal. A Gen.*, vol. 228, no. 1–2, pp. 253–267, Mar. 2002.

[164] J. Lilja, D. Y. Murzin, T. Salmi, J. Aumo, P. Mäki-Arvela, and M. Sundell, “Esterification of different acids over heterogeneous and homogeneous catalysts and correlation with the Taft equation,” *J. Mol. Catal. A Chem.*, vol. 182–183, pp. 555–563, May 2002.

Scheme 22. The CatBio process 2. The step under experimental research in CatBio project process 2 is highlighted with orange (the oxidation step).

Experimental results.

The screening of heterogeneous acid catalysts for reaction of furfural oxidation with hydrogen peroxide were studied in batch reactor with the aim of finding the most selective catalyst for the process. The reaction was performed in aqueous environment, which is compatible with upstream and downstream processes for further valorisation to other valuable products. Different types of acid catalysts were tested in order to find the most selective catalyst for this reaction, including various types of zeolites with different acidities, sulphonated carbon, sulfated zirconia and ion-exchange resins. The highest yield of succinic acid was obtained over Smopex-101. The results of sulphuric acid production were also compared between the catalysts and it was discovered that Smopex-101 gives better performance in comparison to a homogeneous catalyst.

Kinetic studies were conducted to determine the optimum reaction conditions. Different operating conditions were tested to achieve the highest yields of succinic acid. The following parameters were modified in order to get reliable kinetic data: temperature, catalyst-to-furfural ratio and initial hydrogen peroxide and furfural concentrations. The temperatures were screened between 40 - 90 °C. The conversion of furfural was almost complete in all these cases, but the reaction was too slow at lower temperatures. The solubility of furfural was taken into account and it was observed that concentration of furfural was limited by its solubility in water (max 8.3 wt-%). The maximum yield was achieved at 4.5 wt-% of furfural in aqueous phase. At high concentrations and in acidic environment, condensation and degradation products of furfural were easily formed, which mostly comprises of C_2-C_4 acids. The decomposition of hydrogenperoxide was also considered and it was found out that the decomposition is negligible within the operating conditions. The maximum yield of succinic acid was achieved in batch reactor was 67 wt-% with a reaction time of 24 h at 80 °C and molar ratio of (H_2O_2/Furfural= 4). In semi-batch process higher, 80 wt-% yield could be obtained. It was also discovered that the presence of furfural significantly inhibits the side reactions and improves the selectivity of hydrogen peroxide.

Besides, succinic acid, the other valuable products which formed during the oxidation of furfural include maleic acid, formic acid, 2(5H)-furanone and minor quantities of malic and malonic acids.

Yield assumptions used in the value chain calculations.

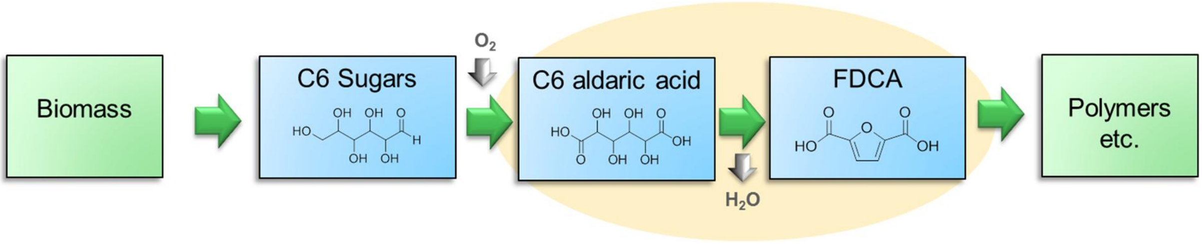
The estimated value chain for the production of succinic acid derived from C_5 sugars is based on 67 wt-% yield of succinic acid for the oxidation process and 70 mol-% for the production of furfural from dehydration process. Furthermore, it is also possible to achieved high yields of succinic acid, if semi-batch operation is considered for oxidation process.

2.8.3. Furchem Process: From C6 sugars to FDCA

General description.

The Furchem Process is described in Scheme 23. The process starts from C6 sugars, which can be obtained from various types of biomass. The C6 sugars are first oxidized into aldaric acids, which are then further dehydroxylated into FDCA. The experimental studies in Furchem project concentrated on the dehydroxylation step. The state-of-the art regarding the oxidation of C6 sugars to aldaric acids was summarized in Chapter 2.5.2. Previous literature regarding the dehydrocylation of aldaric acid to FDCA was found to be limited – this literature is summarized in Chapter 2.5.3.

The dehydroxylation reaction developed in the Furchem project proceeds in dissolved conditions, utilizing commercial heterogeneous catalysts. Various solvents and catalysts have been screened. Both glucaric and galactaric acid have been tested as feedstocks. FDCA can be produced as a pure compound or as its ester.



Scheme 23. The Furchem process. The step under experimental research in Furchem project is highlighted with orange (the dehydroxylation step).

Experimental results.

During the project the highest yield to FDCA or to its ester was 52 mol-%. The main side product is Furoic acid (FCA) or its ester which is formed approximately in 2:1 ratio. 85 mol-% total yield of furan acids (FDCA and FCA or their esters combined) was obtained in the project. The catalyst used is commercial catalyst and temperature approximately 200 - 250 °C.

Yield assumptions used in the value chain calculations.

In the calculations of following chapters, 80 mol-% yield assumption was used for both the oxidation and dihydroxylation steps. Regarding oxidation, the results summarized in Chapter 2.5.2. describe yields ranging between 70 - 95%. Regarding dihydroxylation, 80 mol-% was considered as the target of the development work in Furchem.

2.9. Value chain calculation results

2.9.1. Summary of assumptions used in calculations

Following assumptions and specifications were applied in the value chain calculations.

Process Size

- All processes consume 100 kt of sugar (C5 sugar in CatBio processes and C6 sugar in Furchem process).

Prices

- Sugar price 250 €/ton was applied in the calculations. Raw sugar price has varied between 200 - 550 €/ton in 2010-2015.[165]

Yields

- Bioethanol Reference Process (C6+C5 sugar to ethanol) was calculated with this yield assumption:
    - From C6+C5 sugar to ethanol: 50 w-%

- CatBio Reference Process (C5 sugar to furfuryl alcohol) was calculated with these yield assumptions:
    - From C5 sugar to furfural: 70 mol-%[166]
    - From furfural to furfuryl alcohol: 90 mol-%[167]

- CatBio Process 1 (C5 sugar to 2-methylfuran and other components) was calculated with these yield assumptions:
    - From C5 sugar to furfural: 70 mol-%
    - From furfural to 2-methylfuran: 60 mol-%
    - From furfural to furfuryl alcohol: 5 mol-%
    - From furfural to THFA: 15 mol-%

- CatBio Process 2 (C5 sugar to succinic acid and other components) was calculated with these yield assumptions:
    - From C5 sugar to furfural: 70 mol-%
    - Fom furfural to succinic acid: 67 w-%
    - From furfural to maleic acid: 10 w-%
    - From furfural to formic acid: 5 w-%

- Furchem Process (C6 sugar to FDCA) was calculated with these yield assumptions:
    - From C6 sugar to sugar diacid (aldaric acid): 80 mol-%
    - From aldaric acid to FDCA: 80 mol-%

- Biomass fractionation yield assumptions:
    - Cellulose from biomass: 95 w-% of the theoretical maximum
    - Hemicellulose sugars from biomass (includes hydrolysis): 80 w-% of the theoretical maximum
    - Cellulose + hemicellulose sugars from biomass (includes hydrolysis): 80 w-% of the theoretical maximum
    - Lignin from biomass: 80 w-% of the theoretical maximum

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[165] http://ec.europa.eu/agriculture/sugar/presentations/price-reporting_en.pdf

[166] Cai C.M. et al., Integrated Furfural Production as a Renewable Fuel and Chemical Platform for Lignocellulosic Biomass, 89 (2014), 1, 2-10.

[167] Baijun L. et al. Liquid Phase Selective Hydrogenation of Furfural on raney Nickel Modified by Impregnation of Salts of Heteropolyacids, Applied Catalysis A: General, 171 (1998) 177-122.

Biomass compositions

- Softwood (SW)[168]
    - Cellulose 39 w-% of total SW d.m.
    - Hemicellulose 26 w-% of total SW d.m.
        - SW hemicellulose composition[169]: C6 sugars 69 w-%, C5 sugars 27 w-%, acetyl groups 4 w-%.
    - Lignin 28 w-% of total SW d.m.
    - Softwood density = 416 kg/m^3 [170]

- Hardwood (HW)[168]
    - Cellulose 40.5 w-% of total HW d.m.
    - Hemicellulose 31 w-% of total HW d.m.
        - HW hemicellulose composition[169]: C6 sugars 18 w-% C5 sugars 67 w-%, acetyl groups 15 w-%
    - Lignin 21 w-% of total HW d.m.
    - Hardwood density = 490 kg/m^3 [170]

- Straw [171]
    - Cellulose 35 w-% of total straw d.m.
    - Hemicellulose 22 w-% of total straw d.m.
        - Straw hemicellulose composition: C6 sugars 11 w-%, C5 sugars 89 w-%.
    - Lignin 16 w-% of total straw d.m.

- Recovered paper
    - Mechanical pulp paper: 70 w-% of all recovered paper (rough estimation of Finnish situation)
        - Composition[172]: 57 w-% sugars (84 % C6, 16 % C5), 39 w-% lignin
    - Chemical pulp paper: 30 w-% of all recovered paper (rough estimation of Finnish situation)
        - Composition[172]: 80 w-% sugars (82 % C6, 18 % C5), 10 w-% lignin

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[168] Pine and birch compositions taken from: Seppälä M. (ed.) Kemiallinen metsäteollisuus 1 – Paperimassan valmistus. Opetushallitus 2001.

[169] SW and HW hemicellulose compositions taken from: a) Alen R. (ed). Papermaking science and technology, Volume 4 Papermaking chemistry. Finnish Paper Engineers' Association 2007. b) Sjöström E. Wood chemistry – fundamentals and applications. Gulf Professional Publishing, 1993.

[170] Kangas P. et al. Evaluation of future pulp mill concepts – Reference model of a modern Nordic kraft pulp mill. *Chemical Pulping* 29 (2014) 620-634.

[171] Kallioinen A. Development of pretreatment technology and enzymatic hydrolysis for biorefineries. Dissertation, VTT 2014. http://www.vtt.fi/Documents/2014_S56.pdf

[172] Foyle T et al. Compositional analysis of lignocellulosic materials: Evaluation of methods used for sugar analysis of waste paper and straw. *Biores. Tech.* 98 (2007) 3026-3036. DOI:10.1016/j.biortech.2006.10.013

2.9.2. Summary of value chain calculation results

The results of the value chain calculations are summarized in Table 13. The table shows the calculation results for the three processes studied in CatBio and Furchem projects (CatBio Process 1, CatBio Process 2, and Furchem Process), alongside with three reference processes (Bioethanol Reference, CatBio Reference Process, and Furchem Reference Process.)

The table describes

- *How much biomass is needed to feed a process that uses 100 kt of sugar as raw material*. These have been calculated separately for C5 and C6 sugar processes. The considered (Finnish) biomass sources for C5 sugars were hardwood and straw, whereas the considered (Finnish) biomass sources for C6 sugars were softwood, straw and recovered paper. Softwood utilization was considered in two different ways: either all the C6 sugars or only hemicellulose C6 sugars. The biomass sources were selected based on the availability (See Chapter 2.1.). It was estimated that tens of kilotons of sugars are at least needed for a feasible process. All the selected biomass sources are lignocellulosic, non-food sources. The required biomass amount varies between 220 - 700 kt, depending on biomass composition. This topic is further elaborated in Chapter 2.11.
- *How much product or product mix is obtained with 100 kt sugar feed*. These values were calculated based on the yield assumptions. This topic is further elaborated in Chapter 2.10.
- *What are the sugar costs (€/ton of product).* These values were calculated based on the yield assumptions and sugar price of 250 €/ton. This topic is also further elaborated in Chapter 2.10.
- *What is the predicted value of the product?* These estimations are based either on the current price of the product, or current price of the corresponding product.[173]

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[173] From the sugar platform to biofuels and biochemicals, final report for the European Commission Directorate-General Energy, N° ENER/C2/423-2012/S12.673791, April 2015.

