Overview of Biorefineries based on Co-Production of Furfural, Existing Concepts and Novel Developments

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Abstract

At Delft University of Technology theoretical and experimental research is carried out towards selective production of furfural from renewable biomass. Furfural is an interesting molecule that has been identified as a platform chemical for a multitude of chemical products and fuel (additives).

Acidic biomass hydrolysis and subsequent dehydration of the obtained C_5 sugar xylose leads to furfural. The reaction selectivity is a point of concern for reactor design, as furfural can further react to loss products. The residue of this process mainly consists of the remaining main biomass constituents, cellulose and lignin. Mineral matter is to a large extent extracted to the acid in the primary hydrolysis. This implies that the residue has the potential to be a better feedstock for thermo-chemical conversion, as e.g. alkali and chlorine species—now extracted—potentially cause different types of problems (slagging, fouling, agglomeration etc.).

An interesting option for example might be to convert this improved feedstock into synthesis gas via a gasification process, which then needs to be conditioned and upgraded for the production of green transportation fuels. In this line, a new biorefinery generation is created, which selectively uses the hemi-cellulose part of biomass. An analysis is presented towards current (integrated) concepts for novel,

improved furfural production process. This paper presents some current process concepts and a novel continuous process design.

INTRODUCTION – BIOREFINERIES, SOME CURRENT DEFINITIONS

The world faced an unprecedented high oil price in the first half of 2008 and subsequent fast price decrease related to the current financial crisis. No one can exactly predict its development. Whatever the short-term oil price development will become the reducing amount of available cheap fossil energy, conventional material sources and the need for sustainable, climate neutral production technologies have led to a renewed interest in the utilization of biomass. Biomass is indeed an abundant, renewable, and natural source, which is more evenly spread over the world in both terrestrial and aquatic environments than conventional fossil resources. Its annual global production is of the order of 170-200 billion tons.

The drivers for a biomass based economy are thus clean, sustainable environmental development, economic growth and green politics. In December 2008 the European Parliament approved a Directive which set mandatory targets on the EU-25 Member States in order to increase energy efficiency of 20% from present levels, cut greenhouse gas emissions of 20% compared to the 1990 levels and reach a 20% of renewable energy share of final consumption, within the year 2020 (EC 2008). Of course, biomass, a renewable rich natural energy and material source, is not new; man knows it from his beginning as a diverse source of food, feed and energy in the form of heat generation as well as light production and it is associated with meaningful labor.

This paper deals with biorefineries where furfural is an important (co-) product. A biorefinery is aimed at fractionation and further processing of biomass, which has a complex and to some extend variable composition, to generate versatile (organic) products and is in fact analogue to the petro-chemical refinery. The main constituents of biomass differ from crude oil, the feedstock of a petro-chemical refinery. They are oxygenated species: carbohydrates (cellulose, hemi-cellulose) and lignin. Often as minor compounds (generally <5% of the total as received mass) in biomass proteins, lipids/oils, terpenes, vitamins, dyes, flavors and minerals/salt are present (Kamm, Gruber et al. 2006). A very generic picture of the biorefinery concept is shown in Figure 1. A shift towards bio-based industry is already starting and means nothing less than a worldwide revolution in technology. Although biomass is known from before man's history, the term biorefinery is comparatively new and has come up only towards the end of the 20th century. However, such units in certain forms already have been among us since long times. It both refers to both a factory and a concept. The definitions given nowadays are dealt with in this part.

The American institute NREL (USA) defines the biorefinery as follows (NREL 2009): "A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass." At Iowa State University, active in applied research towards a wide variety of

biorefinery concepts, the following is stated about biorefineries: "A biorefinery is a cluster of biobased industries producing chemicals, fuels, power, products, and materials."
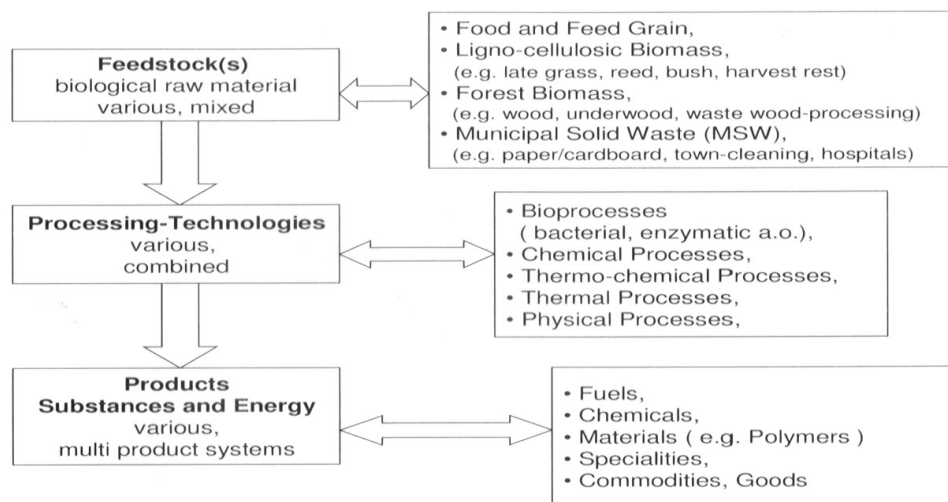

Figure 1. From feedstock to multiple products, adapted from Kamm et al. (Kamm, Gruber et al. 2006).