Table 12. Summary of value chain calculation results.

Value chain / product	Sugar type	Biomass needed for 100 kt sugar	Product (mix) from 100 kt sugar	Sugar costs (€/ton of product)	Product value prediction (€/ton)
Bioethanol Reference / Bioethanol	C6 (+C5) sugar		50	500	500-850
CatBio Reference / Furfuryl alcohol (FA)	C5 sugar	Hardwood: 600 kt /1.2 Mm^3 (hemicellulose utilized) Straw: 640 kt (hemicellulose utilized)	41	610	1000-1500[174]
CatBio Process 1 / 2-Methylfuran (2-MF) Furfuryl alcohol (FA) Tetrahydrofurfuryl alcohol (THFA)	C5 sugar		32	770	1200-4000 (2-MF)[175,176] 1000-1500 (FA) 1000 – 4600 (THFA)[177]
CatBio Process 2 / Succinic acid (SA) Maleic acid (MA) Formic acid	C5 sugar		37	680	2500-2900 (SA)[178] 2400 (MA) 450 (Formic acid)
Furchem Process / FDCA	C6 sugar	Softwood: 220 kt / 0.5 Mm^3 If only hemicellulose utilized: 700 kt / 1.7 Mm^3 Straw: 330 kt Recovered paper: 230 kt	55	450	1100 (Terephthalic acid)
Furchem Ref. (Avantium) / FDCA	C6 sugar		55	450	1100

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[174] ANON. Furfural price. http://www.alibaba.com/trade/search?fsb=y&IndexArea=product_en&CatId=&SearchText=furfural+price. Updated 2014

[175] ANON. High quality 2-methylfuran. http://www.alibaba.com/product-detail/high-quality-2-methylfuran_60131635776.html?s=p, Updated 2015.

[176] ANON. 2-methylfuran. http://www.molbase.com/en/search.html?search_keyword=2-methylfuran&gclid=CjwKEAjw0-epBRDOp7f7lOG0zl4SJABxJg9q4lyw4iLel2CQrk7sMWmMg-aH1EwYA3LdMYXFNwr9nBoCTmTw_wcB, Updated 2013.

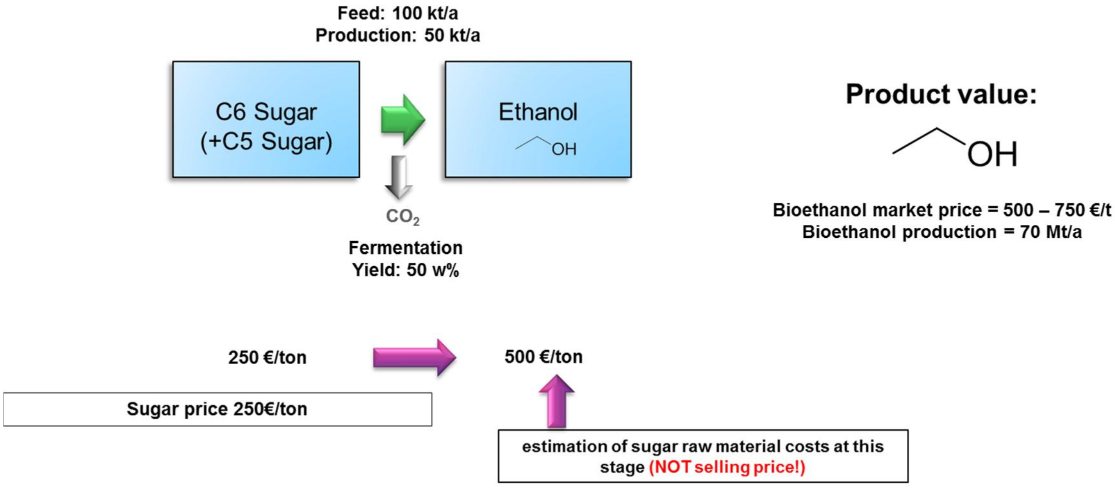
[177] ANON. Tetrahydrofurfuryl alcohol price. http://www.alibaba.com/showroom/tetrahydrofurfuryl-alcohol.html. Updated 2014.

[178] "WP 8.1. Determination of market potential for selected platform chemicals. Itaconic acid, Succinic acid, 2,5-Furandicarboxylic acid," Weastra, S.R.O, 2012.

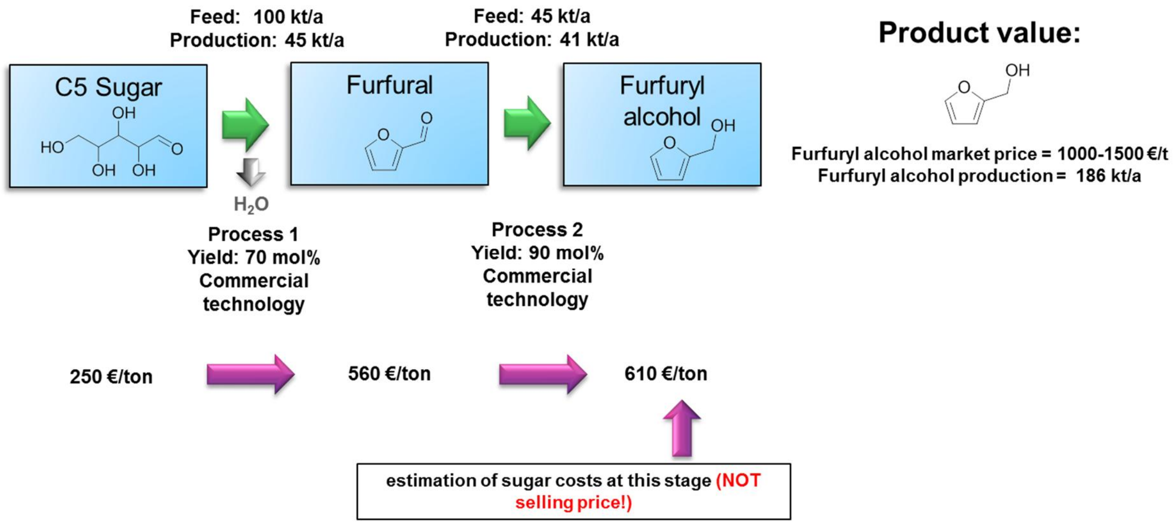
2.10. Sugar costs vs. predicted product value

This chapter presents schemes of the six processes described in Table 13. In the schemes, following points are shown:

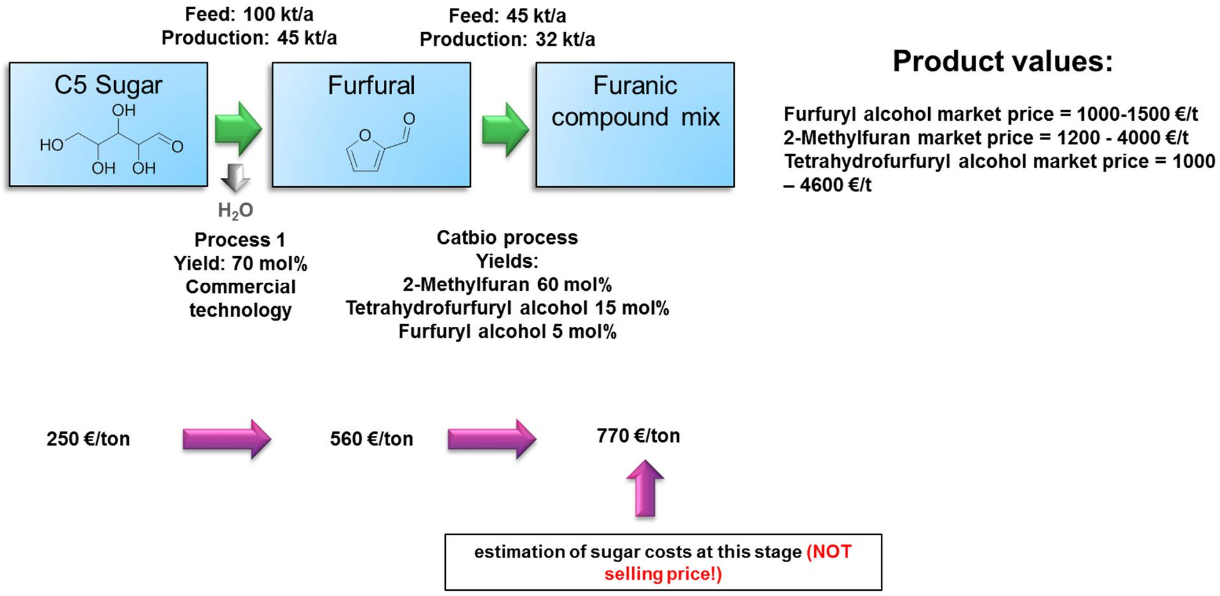
- How the mass flow changes throughout the process, based on yield assumptions. All processes start with 100 kt sugar (C5 or C6).
- How do the sugar (main raw material) costs develop during the process, assuming sugar price at 250 €/ton.
- How do the calculated raw material costs relate with the predicted product value.
-



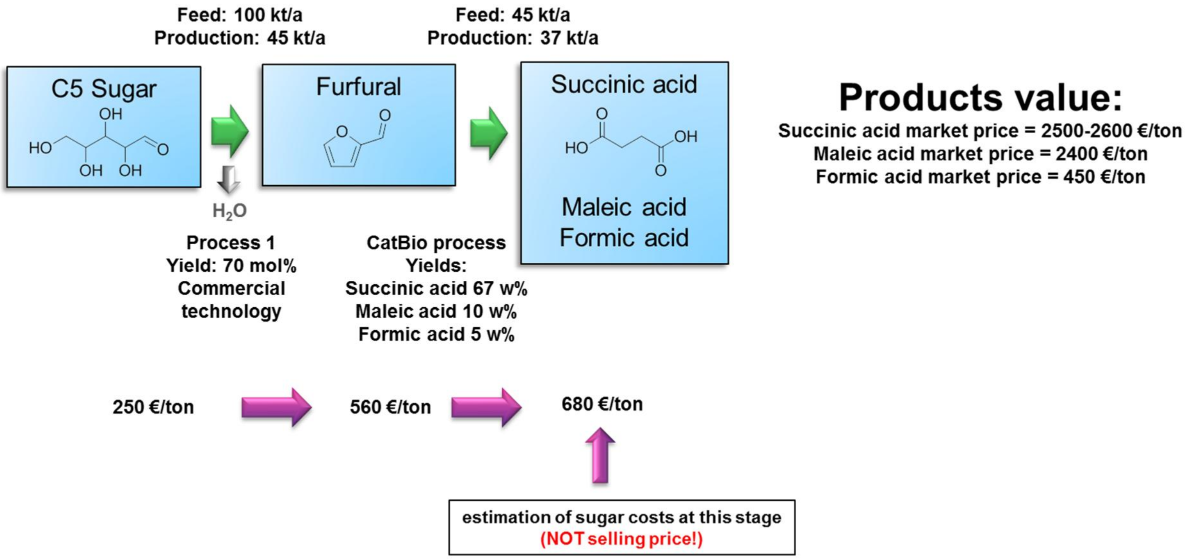
Scheme 24. Bioethanol reference. 500 €/ton costs are estimation of sugar (main raw material) costs - not the selling price.