DOE summarizes its unique features as (EERE 2008): a biorefinery is an overall concept of a promising plant where biomass feed stocks are converted and extracted into a spectrum of valuable products." The National Non-Food Crops Centre in the UK uses a broad definition: "A biorefinery is a manufacturing site involved in the refining of biomass material to yield purified materials and molecules. This conversion can be achieved using biological or thermo-chemical processing or a mixture of both. Downstream manufacturing sites processing materials/molecules from biomass are often termed secondary biorefineries." (NNFCC 2007). In the definitions often two aspects are not considered to their full extend: food and feed co-production and the self supply of heat and electricity of the refinery. IEA has dedicated a separate task (nr. 42) since early 2007 on Biorefineries and has defined the entity clearly emphasizing the driving force from a broader context of sustainable development as (Van Ree and Annevelink 2007): "A biorefinery is the sustainable processing of biomass into a spectrum of marketable products and energy." In biorefinery development different stages can be discriminated, ranked into generations as has been done by Kamm & Kamm (Kamm and Kamm 2004). *Generation I* biorefineries are characterized by the lowest flexibility as feedstock type and products as well as resulting by-products are fixed. An example is the dry-milling ethanol plant using grain as feedstock. *Generation II* units are more flexible in the end products, for instance a wet

milling ethanol production plant can produce different products depending on demand, and they may include ethanol, starch, high fructose syrups, oils and meals. *Generation III* is the most flexible biorefinery, as it can process a multitude of feedstock to variable end products. A schematic of a generation III biorefinery is shown in Figure 2.

The successful further development of biorefineries is an exciting area of multi-discipline science integration. Knowledge of plant biology, chemistry, physics, geoscience, economics, logistics & infrastructure and engineering must be applied in this field.

FURFURAL – A PLATFORM CHEMICAL

Furfural has been identified as one of the key 'green' chemicals produced in the so-called 'ligno-cellulosic' feedstock biorefinery, as shown in Figure 2. Current uses are mainly for the production of furfurylalcohol (resin production), linking foundry sand, lubrication oil extraction, and a novel application is as a nematicide. For the future a role is foreseen in green fuel production, like the furfural derived compound MTHF (methyltetrahydrofuran) in the so-called P-series, developed in the USA (Kar and Deveci 2006). However, it is also considered as a platform chemical for the (near) future: a compound which is pinpointed as important chemical intermediate from biomass, not produced in major quantities in petroleum refineries. A study towards the identification of the most promising platform chemicals supported by US DOE revealed that furfural was ranked within the long list of 30 chemicals and two of the possible derivatives, furan dicarboxylic acid and levulinic acid, as top 10 building block (Werpy, Petersen et al. 2004); C_5 sugar related building blocks identified were xylitol and arabinitol. A good overview on furfural and derivatives is given by (Hoydonckx et al. 2008).

Furfural was discovered already in about 1821 by Johann Wolfgang Döbereiner, officially reported in 1832 (Dunlop and Peters 1953). In 1840 John Stenhouse, a Scottish chemist, discovered that furfural could be produced by distilling food crop materials like corn and oats using sulphuric acid. He also determined the chemical formula and in the early years of the 20th century the chemical structure was elucidated. Its name was derived from the Latin word "furfur" meaning bran, an early source of the product. Already from 1922 Quaker Oats Company started to produce furfural from oat hulls, based on a batch process using concentrated sulphuric acid. Nowadays, most of the furfural on the world market, about 280 kton/yr (Win 2005), is produced in China, representing more than half of the global capacity. This Chinese production capacity is characterized by widespread, inefficient (~50% of the theoretical furfural yield) small-scale fixed bed processes. Large-scale batch production plants are situated in the

Dominican Republic and South Africa. This means that there is a large potential for improvements that may make the process competitive with oil-based products. As described by Zeitsch (Zeitsch 2000), in the reactor the hemi-cellulose part of biomass is first hydrolyzed by a (light) acid catalyzed step to form xylose (reaction R1). Under more severe acidic conditions, xylose is instantaneously cyclo-dehydrated to furfural (reaction R2). Besides furfural, also small amounts of carboxylic acids, mainly acetic acid and formic acid, are produced. These are formed by the hydrolysis of formyl and acetyl side groups of the hemi-cellulose.