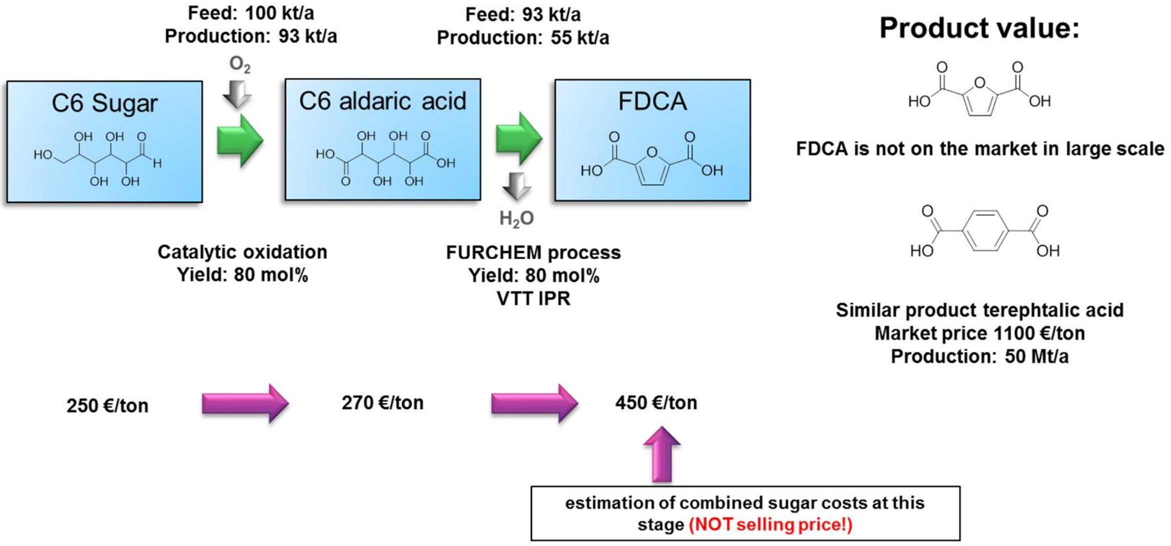
Scheme 25. CatBio reference (from C5 sugars to furfuryl alcohol). 610 €/ton costs are estimation of sugar (main raw material) costs - not the selling price.



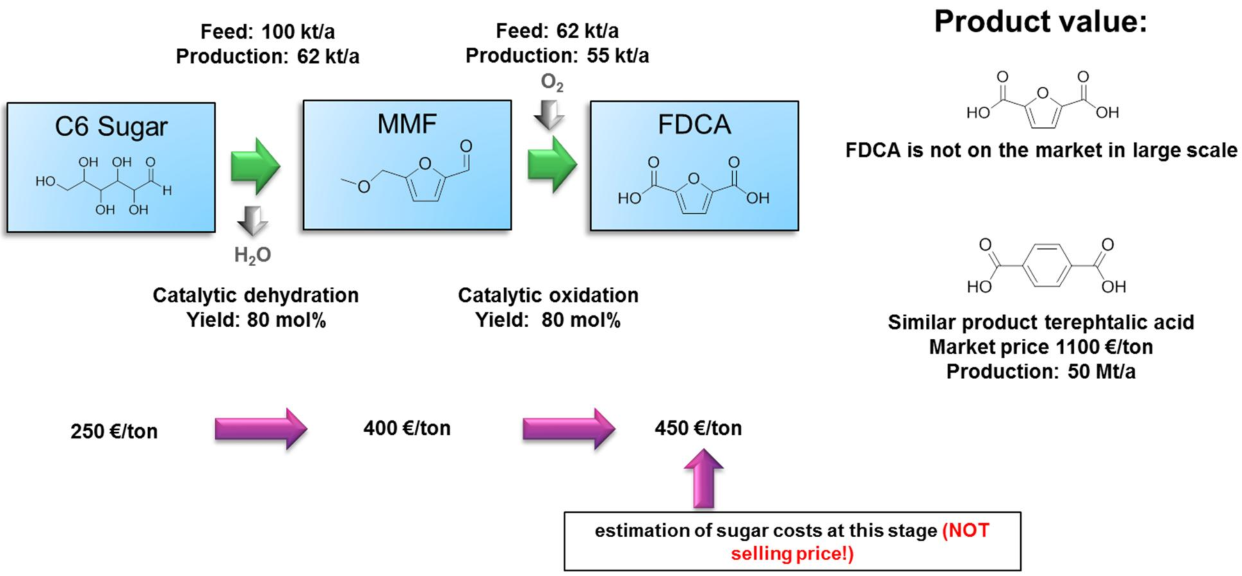
Scheme 26. CatBio Process 1 (from C5 sugars to furanic compound mix, where 2-methylfuran and 2-methyltetrahydrofuran components are applicable as fuel components and furfuryl alcohol and tetrahydrofurfuryl alcohol as solvents). 770 €/ton costs are estimation of sugar (main raw material) costs - not the selling price.



Scheme 27. CatBio Process 2 (from C5 sugars to succinic acid + maleic acid + formic acid). 680 €/ton costs are estimation of sugar (main raw material) costs - not the selling price.



Scheme 28. Furchem process (from C6 sugars to FDCA). 450 €/ton costs are estimation of sugar (main raw material) costs - not the selling price.

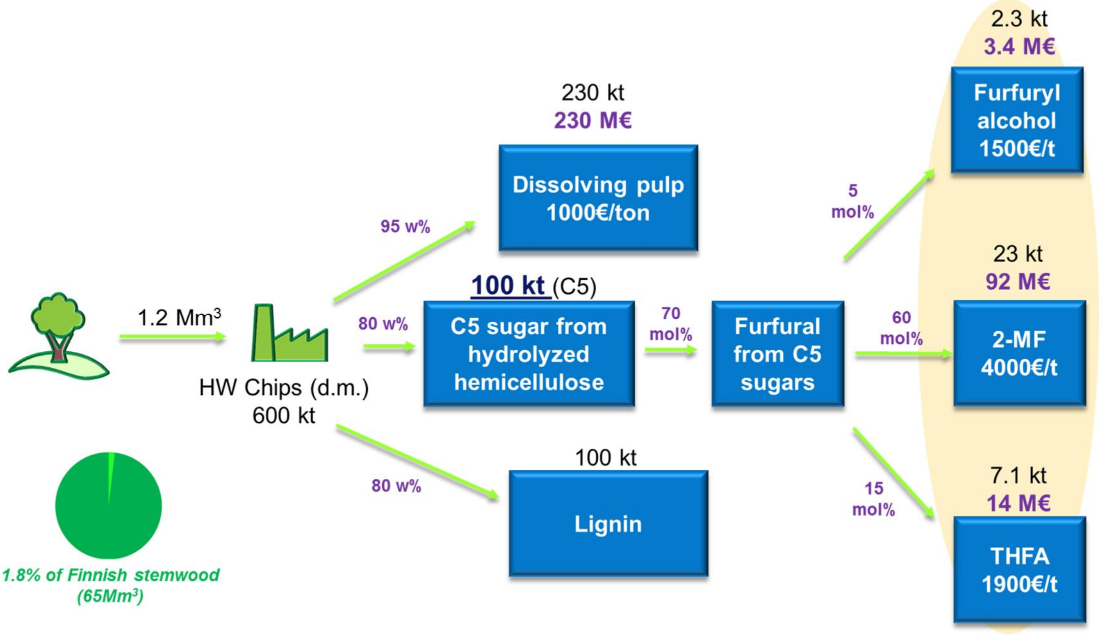


Scheme 29. Furchem reference process (from C6 sugars to FDCA via route used by Dutch company Avantium.) 450 €/ton costs are estimation of sugar (main raw material) costs - not the selling price.

2.11. Biomass source comparisons

This chapter presents schemes of three processes described in Table 13 (CatBio Process 1, CatBio Process 2 and Furchem Process), starting from varying sources of biomass. In the schemes, following points are considered:

- How much biomass is needed to provide **100 kt** of sugar for the processes? (Using assumptions described previously in Chapter 2.9.1.).
- Biomass sources considered for C5 sugar (CatBio Process 1 and CatBio Process 2) were hardwood hemicellulose and straw hemicellulose.
- Biomass sources considered for C6 sugar (Furchem Process) were softwood, softwood hemicellulose, straw, and recovered paper.
- How does the required biomass amount relate to biomass availability in Finland?
- What are the other products that can be produced alongside, depending on biomass?
  - The most important additional product under consideration was cellulose or dissolving pulp. They were produced in schemes that utilized only hemicellulose sugars as feed for the furan production.
- What is the size of the business (turnover) in the total process, if 100 kt of sugar is consumed?



Scheme 30. ***Hardwood hemicellulose*** *as biomass starting material for CatBio Process 1. 1.2 Mm^3 of hardwood is consumed in the process, to allow 100 kt C5 sugar input for the process. This corresponds to 1.8 % of the amount of stemwood harvested in Finland during 2014 (65 Mm^3, SW and HW combined).[179] Hardwood hemicellulose contains 67 w-% C5 sugars and 18 w-% C6 sugars – uses and separation techniques for hemicellulose C6 sugars are out of the scope of this scheme. The process assumes that hemicellulose and cellulose can be fractionated into separate streams. Yield assumptions and turnover numbers are shown* ***in purple*** *in the scheme.The largest turnover in the process comes from the dissolving pulp production, but 2-MF production is also significant.*

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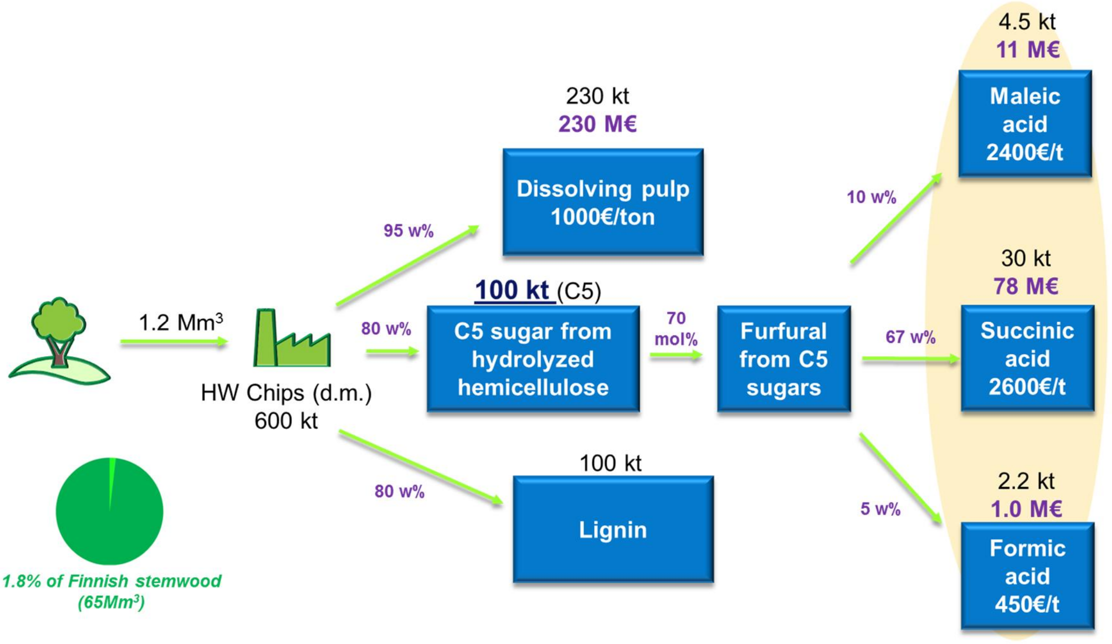
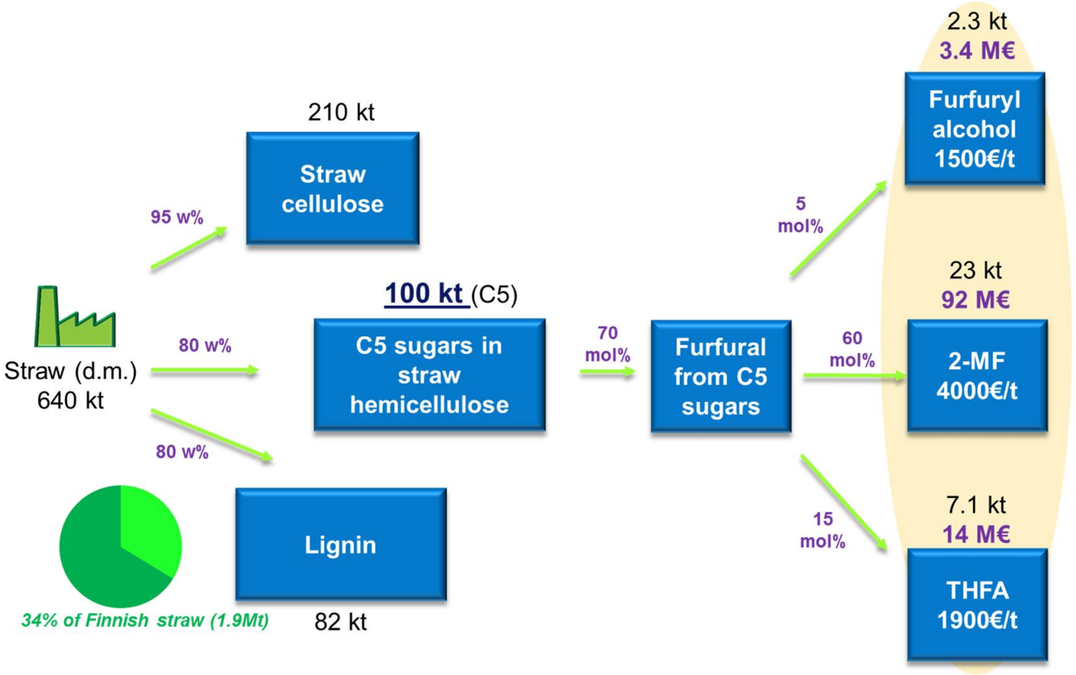
[179] http://www.forestindustries.fi/statistics/The-Finnish-forest-industry-in-figures-1274.html



Scheme 31. ***Hardwood hemicellulose*** *as biomass starting material for CatBio Process 2. The scheme is otherwise same as Scheme 30, just the end products after furfural are different.*



Scheme 32. ***Straw*** *as biomass starting material for CatBio Process 1. 640 kt of straw is consumed in the process, to allow 100 kt C5 sugar input for the process. This corresponds to 34 % of the amount of estimated annual straw production in Finland (1.9 Mt, see Table 2). As a comparison: Suomen bioetanoli has a plan to collect 330 kt of straw annually for bioethanol production in Kouvola.*[180] *Straw hemicellulose contains 89 w-% C5 sugars and 11 w-% C6 sugars – uses and separation techniques for hemicellulose C6 sugars are out of the scope of this scheme. The process assumes that hemicellulose and cellulose can be fractionated into separate streams.*

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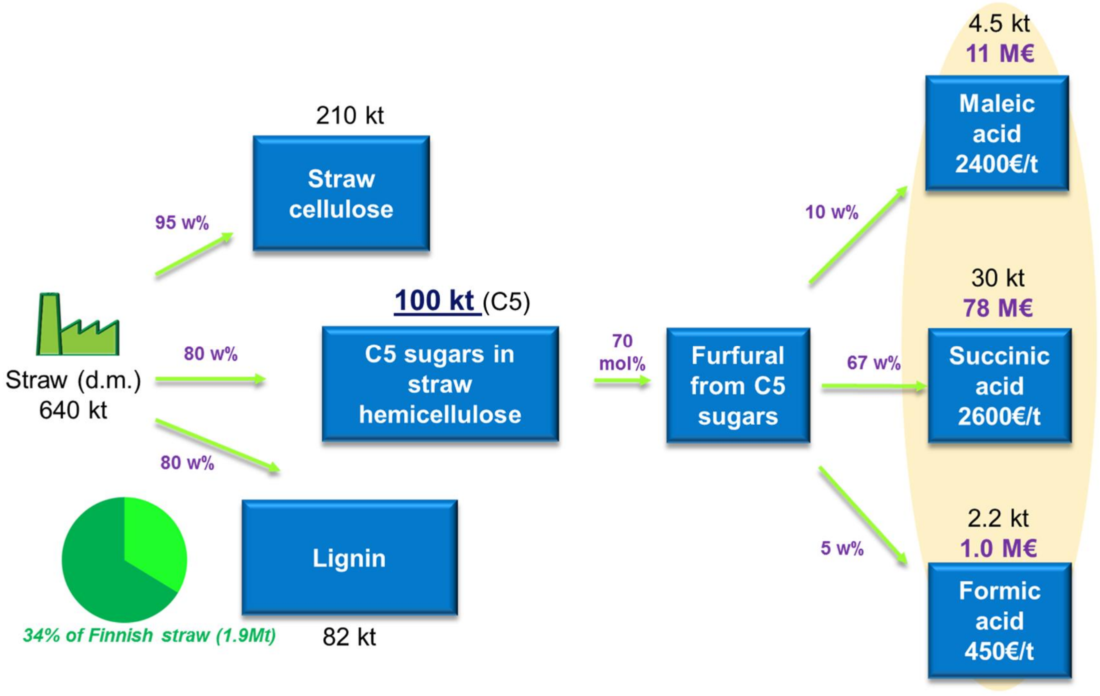
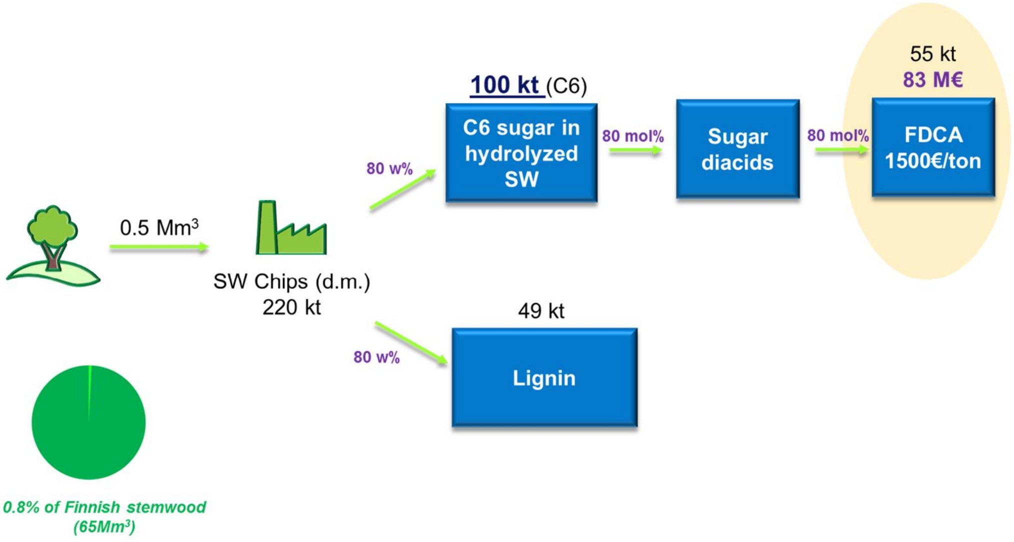
[180] Suomen Bioetanoli website, http://www.sbe.fi/SBE/SBE.html

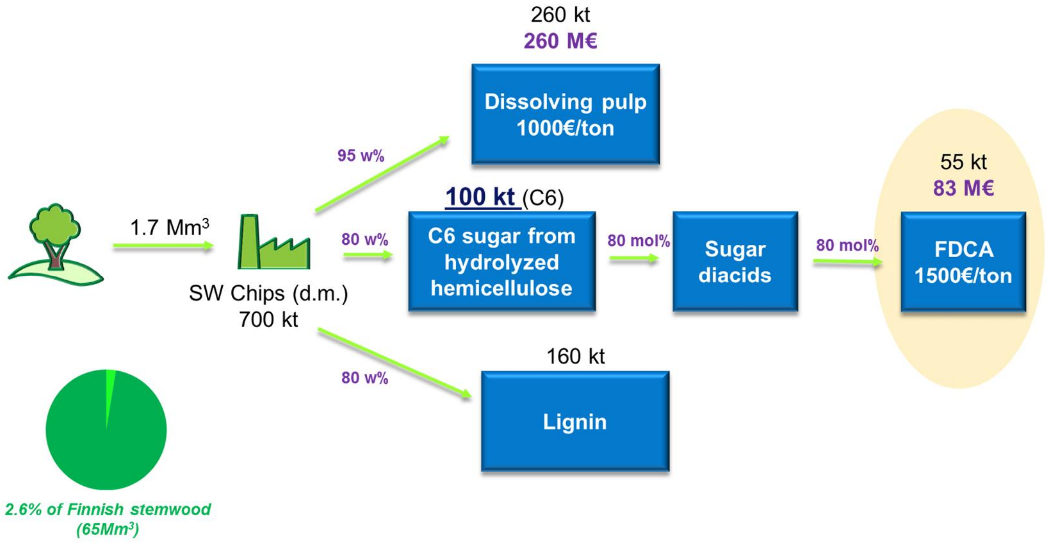


Scheme 33. ***Straw*** *as biomass starting material for CatBio Process 2. The scheme is otherwise same as Scheme 32, just the end products after furfural are different.*



Scheme 34. ***Softwood*** *as biomass starting material for Furchem process. 0.5 Mm^3 of softwood is consumed in the process, to allow 100 kt C6 sugar input for the process. This corresponds to 0.8 % of the amount of stemwood harvested in Finland during 2014 (65 Mm^3, SW and HW combined).*[179] *Softwood carbohydrate fraction contains 89 w-% C6 sugars and 11 w-% C5 sugars (cellulose and hemicellulose combined) – uses and separation techniques for C5 sugars are out of the scope of this scheme.* ***Note: Sawdust*** *is sometimes considered as biorefinery feedstock, and SW sawdust could be applied as feedstock in this scheme. A large Finnish sawmill can have an annual*

production rate at 400 000 m^3.[181] If ca. 10% of the wood is turned into sawdust, it can be estimated that ca. 15-20 kt of sawdust (d.m.) is produced at one large site annually – this is <10% of the biomass amount required in this scheme.



Scheme 35. ***Softwood hemicellulose*** *as biomass starting material for Furchem process. 1.7 Mm^3 of softwood is consumed in the process, to allow 100 kt C6 sugar input for the process. This corresponds to 2.6 % of the amount of stemwood harvested in Finland during 2014 (65 Mm^3, SW and HW combined).[179] Softwood hemicellulose contains 69 w-% C6 sugars and 27 w-% C5 sugars – uses and separation techniques for hemicellulose C5 sugars are out of the scope of this scheme. The process assumes that hemicellulose and cellulose can be fractionated into separate streams. The largest turnover in the process comes from the dissolving pulp production, but FDCA production is also significant.*

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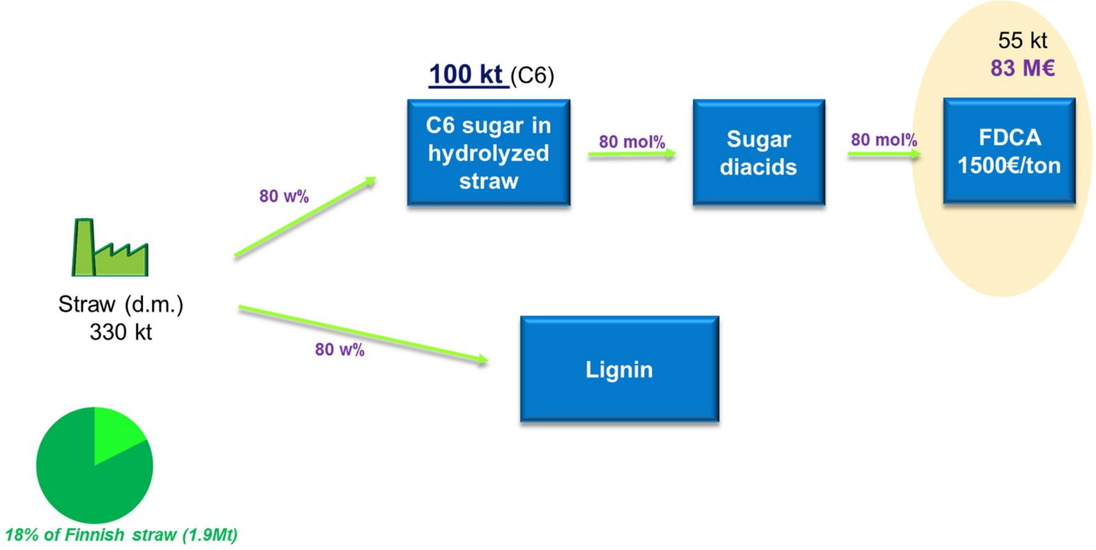
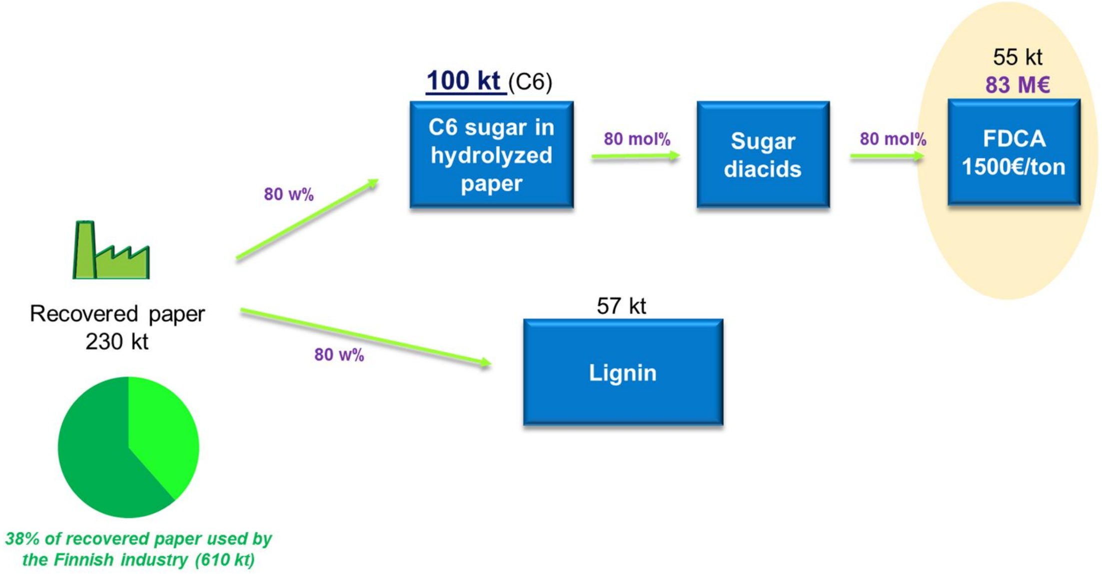
[181] Keitele Forest pian Suomen suurin saha. http://www.savonsanomat.fi/uutiset/talous/keitele-forest-pian-suomen-suurin-saha/1183749 (Published 04.04.2012).