$$\left(C_5H_8O_4\right)_n + n\,H_2O \xrightarrow{\text{pH} < 3} n\,C_5H_{10}O_5 \qquad \text{(R1)}$$

$$C_5H_{10}O_5 \xrightarrow{\text{pH} < 1} C_5H_4O_2 + 3\,H_2O \qquad \text{(R2)}$$
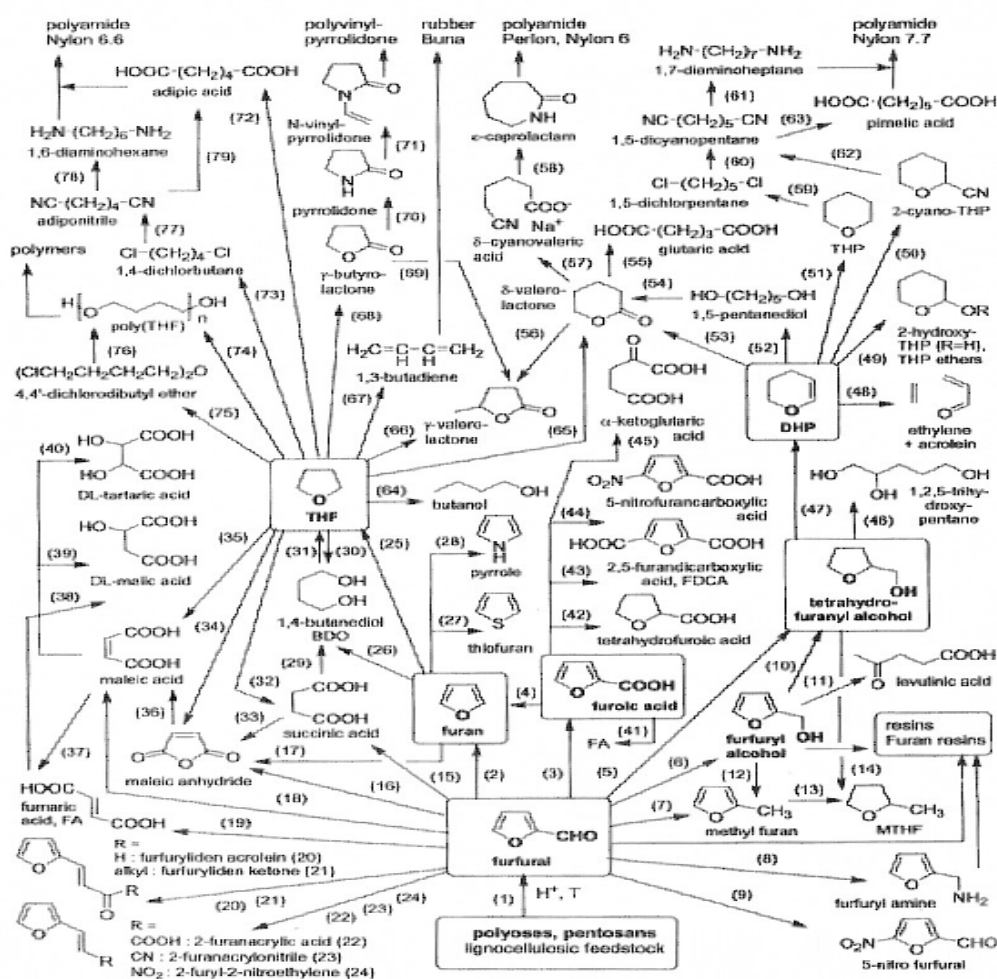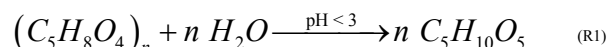

Figure 2. Chemical routes based on furfural.

The furfural formed can decompose into resins and formic acid in an acid medium. Resins are formed in two types of reaction: furfural reacting with intermediates in the xylose-to-furfural conversion, or furfural reacting with itself.

With O_2 present, furfural can be oxidized to some acidic products that are not specified yet. Acetic acid is derived from acetyl groups in hemi-cellulose at ~120 ^{o}C in acid medium. 5-methylfurfural (5-MF) is also detected in the furfural product stream in industrial production (Arnold and Buzzard 2003).

BIOREFINERY CONCEPTS FOR CO-PRODUCTION OF FURFURAL

Among all the pre-treatments (dilute) acid hydrolysis is found to be most effective and inexpensive so far (Mamman, Lee et al. 2008); so this paper concentrates on technologies comprising this pretreatment technology, with the exception of an excurs on organosolv which also ensures an acid pretreatment environment.