Scheme 36. ***Straw*** *as biomass starting material for Furchem process. 330 kt of straw is consumed in the process, to allow 100 kt C6 sugar input for the process. This corresponds to 38 % of the amount of estimated annual straw production in Finland (1.9 Mt, see Table 2). As a comparison: Suomen bioetanoli has a plan to collect 330 kt of straw annually for bioethanol production in Kouvola.[180] Straw carbohydrate fraction contains 66 w-% C6 sugars and 34 w-% C5 sugars (cellulose and hemicellulose combined) – uses and separation techniques for C5 sugars are out of the scope of this scheme.*



Scheme 37. ***Recovered paper*** *as biomass starting material for Furchem process. 230 kt of recovered paper is consumed in the process, to allow 100 kt C6 sugar input for the process. This corresponds to 38 % of the estimated amount of recovered paper used by the Finnish industry (610 kt, see Table 2). Recovered paper carbohydrate fraction contains 83 w-% C6 sugars and 17 w-% C5 sugars (cellulose and hemicellulose combined) – uses and separation techniques for C5 sugars are out of the scope of this scheme.*

4. Results of company interviews

Company interviews were conducted in order to investigate how representatives of the Finnish industry see the value chains around bio-based furan compounds. Altogether **eight companies were interviewed**. The companies had interests in a wide range within the potential bio-furan value chains (Figure 27). In the interview results, the company answers are roughly categorized into three different groups, depending on the company's role in the value chain:

1. Biomass providers (companies which can also provide certain feedstock)
2. Middle placement (companies that were most interested in fractionation and chemical conversions)
3. End placement (companies that were most interested on the applications and end products)

It can be noted that many of the companies fitted into more than one of these groups.

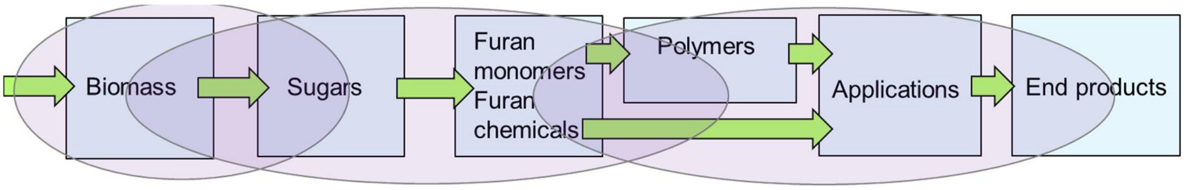


Figure 27. The range of interests of the interviewed companies in relation to potential furanic value chains. Companies were divided into three different groups based on their role – these groups are shown as purple circles in the scheme.

Following topics were discussed during the interviews:

- What role does the company see for itself within the value chain?
- Figure 27 was generated based on these discussions.
- Does the company have an opinion regarding the **biomass feedstocks**, i.e. does it make a difference which biomass raw material is applied?
- What kind of **applications** could be interesting?
- The most desired **end results** of Furchem & CatBio research projects from the company's point of view?

Biomass feedstock discussions – list of company answers. (Companies categorized into three groups.)

1. Biomass providers:
   - Sugars should come from second generation biomass.
   - Cellulose/pulp is too expensive to be applied in chemical production – e.g. prehydrolysis sugars and hemicelluloses should be looked into as alternatives.
   - We want to create biorefinery concepts where all the components in wood are utilized.
   - Our view of suitable production capacity is 10 - 50 kt/a of biochemical product.

2. Middle placement in the value chain (fractionation, chemistry):
   - Production volumes need to be large. Lignocellulosics most probable in Finland. Some side streams and wastes also possible but also then volumes must be large.
   - 100 kt sugar production is possible in Finland, when various biomass sources (straw, wood, etc.) are combined.
   - If glucose is the main product from biomass fractionation, valuable side products may allow profitability.

- All sugar types are interesting, also lignocellulosic sugars (especially those that can be double-counted.)
- Regarding agro biomass – logistics can become a problem in Finland.
- Sugars need to be produced from biomass (e.g. cellulose) as easily as possible – pulp should not be turned into sugars.
- Raw material cost can be the largest cost of bio-based product.
- The raw material base is global in principle.
- Sustainability, land use, indirect effects and GHGs must be taken into account – often strict regulations e.g. in fuel components.

3. End placement in the value chain:
    - There must be enough feedstock to ensure availability.
    - In order to be interesting, the bio-monomer should be produced at least in 10 - 100 kt/a scale.
    - Food-based or unethical feedstock can become a problem.
    - Bio-based raw material can help in marketing and differentiation – however, bio-products do not sell only because of bio-label. Also price / properties must be in place.
    - We cannot increase price because of bio-based raw material – our customers want new products to be cheaper.

Applications of furan compounds – list of company answers. (Companies categorized into three groups.)

1. Biomass providers:
    - The final application matters a lot as the attractiveness of the potential business is determined by the market.
    - Platform chemicals are interesting. E.g.for polymers, cosmetics and pharmaceuticals.
    - The economy of the whole process is important.

2. Middle placement in the value chain (fractionation, chemistry):
    - Bio-based fuel components are interesting. Also biochemicals are interesting as a side product. Especially platform chemicals that can be used in many applications.
    - Platform chemicals from glucose are interesting.
    - Liquid fuels are especially interesting to us.
    - Fuel component from furfural would be interesting, e.g. 2-MTHF.
    - Our glucose has already been tested as raw material in many products.
    - Fuels and platform chemicals are interesting.
    - The properties of the fuel components are important.

3. End placement in the value chain:
    - FDCA is interesting if it has good properties in polyesters / polyamides / polyester resins.
    - FDCA is interesting if price can be decreased to the level of terephthalic acid.
    - Legislation (e.g. EU packaging legislation) must be in order.
    - It would be interesting if PEF would turn out to be a bio-based material that is truly applicable in packaging.
    - In most polymers we are involved with, price of specific monomers is more important than properties. If the bio-monomer price is low, we can offer broad uses for the monomer. If again the bio-monomer price is high, then it would be applicable only to some high performance speciality products.
    - If commercial PEF is available, and has interesting properties we could test it in our packaging films. But PEF etc. needs to be close to commercial production. Producer needs to

be defined, e.g. VTT piloting is not enough. It must be fairly certain, that commercial product will be on the market. More than one producer would be beneficial.

- Other furanic monomers besides FDCA, e.g. thermoreversible monomers, can be interesting if good case is presented.
- New biomaterial needs to fulfil many requirements: e.g. processability with current equipment, compatibility/adhesion with other product components, no color/odour, no degradation under moisture.

Most desired end results of Furchem and CatBio – list of company answers. (Companies categorized into three groups.)

1. Biomass providers:
    - Knowledge on the markets and business areas.
    - New sustainable technologies developed.
    - New methods for the formation of furan ring from carbohydrates.
    - A new reaction route to FDCA.
    - Technologies that provide end products without fermentation are interesting.

2. Middle placement in the value chain (fractionation, chemistry):
    - Technology to produce fuel components with good economics and sustainability. Side products ok, if they can be also applied somewhere.
    - Clarification on the possible feedstocks.
    - Project would help in the initiation of bio-based chemical production in Finland. It is important to us that bioeconomy would go forward!
    - Roadmap is interesting.
    - Applications for the components present in our current process.
    - Networking
    - Linkages between domestic and foreign parties.

3. End placement in the value chain:
    - Economic technology to produce and upscale FDCA, enabling FDCA production to start within reasonable future.
    - FDCA technology licenced, production started ASAP.

5. Conclusions and recommendations

The purpose of the generation of this roadmap was to review new potential value chains and business opportunities for the Finnish industry, based on furan biorefinery concepts. The roadmap was generated by Tekes strategic opening projects CatBio and FURCHEM. In this roadmap an information package into furan compounds and an comprehensive description of the state-of-the-art of various furan-related topics was presented. Moreover, value chain schemes were generated for the most potential alternatives. Furthermore, recommendations have been included regarding implementation of furan-based value chains in near and long-term future. These recommedations were partly based on company interviews and workshop events carried out during the projects. The results of the interviews and workshops were also summarized in this final version of roadmap.

The purpose of both FURCHEM and CatBio projects was to generate general understanding on the potential of various furan-based biorefinery concepts and find alternative efficient and selective bio-based production routes to current fossil resource based alternatives. In addition, more focused technology development was carried out in both projects. In FURCHEM project the technology development concentrated on the production of furan dicarboxylic acid (FDCA) from C6 sugars and sugar acids and in CatBio project the technology development concentrated on the production of furanic fuel components and succinic acid from furfural (originating from C5 sugars). In this final version of roadmap the results obtained in both projects were also presented.

Company interviews performed for this roadmap have given a good understanding of what are the opinions and needs of Finnish industry of furan-based chemistry. In the interviews a wide range of interest towards furan chemistry was shown, all the way from raw materials to the end products. Many of the interviewed companies were working in multiple sections and the production chain would be well covered by some companies.

Recommendations received from the company interviews were that the price and properties of furan based products must be in place, only having the bio-label on the product does not sell. Customers will not pay more of new products, new products developed need to be cheaper to attract interest. Also, the economy of whole process to produce furan-based products is important.

This roadmap functions as a good start for furan-based economy and a well started work should be finished. Based on the two strategic projects now performed (CatBio and FURCHEM) actual process development work should be started in a continuation project. The coming projects should focus on further intensificiation of value chain processes to value added furan-based products. Yields and selectivitites of individual steps have to be enhanced in order to promote the profitability of the processes. Furthermore, the processes for furan-based products should be studied together with concepts of biorefineries to ensure overall feasibility of value chains. Emphasize should especially be directed to on-going biorefienery projects in Finland.

Furthermore, studies should be directed both the evaluation of potential raw material streams and evaluation of application of proposed products. This work should be solely carried out together with companies in the field and it should be linked to the on-going development work of the companies. Potential streams could be found e.g. from on-going biorefinery concept studies and investment project. Companies interested in applications of proposed products should be identified and application testing products should be started together with these companies.

Appendix 1 Patent survey tables

Appendix 1, Table 1. Relevant patents related to FDCA polymers. 91 patents altogether.

Patent /application number	Publ. Year	Assignee	Title, **general topic**, and remarks
GB545609 A	1942	Geigy	Manufacture of furan carboxylic acid amides and acid ester amides **Polyamide.** Not exactly perhaps FDCA, but quite close!
GB621971	1946	Celanese	Polyesters from heterocyclic components **Polyester**. Melt polycondensation with e.g. Na/Mg methoxide as catalyst -> yielded filaments
US4806623 A	1988	Stamicarbon (Gandini)	Poly(p-phenylene-2,5-furandicarbonamide), anisotropic solution, filament, film thereof **Aramide**. FDCA with aromatic diamine, p-phenylene. Anisotropic solutions, filaments, films
US4876327A	1988	Stamicarbon	Aromatic polyester **Polyester**. Fully aromatic polyester with liquid-crystalline properties. Replacement of part of aromatic acids by FDCA leads to melting point reduction.
US5504182A	1991	Hoechst	Thermoplastically processable aromatic polyether amide **Aramide.** FDCA chloride has been applied in examples
US5536408A	1993	Hoechst	Hydrophilic, asymmetric, chemically-resistant polyaramide membrane **Aramide**. FDCA chloride just mentioned as one potential component
US6342300B	1999	Aventis /Celanese	Biodegradable polymers based on natural and renewable raw materials especially isosorbite **Polyester**. FDCA claimed as one alternative for diacid
US5958581A	1999	DuPont	Polyester film and methods for making same **Polyester**. Mainly concentrates on isosorbides, but FDCA listed as one potential monomer component
US5959066A	1999	DuPont	Polyesters including isosorbide as a comonomer and methods for making same **Polyester**. Mainly concentrates on isosorbides, but FDCA listed as one potential monomer component
US6063495A	1999	DuPont	Polyester fiber and methods for making same **Polyester.** Mainly concentrates on isosorbides, but FDCA listed as one potential monomer component.
US6025061A	1999	DuPont	Sheets formed from polyesters including isosorbide **Polyester.** Mainly concentrates on isosorbides, but FDCA listed as one potential monomer component.
US6126992A	1999	DuPont	Optical articles comprising isosorbide polyesters and method for making same **Polyester.** Mainly concentrates on isosorbides, but FDCA listed as one potential monomer component.
US6063464A	1999	DuPont	Isosorbide containing polyesters and methods for making same **Polyester.** Mainly concentrates on isosorbides, but FDCA listed as one potential monomer component.
US6063465A	1999	DuPont	Polyester container and method for making same **Polyester.** Mainly concentrates on isosorbides, but FDCA listed as one potential monomer component.
US6140422A	1999	DuPont	Polyesters including isosorbide as a comonomer blended with other thermoplastic polymers **Polyester.** Mainly concentrates on isosorbides, but FDCA listed as one potential monomer component.
DE19928927A1	2000	Univ. Rostock	New polyurethanes containing 2,5-disubstituted furan rings, useful for preparing flexible foams with surface-bonded active agents for medicinal applications, especially as breast prostheses **Polyurethane/polyester.** Furan compounds used in polyester polyols for flexible foam preparation

US2005089690A	2001	DLW	**Storable moldable material and flat articles produced from renewable raw materials** Some kind of **crosslinked material.** FDCA listed as one of many alternatives.
US2002020128A	2002	DLW	**LINOLEUM-BASED PLANAR STRUCTURE AND PROCESS FOR MAKING SAME** **Polyester.** FDCA listed as one of many alternatives, polyester with polyol.
WO07052847	2007	Canon	**POLYMER COMPOUND AND METHOD OF SYNTHESIZING THE SAME** **Polyester.** DP = 185-600. Tin or Titanium catalyst. Melt condensation + solid condensation, purification in HFIP in between. Dark colour reason for purification?
US2008081883A	2008	BATTELLE MEMORIAL INST	**POLYESTER POLYOLS DERIVED FROM 2,5-FURANDICARBOXYLIC ACID, AND METHOD** **Polyester/polyol**. Containd FDCA and epoxide to form polyester.
US2009018264	2008	Canon	**RESIN COMPOSITION** **Polyester.** FDCA polyester + layered silicate structure.
US2008125517A	2008	BATTELLE MEMORIAL INST	**ACCELERATED FURANIC AGGREGATE BINDERS FROM BIO-DERIVED COMPONENTS** This patent contains multitude of furanic structures, including BHF
KR100952724B	2008	LG Chemical	**Method for Synthesizing Biodegradable Polyester Containing Aliphatic and Aromatic Compound** **Polyester.** FDCA+aliphatic diol+lactide, possibly also other components. Ring opening polymerization of FDCA!?
US2008207795A	2008	BATTELLE MEMORIAL INST	**BINDER FORMULATIONS UTILIZING FURANIC COMPONENTS** This patent contains multitude of furanic structures, including FDCA.
US2008207847A	2008	BATTELLE MEMORIAL INST	**FURANIC-MODIFIED AMINE-BASED CURATIVES** **Crosslinker.** FDCA incorporated into bisamide based crosslinker.
JP2008291243A	2008	Mitsubishi	**THERMOPLASTIC RESIN INCLUDING FURAN STRUCTURE**
JP2008308578	2008	Canon	**PROCESS FOR PREPARING POLYARYLATE RESIN CONTAINING FURAN RING** **Polyester** PEF etc. with Titanium tetrabutoxide / magnesium acetate catalyst system
US2009043018	2009	Canon	**RESIN COMPOSITION AND MOLDED ARTICLE** **Polyester.** Especially PBF resin. Contains hematoporphyrin dihydrochloride (for increased crystallization rate?)
JP2009062465	2009	Canon	**POLYESTER RESIN, METHOD FOR PRODUCING THE SAME, COMPOSITION FOR MOLDED ARTICLE AND MOLDED ARTICLE** **Polyester.** FDCA. Contains also itaconic acid.
US2011021740A	2009	DSM	**FURAN BASED RESIN, PROCESS FOR THE PREPARATION THEREOF, AND USE OF THE COMPOUND** **Resin.** Seems to be connected to furfuryl alcohol resins, but includes lot of potential stuff, also FDCA.
US2010184900	2009	Canon	**RESIN COMPOSITION AND MOLDED ARTICLE** **Polyester.** PEF with reduced long-term crystallization tendency. Contains sodium montanate.
US2010184888	2009	Canon	**RESIN COMPOSITION AND MOLDED ARTICLE** **Polyester.** PEF with high crystallization rate. Contains pyrimide thiol.
US2010174044	2009	Canon	**POLYESTER RESIN, METHOD OF PRODUCING THE SAME, COMPOSITION FOR MOLDED ARTICLE AND MOLDED ARTICLE** **Polyester.** PEF or polyester with diethylene glycol.
JP2009215467	2009	Canon	**MANUFACTURING METHOD OF POLYETHYLENE-2,5-FURAN DICARBOXYLATE** **Polyester.** PEF with scandium triflate catalyst.
US2011020660A	2009	Novamont	**BIODEGRADABLE POLYESTER, PREPARATION PROCESS THEREOF AND PRODUCTS COMPRISING SAID POLYESTER** **Polyester.** Aromatic-aliphatic biodegradable structure with long-chain branches. FDCa as one monomer option.
US2011071238A	2009	Novamont	**ALIPHATIC-AROMATIC BIODEGRADABLE POLYESTER** **Polyester.** Aliphatic-aromatic polyester, FDCA as monomer.

JP2009263509A	2009	National institute of adv. Ind. Sci and tech.	**BIODEGRADABLE HIGH MOLECULAR-WEIGHT ALIPHATIC POLYESTER AND METHOD FOR MANUFACTURING THE SAME** **Polyester.** Aromatic-aliphatic biodegradable structure.
US2011183099A	2010	Arkema	**BLOCK COPOLYMER DERIVED FROM RENEWABLE MATERIALS AND METHOD FOR MAKING SUCH BLOCK COPOLYMER** **Polyester.** Concentrates on tetrahydrofuran block, for other blocks claims almost everything. FDCA included.
US2011281972A	2010	HEXION SPECIALTY CHEMICALS	**POWDER COATING COMPOSITIONS FOR LOW TEMPERATURE CURING AND HIGH FLOW** **Polyester.** FDCA listed as one of many possible component.
WO10077133	2010	Furanix (Avantium)	**PROCESS FOR PREPARING A POLYMER HAVING A 2,5-FURANDICARBOXYLATE MOIETY WITHIN THE POLYMER BACKBONE AND SUCH (CO)POLYMERS** **Polyester.** Mn > 10 000 g/mol, prepolymerization+polycondensation+(solid state polymerization) tin(IV) and/or tin (II) catalyst. Colour not good enough for bottle use?
JP2010254827A	2010	National institute of adv. Ind. Sci and tech.	**HIGH-MOLECULAR WEIGHT ALIPHATIC POLYESTER ETHER USING BIOBASE RAW MATERIAL AND METHOD FOR PRODUCING THE SAME** **Polyester.** General. Different FDCA polyesters.
CN101899145A	2010	JIANGNAN UNIVERSITY	**PREPARATION METHOD OF 2, 5-FURAN DIFORMYL POLYESTER** **Polyester.** General. Different FDCA polyesters.
US2012065356	2010	Canon	**POLYESTER RESIN, METHOD OF PRODUCING THE RESIN, AND MOLDING PRODUCT** **Polyester.** FDCA + certain diols.
US2012220507A	2011	Evonik	**2,5-FURAN DICARBOXYLATE DERIVATIVES, AND USE THEREOF AS PLASTICIZERS** **Plasticizer.** Especially for PVC.
US2012202725A	2011	Evonik	**2,5-FURAN DICARBOXYLATES COMPRISING ISODECANOLS, AND USE THEREOF** **Plasticizer.** Especially for PVC.
US2012178896A	2011	Novamont	**BIODEGRADABLE POLYESTER** **Polyester.** Unsaturated end groups. FDCA one option.
US2012220680A	2011	Novamont	**BIODEGRADABLE ALIPHATIC-AROMATIC POLYESTER** **Polyester.** Aliphatic-aromatic polyester, FDCA as monomer.
CN102050941A	2011	TORAY FIBER res. Inst.CHINA	**MACROMOLECULAR POLYMER AND PRODUCTION METHOD THEREOF** **Polyester.** Quite general, FDCApolyesters.
US2011124839	2011	Canon	**FLAME-RETARDANT POLYESTER COPOLYMER, AND PRODUCTION PROCESS AND MOLDED ARTICLE THEREOF** **Polyester.** FDCA with various other components, including phophorus-containing compounds
US2011120902A	2011	Procter &Gamble	**SUSTAINABLE PACKAGING FOR CONSUMER PRODUCTS** **Polyester.** FDCA polyesters listed as one of many alternatives.
US2011130498	2011	Canon	**FLAME RETARDANT RESIN COMPOSITION AND MOLDED ARTICLE THEREOF** **Polyester**. FDCA with various other components, including phophorus-containing compounds.
CN102190785A	2011	CHANGCHUN inst. Appl. Chem.	**Poly(ethylene 2,5-furandicarboxylate), and preparation method thereof** **Polyester.** PEF production route. Seems not very mild.
US2013022771A	2011	Arkema	**BLOCK COPOLYMER DERIVED FROM RENEWABLE MATERIALS AND METHOD FOR MAKING SUCH A BLOCK COPOLYMER** **Polyester.** Concentrates on PEO/PPO block, for other blocks claims almost everything. FDCA included.
US2013071588A	2011	Novamont	**ALIPHATIC-AROMATIC COPOLYESTERS AND THEIR MIXTURES** **Polyester.** Aliphatic-aromatic polyester, FDCA as monomer.
WO12005645A1	2012	Perstorp	**Alkyd resin.** **Polyester.** Contains FDCA as one monomer.
US2013136879A	2012	Novamont	**POLYPHASE BIODEGRADABLE COMPOSITIONS CONTAINING AT LEAST ONE POLYMER OF VEGETABLE ORIGIN** **Polyester.** FDCA one possible monomer.