Biofine process

A recent refinery concept for biomass leading to furfural as an intermediate product in the production of levulinic acid is the Biofine process, which was already patented in 1990 (Fitzpatrick 1990). A schematic is shown in Figure 3 (adapted from Girisuta (Girisuta 2007)).
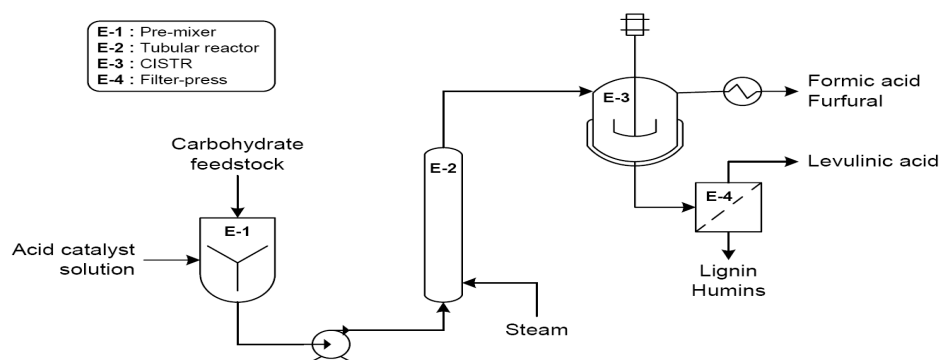

Figure 3. The Biofine process (Girisuta 2007).

It comprises two reactors in which diverse biomass types are processed via acid hydrolysis (1.5-3% dilute sulfuric acid, depending on the feedstock's alkalinity contribution). The first reactor downstream a pre-mixer is a short residence time, plug flow reactor where at 210-220 ^{o}C and 25 bar cellobiose is hydrolyzed using steam. The second reactor is a well-mixed reactor type with conditions favorite for Levulinic Acid formation, i.e. 190-200 ^{o}C, approximately

20 min. residence time and 14 bar pressure; here also previously formed furfural is converted, however it could be retrieved separately. Regarding the mass yield of furfural, based on the principle of the process a value of approximately 70% of the theoretical yield is given of the theoretical yield from C_5 sugars obtained from the biomass, which is about equal to 50% of the mass. The remainder is reported to be incorporated in the char produced (Hayes et al. 2006). LeCalorie S.p.A. in Caserta (Italy) is reported to operate the process on a 3 kton/year scale, processing tobacco plant residue and paper mill sludges (Ritter 2006) .

Vedernikovs process

At the Latvian State Institute of Wood Chemistry, a new process to enhance furfural production yields and minimize cellulose loss has been put forward as an alternative to the conventional dilute acid process (Gravitis, Vedernikov et al. 2001). The process applies small aliquots of strong acid catalysts and use of salts to ensure differential catalysis of hydrolysis and dehydration reactions. The process has been patented from about 10 years ago, covering different production aspects (Verdernikovs 1996; Vedernikovs 1998; Vedernikovs 1998).

A process schematic is depicted in Figure 4. This development in the hydrolysis process has solved two notorious problems: the furfural yield has increased from 55% to 75% of the theoretical value and the degree of cellulose degradation has been reduced fivefold. On the basis of fundamental studies, a new technology including two-step selective catalysis of wood and other pentosan-containing raw materials has been devised. This paper considers alternative routes of chemical processing of the cellulose residues into valuable monomers such as levoglucosan and ethanol as well as integration with other biomass treatment methods such as steam explosion.
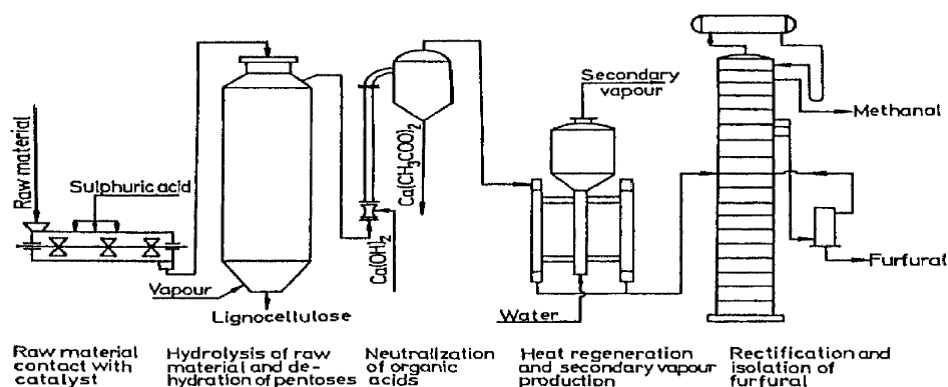

Figure 4. Furfural production process invented by Vedernikovs (Gravitis, Vedernikov et al. 2001).