US2013171555A	2012	Kao Corp	**BINDER RESIN FOR TONERS Polyester.** FDCA containing binder,
US2013281560A	2012	Novamont	**POLYESTER COMPOSITION Polyester.** Mixtures that contain aromatic and aliphatic components. FDCA seems to be favored, e.g. PBF mixed with aliphatic-asromatic furan copolymer.
CN102516513A	2012	JIANGNAN UNIVERSITY	**Preparation method of low-yellowing 2,5-furandicarboxylic acid-based polyester Polyester.** PEF in mild conditions.
JP2012122023A	2012	Unitika	**LIQUID CRYSTALLINE POLYESTER Polyester.** Contains PEF, aromatic diacid, and phosphorus-containing diol. Material is heat and flame resistant.
WO12091573	2012	Furanix (Avantium)	**PROCESS FOR THE DEPOLYMERIZATION OF A FURANDICARBOXYLATE CONTAINING POLYESTER Polyester.** PEF depolymerization. Relates to recycling/reuse of the polymer.
US2014024754A	2012	Evonik	**PENTYL ESTERS OF FURANDICARBOXYLIC ACID AS SOFTENERS Plasticizer.** Especially for PVC.
US2014024754A	2012	Evonik	**HEPTYL ESTERS OF FURAN DICARBOXYLIC ACID AS SOFTENERS Plasticizer.** Especially for PVC.
US2013338276A	2012	Evonik	**C11 TO C13 DIALKYL ESTERS OF FURANDICARBOXYLIC ACID AS SOFTENERS Plasticizer.** Especially for PVC.
US2012238170A	2012	Procter &Gamble	**FLUID PERMEABLE STRUCTURED FIBROUS WEB Polyester.** PEF listed as one of many alternatives.
US2012237718A	2012	Procter &Gamble	**STRUCTURED FIBROUS WEB Polyester.** PEF listed as one of many alternatives.
US2012238981A	2012	Procter &Gamble	**FLUID PERMEABLE STRUCTURED FIBROUS WEB Polyester.** PEF listed as one of many alternatives.
US2012238982A	2012	Procter &Gamble	**STRUCTURED FIBROUS WEB Polyester.** PEF listed as one of many alternatives.
US2012238978A	2012	Procter &Gamble	**FLUID PERMEABLE STRUCTURED FIBROUS WEB Polyester.** PEF listed as one of many alternatives.
US2012238979A	2012	Procter &Gamble	**STRUCTURED FIBROUS WEB Polyester.** PEF listed as one of many alternatives.
KR20120107573 A	2012	KOREA inst. Ind. Tech.	**FURAN BASED COPOLYESTER AND METHOD FOR PREPARING THE SAME Polyester.** Seems to be quite general FDCA polyester claim.
US2012258299	2012	Canon	**Plastic film Polyester.** e.g. PEF with good barrier properties.
US2012288692A	2012	Procter &Gamble	**RENEWABLY SOURCED FILMS AND METHODS OF FORMING SAME Polyester.** PEF listed as one of many alternatives.
CN102796250A	2012	Beijing Jinjiao Biomass Chemical Co.	**Biobased polyarylester and preparation method thereof Polyester.** FDCA+aromatic diol.
CN102827361A	2012	Beijing Jinjiao Biomass Chemical Co.	**BIOLOGICAL-BASED POLYESTER AND PREPARATION METHOD THEREOF Polyester.** FDCA+pentanediol. high in strength, toughness, heat stability and chemical resistance, easy to process
WO13034305	2013	Nitto Denko Europe	**POLYCONDENSATE-BASED PRESSURE-SENSITIVE ADHESIVE CONTAINING FURAN MOIETIES Polyester.** Pressure sensitive adhesives. Claims both FDCA and BHMF, example only with FDCA.
JP2013006963A	2013	Unitika	**POLYAMIDE AND MOLDED ARTICLE THEREOF Phtalamide.** FDCA+aliphatic diamine C5-C12. Excellent mechanical properties.
US2013023608A	2013	Procter &Gamble	**BIO-POLYMERS IN MULTICOMPONENT FIBERS Polyester.** PEF listed as one of many alternatives.
CN102952253A	2013	NINGBO INST MAT TECH AND ENG	**EPOXY RESIN BASED ON 2,5-FURANDICARBOXYLIC ACID, PREPARATION METHOD AND APPLICATION THEREOF Polyester/crosslinked?** Contains FDCA, other ingredients not clear.
KR20130034808 A	2013	LOTTE CHEMICAL CORP	**POLYESTER RESIN COMPOSITION USING BIOMASS EXTRACT AND METHOD FOR PREPARING THE SAME Polyester.**

			FDCA+perhaps some other aromatic compounds. Mechanical strength, heat resistance.
US2013095263A	2013	Eastman Chemical Company	**POLYESTER COMPOSITIONS CONTAINING FURANDICARBOXYLIC ACID OR AN ESTER THEREOF, AND 2,2,4,4-TETRAMETHYL-1,3-CYCLOBUTANEDIOL** **Polyester.** FDCA+cyclic diol+ optionally aromatic or aliphatic diacids.
WO13062408	2013	Furanix (Avantium)	**A PROCESS FOR PREPARING A POLYMER PRODUCT HAVING A 2,5-FURANDICARBOXYLATE MOIETY WITHIN THE POLYMER BACKBONE TO BE USED IN BOTTLE, FILM OR FIBRE APPLICATIONS** **Polyester.** Mn > 25 000 g/mol. Transesterification + polycondensation + crystallization + post condensation. Various catalysts, different in each step, e.g. Ca and Zn acetate. No discoloration? It is stated that discoloration is caused by typical PET catalysts (Mg, Co,Ge), and if high >250oC temperature is applied
CN103113577A	2013	SUZHOU UHNHI CHEMICAL CO	**ALCOHOL-SOLUBLE COPOLYAMIDE AND PREPARATION METHOD THEREOF** **Phtalamide.** FDCA+other caroboxylic acid/diamine/lactam, alcohol soluble copolyamides are obtained
WO13092667A1	2013	Teijin Aramid	**LIQUID CRYSTALLINE FURANDICARBOXYLIC ACID-BASED AROMATIC POLYESTERS** **Aramides.** FDCA+ different comonomers: aromatic diol/p-hydroxybenzoic acid/aromatic monocarboxylic acid. Liquid crystalline structures.
WO13097013A1	2013	NATURA COSMETICOS	**PROCESS FOR THE PRODUCTION OF POLY (ETHYLENE 2,5-FURANDICARBOXYLATE) FROM 2,5-FURANDICARBOXYLIC ACID AND USE THEREOF, POLYESTER COMPOUND AND BLENDS THEREOF** **Polyester.** Some general PEF stuff.
US2013171397A	2013	Pepsico	**2,5-FURAN DICARBOXYLIC ACID-BASED POLYESTERS PREPARED FROM BIOMASS** **Polyester.** Different PET replacement copolyester candidates. FDCA+TPA/C3-C10 diol/isosorbide (etc?)
CN103333325A	2013	CHANGCHUN Inst. Appl. Chem.	**POLY FURAN-2,5-DICARBOXYLIC ACID-2,3-BUTANEDIOL DIACRYLATE AND PREPARATION METHOD THEREOF** **Polyester.** Synthesis description.
WO13149221	2013	DuPont	**POLYESTERS AND FIBERS MADE THEREFROM** **Polyester.** Poiy(trimethylene furandicarboxylate) (PTF), and PTF based copolymers
WO13149222	2013	DuPont	**POLYESTERS AND FIBERS MADE THEREFROM** **Polyester.** Poiy(trimethylene furandicarboxylate) (PTF), and PTF based copolymers
WO13149180	2013	DuPont	**FURAN BASED POLYAMIDES** **Aramide.** Polyamides with m-phenylene diamine (aramide structure)
WO13144525A1	2013	Roquette Freres	**POLYMERS, THE PROCESS FOR THE SYNTHESIS THEREOF AND COMPOSITIONS COMPRISING SAME** **Polyester.** On particular poly(butylenesuccinate-co-furanoate) (PBSF) copolymers (advantageous mechanical properties).
US2013270212	2013	Procter &Gamble	**PLASTIC BOTTLES FOR PERFUME COMPOSITIONS HAVING IMPROVED CRAZING RESISTANCE** **Polyester.** Made of PEF.
US2013273467A	2013	Kao Corp	**TONER FOR ELECTROSTATIC IMAGE DEVELOPMENT** **Polyester**. Binder containing FDCA
JP2013222044A	2013	Kao Corp	**BINDER RESIN FOR TONER** **Polyester**. Binder containing FDCA
JP2013228488A	2013	Kao Corp	**METHOD FOR MANUFACTURING ELECTROPHOTOGRAPHIC TONER** **Polyester**. Binder containing FDCA
US2014024793A	2014	Hitachi	**POLYESTER PRODUCTION PROCESS AND APPARATUS** **Polyester.** PEF production process.
WO14019459 A1	2014	Shanghai Genius Adv. Mat. Group	**BIODEGRADABLE COPOLYESTER CONTAINING 2,5-FURANDICARBOXYLATE, PRODUCT THEREOF, PREPARATION METHOD THEREFOR AND USE THEREOF** **Polyester.** Aromatic-aliphatic biodegradable structure.
US2014044904A	2014	Procter &Gamble	**DEEP GLOSS CONTAINERS, AND PREFORMS FOR MAKING THEM** **Polyester.** Concentrates on container structure. PEF listed as one of many material alternatives.

WO14032730A1	2014	EAUX MINERALES D EVIAN	**BOTTLE, METHOD OF MAKING THE SAME AND USE OF FDCA AND DIOL MONOMERS IN SUCH BOTTLE Polyester.** PEF bottle.
WO14032731A1	2014	EAUX MINERALES D EVIAN	**METHOD OF MAKING A BOTTLE MADE OF FDCA AND DIOL MONOMERS AND APPARATUS FOR IMPLEMENTING SUCH METHOD Polyester.** PEF bottle.
WO14054940A2	2014	STICHTING DUTCH POLYMER INST	**POLYMER, PROCESS FOR PRODUCING SUCH POLYMER AND COMPOSITION COMPRISING SUCH POLYMER Polyester.** Mainly concentrates on isosorbides and similar, FDCA listed as one of potential comonomers.

Appendix 1, Table 2. Relevant patents related to termoresponsive polymeric materials, utilizing furans in Diels-Alder chemistry.26 patents altogether.

Patent /application number	Publ. Year	Assignee	**Title, general topic**, and remarks
US4617348A, US4565852A	1986	DuPont, Ford	**Crosslinkable composition comprising modified aminoepoxy resins-II Thermoreversible stabilization.** Cured to network at elevated T.
US4656235A	1987	New York Polytech Inst.	**Siloxane-containing polyimide coatings for electronic devices Linear polymerization.** Aromatized.
US4657979A	1987	DuPont	**Blocked dieneophile functional modified aminoepoxy resins Thermoreversible stabilization.** Cured to network at elevated T.
US5643998A	1995	Toyota	**Recyclable polymer, process for producing the same, method for recovering the same, and method for regenerating the same Thermoreversible network**
US5641856A	1996	Shell	**Cross-linked resin Thermoreversible network.**
US5654368A	1996	Toyota	**Recyclable cross-linked polymer, method for producing a molded article, and method for recycling the same Thermoreversible network.** Thermoplastic elastomer.
US5844020A	1998	Xerox	**Phase change ink compositions Thermoreversible network.** Ink that is solid at RT but flows at elevated T.
US2002086952A	1999	Yokohama Rubber Co.	**ELASTOMER COMPOSITION Thermoreversible network.** Thermoplastic elastomer.
US6271335B	2001	Sandia Corp, US department of energy	**Method of making thermally removable polymeric encapsulants Thermoreversible network.** Thermally removable encapsulant for electric component protection.
US2004014933A	2004	UCLA	**Thermally re-mendable cross-linked polymers Self-healing.** Thermoreversible material prepared with non-linear polymerization.
US2004266954A	2004	Washington university	**Reversible crosslinking method for making an electro-optic polymer Thermoreversible network.** Some kind of crosslinkable non-linear optical polymer.
WO04076567A1	2004	TNO	**OW SOLVENT COATING PROCESS FOR APPLYING THE COATING TO AN OBJECT COATED OBJECT OBTAINABLE WITH THE PROCESS AND PROCESS FOR LEVELING A COATING APPLIED TO AN OBJECT Thermoreversible coating.**
US2005067373A	2005	Hitachi	**STABLE ENCAPSULANT FLUID CAPABLE OF UNDERGOING REVERSIBLE DIELS-ALDER POLYMERIZATION Themoreversible stabilization.** Reversibly networked polymer is formed upon heating.
US2006173125A	2006	Washington university, US Air Force	**NANOIMPRINT LITHOGRAPHY METHOD AND PRODUCT** Cladding material. Somehow conductivity affected by temperature.
US2009297609A	2008	Univ. Toronto	**METHOD OF BIOMOLECULE IMMOBILIZATION ON POLYMERS USING CLICK-TYPE CHEMISTRY** Biomolecule **encapsulation.** This example not thermoreversible