CIMV process

CIMV has developed a continuous process for fractionation of biomass based on acid hydrolysis using organic acids (Delmas and Benjelloun-Mlayah 2008). Whitened paper pulp, sulfur—free linear lignin and xylose syrop are the main products. The last can be used to produce furfural. The first CIMV production plant which processes 180 kton of straw per year will start January 2010 in France and is accompanied with an investment cost of circa 130 MEuro. Figure 5 gives a schematic overview of the process.
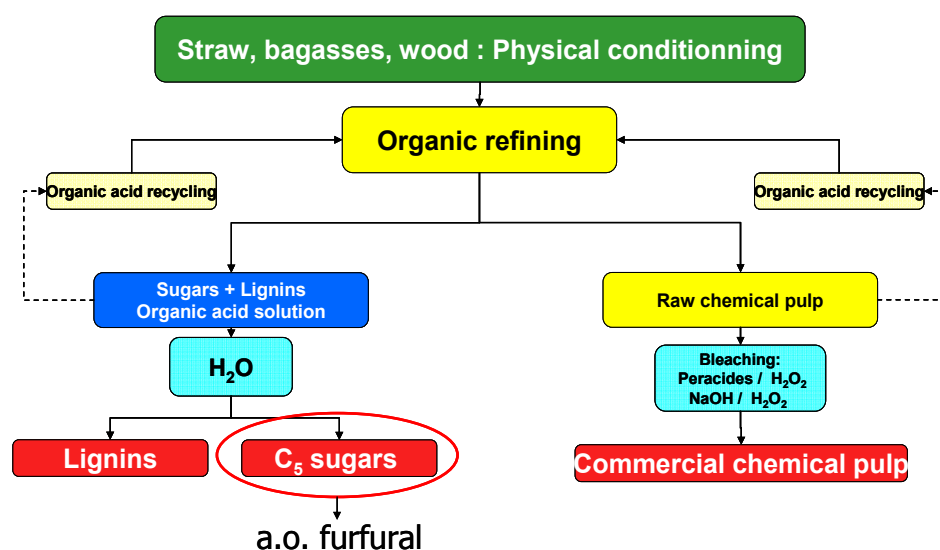

Figure 5. Fractionation principle of the CIMV process and pilot plant, adapted from Delmas et al. (Delmas 2006).

Lignol biorefinery technology

The company Lignol Innovations Corporation has developed a continuous biorefinery process employing an *organosolv* pretreatment step to separate lignin, hemi-cellulose, and extractives from the biomass matrix aimed at the production of ethanol with enzymatic cellulose hydrolysis with subsequent fermentation. The liquor obtained with the organosolv pretreatment is further worked up using well-established chemical engineering practices to produce furfural, xylose, acetic acid, lipophylic extractives and lignin, see Figure 6 (Arato 2002; Arato, Pye et al. 2005). The philosophy behind such a process scheme is that producing only

ethanol is not economically attractive, in particular for the scale of e.g. a typical sawmill (~100 ton/day dry wood).

Lignol Energy Corporation recently announced it has completed the first end-to-end production of cellulosic ethanol from its fully integrated industrial-scale biorefinery pilot plant in Burnaby, British Columbia (Lignol 2009). Several patents are related to this technology (Hallberg, O'Connor et al. 2008-2009).
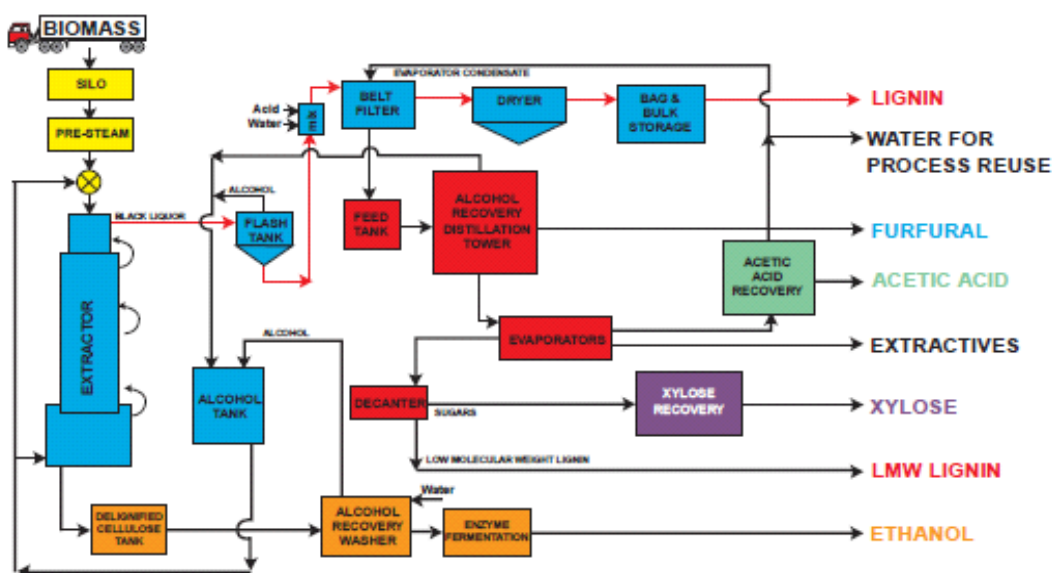

Figure 6. Process schematic, adapted from Arato (Arato 2002).

Suprayield[®] process

Another acid hydrolysis pretreatment based technology is the Suprayield[®] process, which has been patented recently (Zeitsch 2000) and is also described by Zeitsch (Zeitsch 2000) in his comprehensive book on furfural production. It offers an innovative concept where furfural, once formed, is quickly removed from the reacting, acid liquid phase.

This is realized via keeping the reaction medium boiling which often in industrial processes cannot be achieved with condensing stripping steam for the aqueous pentose solution which has an increased boiling point due to the dissolved components. Taking furfural away from the reaction medium is needed to prevent follow up reactions that cause a significant yield loss. SupraYield[®] claims higher yields (50-70 per cent furfural) than the traditional batch processes (O'Brien 2006). A schematic retrieved from the patent is shown in Figure 7.
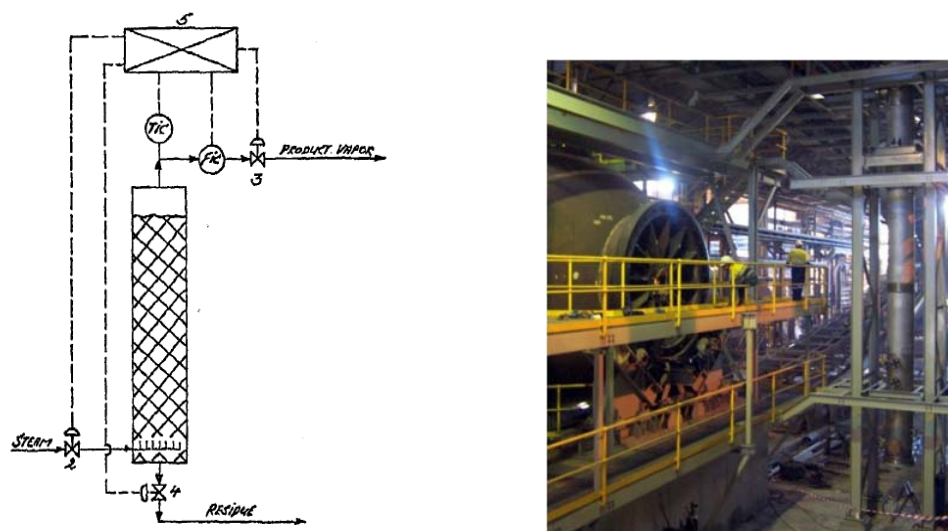
Figure 7. Acid hydrolysis reactor with Suprayield® technology (Zeitsch 2000) (left), picture of the plant at Proserpine sugar mill (Prosugar 2009).

The technology will be applied in a few novel plants. In Queensland (Australia) at the Proserpine sugar mill a unit has been built with support from the Australian Government for the biomass-based annual production of 5 kton furfural (Daff 2009); commissioning is expected to be carried out in the second half of 2009 (ABC 2009). Next to furfural, soil conditioner is reported to be produced. In India Arcoy Biorefinery Private Ltd. is also active in constructing a furfural plant (11 kton/yr) at Panoli, Ankleshwar (Gujarat Province) based on this novel acid hydrolysis technology (Prosugar 2009). The furfural produced is foreseen as feedstock for furfuryl alcohol production.

MTC process

A new process is developed at TU Delft for furfural, first aimed at a production capacity of approximately 10 kton/year, which is near 3% of the current market production capacity. Figure 10 shows a block scheme in which the main unit operations are shown. The reaction part is the biomass pretreatment and the hydrolysis reactor producing a gaseous raw furfural stream and a solid residue. The purification part (extraction with base added to aqueous phase and toluene is applied as organic phase; furthermore subsequent distillation section) is where

furfural is produced on-spec. Finally, filtration to obtain the cellulose-lignin solid fraction. Figure 11 shows the detailed P&ID of the process.

Straw is initially chosen as the feedstock, as it is available, relatively cheap and its hemi-cellulose content is comparatively high. During pretreatment straw must be milled and the air in the straw removed. The milling is necessary to improve the hydrodynamic behavior as a slurry during transport to the reactor and reaction. The air within the straw prevents the wetting with the acidic reaction liquid. Furthermore, straw containing air floats on the fluid. Oxygen in the liquid reacts with furfural causing a yield loss (Zeitsch 2000).

The solid concentration in the slurry is crucial as when this is too high, clogging of the equipments will result. In addition, the slurry density also influences the steam consumption in the reactor section, which is foreseen to be an important influencing factor in economical prospect. A straw/water mass ratio of approximately 1:10 entering the reactor is considered to be on the safe side.
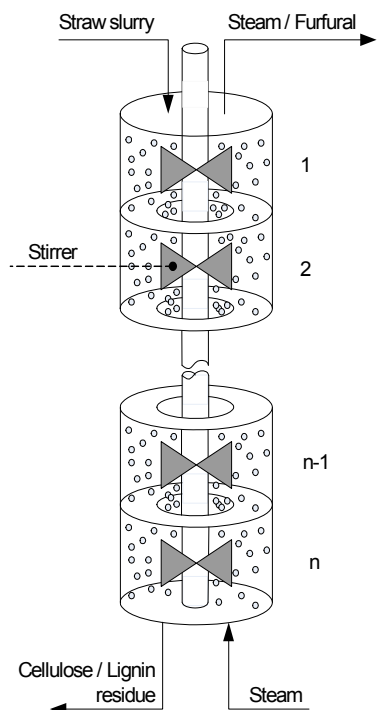

Figure 8. The MTC reactor.