US2009318045A	2008	TNO	**FUNCTIONAL SURFACE FINISH AND METHOD OF ITS APPLICATION TO A MATERIAL SURFACE** **Thermoreversible functionalization.**
US2011190458A	2010	Univ. Groningen	**RE-MOULDABLE CROSS-LINKED RESIN, A COMPOSITION, A SUBSTITUTED FURAN, AND PROCESSES FOR PREPARING THE SAME** **Thermoreversible network.** Furfurylamine as starting compound.
JP2010265377A	2010	Nat.Inst.Adv.Ind.Sci. (Japan)	**THERMOREVERSIBLY REACTIVE POLYMER COMPOUND** **Thermoreversible network.** Lignin based networks.
US2013059988A	2011	Univ. Drexel, US Army	**REMENDABLE INTERFACES FOR POLYMER COMPOSITES** **Self-healing. Thermoreversible composite** interface.
US2013244179A	2012	University of Colorado	**NOVEL THERMOREVERSIBLE NETWORK SCAFFOLDS AND METHODS OF PREPARING SAME** Litography. **Thermoreversible network** is transferred to non-reversible with UV light.
US2012182693A	2012	IBM	**REVERSIBLY ADHESIVE THERMAL INTERFACE MATERIAL** **Thermoreversible adhesive.**
US2012261064A	2012	IBM	**THERMALLY REVERSIBLE CROSSLINKED POLYMER MODIFIED PARTICLES AND METHODS FOR MAKING THE SAME** **Thermoreversible adhesive.** Thermal interface layer between heat generating layer and sink layer. Thermally reversible adhesive that can be easily removed.
US2013137817A	2013	Hutchinson	**CURE-ON-DEMAND LIQUID SEALANT COMPOSITION, PROCESS FOR THE PREPARATION THEREOF AND USES THEREOF** **Thermoreversible stabilization.** Maleimide crosslinker is protected with furan
WO13135235A1	2013	AME Trade & Development	**PROCESS FOR PRODUCING AND USING A GEL SYSTEM FOR OILFIELD AND GASFIELD APPLICATIONS, SUCH AS FRACKING AND WELL CLEANING, AND GEL SYSTEM PRODUCED BY THIS PROCESS** **Thermoreversible viscosity.** Intended for oil&gas applications, fracking etc.
WO13164843A1	2013	Reliance Ind (India)	**THERMO-REVERSIBLE POLYBUTADIENE RUBBER BLEND WITH SELF-HEALING NATURE** **Thermoreversible network.** PIB
WO14025986A2	2014	Univ Akron	**NOVEL POLYISOBUTYLENE-BASED THERMOPLASTIC ELASTOMERS** **Thermoreversible network.** PIB end-capped with furan + multifunctional maleimide

Appendix 1, Table 3. Relevant patents related to 2,5-Bis(hydroxymethyl)furan (BHMF) polymers. 34 patents altogether.

Patent /application number	Publ. Year	Assignee	**Title, general topic**, and remarks
US4316935	1982	Celotex Corp.	**POLYISOCYANURATE FOAM AND LAMINATES THEREOF AND PROCESS FOR PRODUCING THEM .** **Polyisocyanurate**. BHMF as a component.
US4318999	1982	Quaker Oats Co., Penn Specialty Chemicals	**Low fire hazard rigid urethane insulation foam, polyol mixtures used in the manufacture thereof, and method for manufacture thereof.** **Polyurethane**. BHMF as a component.
US4426460	1984	Quaker Oats Co.	**Polyurethanes or isocyanurates from alkoxylated hydroxymethylfuran.** **Polyurethane**. BHMF based polyethers as polyols in polyurethane
US4973715	1988	Centre Scient Tech Batiment	**Furan polyols.** **Polyurethane**. Various furanic compounds claimed for polyol production, including BHMF.
DE19928927A1	2000	Univ. Rostock	**New polyurethanes containing 2,5-disubstituted furan rings, useful for preparing flexible foams with surface-bonded active agents for medicinal applications, especially as breast prostheses.** **Polyurethane/polyester**. Furan compounds used in polyester polyols for flexible foam preparation

JP2008303237A	2008	Univ. of Tokyo	**POLYMER COMPOUND PREPARED BY CROSSLINKING POLYESTER COMPOUND HAVING FURAN RING IN MAIN CHAIN WITH POLYVALENT MALEIMIDE . Polyester/crosslinked**. Maleimide crosslinking.
US2010062276	2009	Transfurans Chemicals	**METHOD FOR MODIFYING WOOD AND WOOD THEREBY OBTAINED Resin**. BHMF as one component in crosslinked resin.
WO11144608	2010	Kebony ASA	**PROCESS FOR POLYMER IMPREGNATING WOOD Resin**. BHMF one possible component in resin that can be used to impregnate wood.
DE102009045225	2011	Hüttenes Albertus	**Furfuryl alcohol-formaldehyde resin composition, useful e.g. as a component of casting binder system, comprises mixture of furan compounds, 2,5-bis(hydroxymethyl)furan, furfuryl alcohol, hydroxy compound, formaldehyde, and metal ion.**
WO13034305	2013	Nitto Denko Europe	**POLYCONDENSATE-BASED PRESSURE-SENSITIVE ADHESIVE CONTAINING FURAN MOIETIES Polyester**. Pressure sensitive adhesives. Claims both FDCA and BHMF, example only with FDCA.
JP2013095859	2013	Sekisui Chemical Co.	**FURFURYL ALCOHOL-FORMALDEHYDE COPOLYMER COMPOSITION AND METHOD FOR PRODUCING THE SAME Crosslinked resin**. Contains 10% BHMF.
US2014099848	2014	Univ Syracuse	**WATERBORNE SHAPE MEMORY POLYMER COATINGS Shape memory polymer**. BHMF incorporated to polymer chain, and can be crosslinked through diene/dienophile reaction.
US2014139591	2014	Xerox Corp.	**INK COMPOSITIONS INCORPORATING ESTER RESINS Small ester**. Crystalline phase-change agent in ink formulation. BHMF only one component in a list.

Series title and number

VTT Technology 326

Title	**From biomass to value-added furan-based platform chemicals** FURCHEM and CatBio roadmap
Author(s)	Leena Nurmi, Salla Jaatinen, Farhan Saleem, Martta Asikainen, Anna Kalliola, Eva-Lena Hult Mori, Reetta Karinen, Juha Lehtonen, Juha Linnekoski & Dmitry Murzin
Abstract	This is the roadmap "From biomass to value-added furan-based platform chemicals", generated together by FURCHEM and CatBio projects. Both of the projects are funded by Tekes, FURCHEM for time period of 1.1.2014–31.4.2016 and CatBio for time period 1.1.2014–31.12.2016. The purpose of this roadmap is to look for new potential value chains and business opportunities for the Finnish industry, based on furan biorefinery concepts. The first version (v. 1.0) could be considered to be an information package into furan compouds. Version 1.0 was generated shortly after the mid-point of the projects, and it contained a comprehensive description of the state-of-the-art of various furan-related topics. In addition, value chain schemes were generated into the roadmap, and the purpose was to further evaluate the proposed value chain schemes during the remaining project time. A new and final version (v. 2.0) of the roadmap is now generated at the end of the projects. In addition to the content in first roadmap version, this version contains recommendations on how implementation of furan-based value chains can be carried out in near and long-term future. These recommedations are partly based on company interviews and workshop events carried out during the projects. The purpose of both FURCHEM and CatBio projects is to generate general understanding on the potential of various furan-based biorefinery concepts. In addition, more focused technology development is being carried out in both projects. In FURCHEM project the technology development concentrates on the production of furan dicarboxylic acid (FDCA) from C6 sugars and sugar acids. In CatBio project the technology development concentrates on the production of furanic fuel components and succinic acid from furfural (originating from C5 sugars). In this final version of roadmap the results obtained in both projects are also presented.
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Julkaisun sarja ja numero

VTT Technology 326

Nimeke	**Biomassasta furaanipohjaisia platformikemikaaleja** FURCHEM- ja CatBio-projektien tiekartta
Tekijä(t)	Leena Nurmi, Salla Jaatinen, Farhan Saleem, Martta Asikainen, Anna Kalliola, Eva-Lena Hult Mori, Reetta Karinen, Juha Lehtonen, Juha Linnekoski & Dmitry Murzin
Tiivistelmä	Tämä on FURCHEM- ja CatBio-projekteissa työstetty tiekartta "Biomassasta furaanipohjaisia platformikemikaaleja". Tämä tiekartta valmistui yhteistyönä FURCHEM- ja CatBio-projekteissa. Molemmat projektit olivat Tekes-rahoitteisia strategisia avauksia (pieniä). FURCHEM-projektin kestoaika oli 1.1.2014–31.4.2016 ja CatBio-projektin 1.1.2014–31.12.2016. Tiekartan tarkoituksena on etsiä uusia arvoketjuja ja liiketoimintamahdollisuuksia suomalaiselle teollisuudelle lähtien furaanipohjaisista biojalostamokonsepteista. Tiekartan ensimmäinen versio valmistui projektien ollessa puolivälissä, ja se oli lähinnä informaatiopaketti furaaniyhdisteistä. Siitä löytyi kattava kuvaus furaanikemiasta. Tiekartan ensimmäisestä versiosta löytyi myös alustavat arvoketjut, joita on tarkasteltu tarkemmin projektien aikana. Tiekartta valmistui projektien jälkeen, ja se sisältää myös ehdotuksia siitä, miten furaanipohjaisia arvoketjuja tulisi rakentaa pitkällä ja keskipitkällä aikavälillä. Nämä näkemykset pohjautuvat projektien aikana yhdessä yritysten kanssa pidetyille seminaareille sekä yrityshaastatteluille. FURCHEM- ja CATBIO-projektien tavoitteena oli tuottaa yleistä tietämystä furaanipohjaisten komponenttien mahdollisuudesta luoda arvoa erilaisissa biojalostamoissa. Lisäksi kummassakin projektissa valittiin selkeä teknologian kehittämiskohde. FURCHEM-projektissa kehitettiin katalyyttistä menetelmää valmistaa furaanidikarboksyylihappoa (FDCA) C6-sokereista ja sokerihapoista. CATBIO-projektissa keskityttiin kehittämään teknologiaa furaanisten polttoainekomponenttien ja meripihkahapon valmistamiseksi furfuraalista (raaka-aineena C5-sokerit). Projekteissa saadut tulokset esitellään myös.
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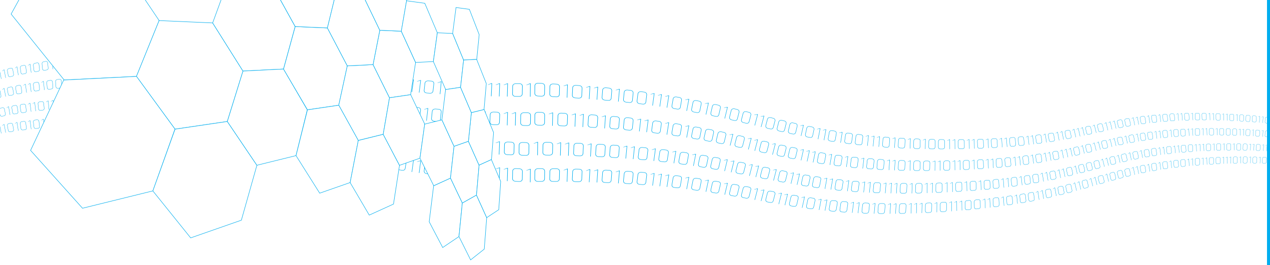

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