In the proposed MTC process, furfural is produced in a novel reactor, a **M**ulti-**T**urbine-**C**olumn (MTC, see Figure 8). Acid hydrolysis of hemi-cellulose from straw to form xylose and further conversion to furfural occurs in this continuous reactor. It has a significantly higher potential yield due to continuous removal of furfural from the reacting mixture, less by-products and lower energy consumption compared to current prevailing batch processes.

The straw slurry enters the MTC from the top while steam rises up from the bottom. This creates the main advantage of this reactor that the produced furfural is directly removed by stripping from the liquid phase, preventing largely subsequent irreversible resinification and possible condensation reactions.

The vapor-liquid equilibrium behavior of water-furfural is such that an azeotrope is formed, also at higher pressures (Curtis and Hatt 1948). Figure 9 depicts this two phase behavior (Zeitsch 2000) for the part in which the vapor phase is enriched in furfural.
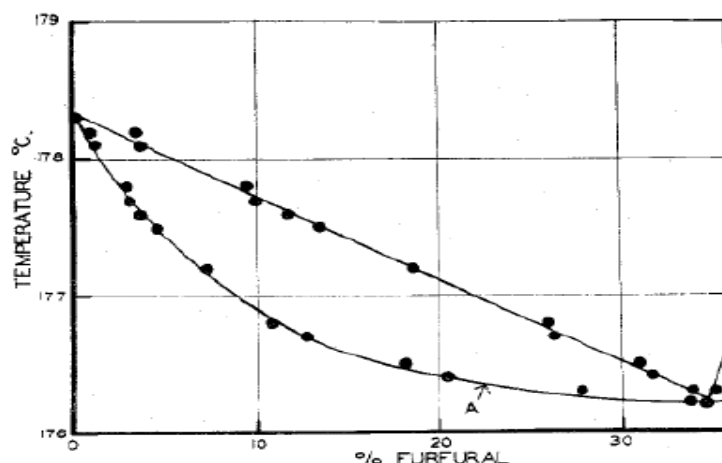
Figure 9. Vapor-liquid equilibrium of furfural/water system (mass percentages, 10 bar).

　　　　The fast removal of furfural from the liquid phase is essential in the prevention of any detrimental follow-up reactions that can take place in the liquid phase. Furfural leaves the reactor at the top in a vapor stream. Its concentration is kept low: the vapor stream consists primarily of water (steam), furfural and small amounts of 5-methyl furfural, acetic acid and formic acid. The distribution of the by products in vapor and liquid phase is determined by the vapor-liquid equilibria under the operation conditions.
　　　　Related to this phase equilibrium, a simple model for the reactor was made with the aim to calculate the steam to furfural ratio. The model simulates a tray column regarding each chamber as a stage. Modifications were made applying unequal mass distribution of furfural in each chamber. For instance, furfural is more concentrated on the top stage than in other stages. Overall furfural concentration in the liquid phase is very low, less than 2% mass based on the low solid content in the diluted straw slurry. Bottom concentration is 0.12 %mass. With a ratio of 4 between the mass fraction of furfural in the vapor phase and that in the liquid phase the tray model resulted in 12.5 ton steam consumption per ton of furfural produced with 10 stages (stirred cells) in the reactor. For details concerning the model, see (Ma 2006). HMF (hydroxyl methyl furfural) and resins are less likely to be produced. HMF will react very fast to formic acid and levulinic acid. Characteristics of the expected product are given in Table 1.
The kinetics of the conversion of hemi-cellulose into xylose sugar was obtained from work of Dunning and Lathrop (Dunning and Lathrop 1945) and Bryner et al.

(Bryner, Christensen et al. 1936), as quoted by Zeitsch (Zeitsch 2000), the expression for the dependence of the rate constant on temperature is:

$$k_0 = 7.832.10^4 * c[H^+] * \exp(-5163/T)$$

with

$C[H^+]$: *mol / liter, the initial hydrogen ion concentration at room temperature*

T : K, *temperature.*

k_0 : $\min^{-1}$ *rate const.*

Dunlop (Dunlop 1948) was the first researcher who studied the rate of furfural formation from pure xylose. His experiments were conducted at 160 °C using hydrochloric acid at two different concentrations: 0.05 mol/l and 0.1 mol/l. The rate constants measured were $9.7.10^{-3}$ (min^{-1}) and $18.9.10^{-3}$ (min^{-1}), respectively. Root et al. (Root, Saeman et al. 1959) published a more detailed study, which covered the measurements over a temperature range of 160 to 280 °C using sulfuric acid at the concentration ranged from 0.00625 to 0.8 mol/l. Based on Dunlop and Root's work, a correlation is derived and quoted by Zeitsch (Zeitsch 2000); Furfural destruction reaction kinetics was neglected for this study:

$$k_1 = 9.306.10^{15} * c[H^+] * \exp(-16894/T)$$

$C[H^+]$: *mol / liter, the initial hydrogen ion concentration at room temperature*

T : K, *temperature.*

k_1 : $\min^{-1}$ *rate const.*

For the MTC reactor plug flow behavior was assumed; a residence time of 24.6 min was calculated to realize a conversion of hemi-cellulose to furfural higher than 86%.

Table 1. Typical raw product and required furfural quality.

Component	Raw product stream [%wt]	Required Furfural product quality [%wt]
Water	91.68	< 0.20
Furfural	6.83	99.5
Acetic acid	1.38	20 [mEq/l]
Formic acid	0.06	
5 − MF (5-methyl furfural)	0.04	-
Residue	-	<0.50
TOTAL	100	100

In the purification section downstream the MTC (see Figure 10 and 11) furfural needs to be selectively removed from a very dilute stream in which small amounts of organic acids are present. The main component of this stream is saturated steam. There are different technologies to realize the separation necessary to obtain on-spec quality furfural. Today's processes use an azeotropic distillation to remove the bulk of the water (Zeitsch 2000). The high temperature in the presence of organic acids in the fluid will lead to loss of furfural. That is why the final distillation has been carried out under reduced pressure and temperature. Separations at about room temperature are preferable in view of the executive reactions of furfural. Extraction of furfural with toluene has been chosen as the step to separate the water bulk and most of the organic acids from furfural. Furfural is recovered from the toluene by a vacuum distilation as a side stream at 83°C.

An Aspen Plus^{TM} simulation shows that 5-methylfurfural can be separated from furfural as a bottom product. Furfural can be obtained at 99.9% purity. Toluene leaves the column over the top together with water and most of the organic acids. At a temperature of 83°C polymerization of furfural will hardly occur. For the future, a development is foreseen of selective absorption using **H**yper **B**ranched thoroughly **P**olymers as the first separation step. The advantages of these HBP's are that they hardly have a vapour pressure and they can be fine-tuned for this application. An HBP can theoretically be completely separated from its absorbed compound by use of e.g. a flash vessel.

The cellulose-lignin residue obtained by belt filtration with acid recycle can be processed via different ways or used as a product itself after neutralization (adsorbent, soil improvement). It could be (co-)fired to produce combined heat and power (CHP), which needs co-siting. Alternatively, after drying it could be gasified using e.g. steam/oxygen to produce synthesis gas with multi-product output possibilities. It is considered to be beyond the scope of this paper to extensively deal with the downstream processing options for this major solids stream. Table 3 presents the overall mass balance of the process.
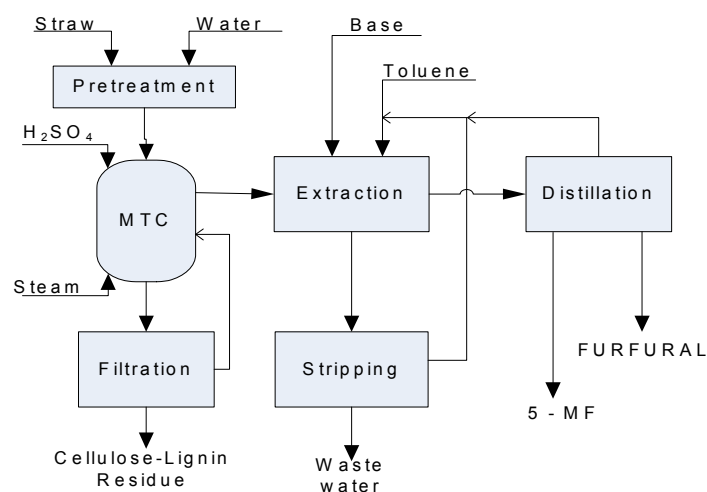
Figure 10. MTC process schematic.

Table 2. List of equipment in the P&ID.

|		
B01 Weighing belt	F01 Filter press	P12 Water pump
C01 Truck	F02 Filter press	P13 Toluene recycle pump
C02 Biomass Crusher	P01 Compressor pump	R01 MTC reactor
C03 Truck	P02 Pump	S01 Extractor
CH1 Chopper	P03 Vacuum pump	S02 Distillation column
E01 Heat Exchanger	P04 Reflux pump	S03 Stripper
E02 Condensor	P05 Furfural pump	T01 Slurry tank
E03 Condensor	P06 5-MF pump	T02 Neutralization tank
E04 Condensor of S2	P07 Wastes pump	T03 Neutralization tank
E05 Condensor	P08 Pump	T04 Reflux drum
E06 Reboiler of S2	P09 Sulphuric Acid pump	T05 Furfural storage tank
E07 Heat Exchanger	P10 Toluene make-up pump	T06 5-MF storage tank
E08 5-MF condensor	P11 Pump	V01,V02 valves
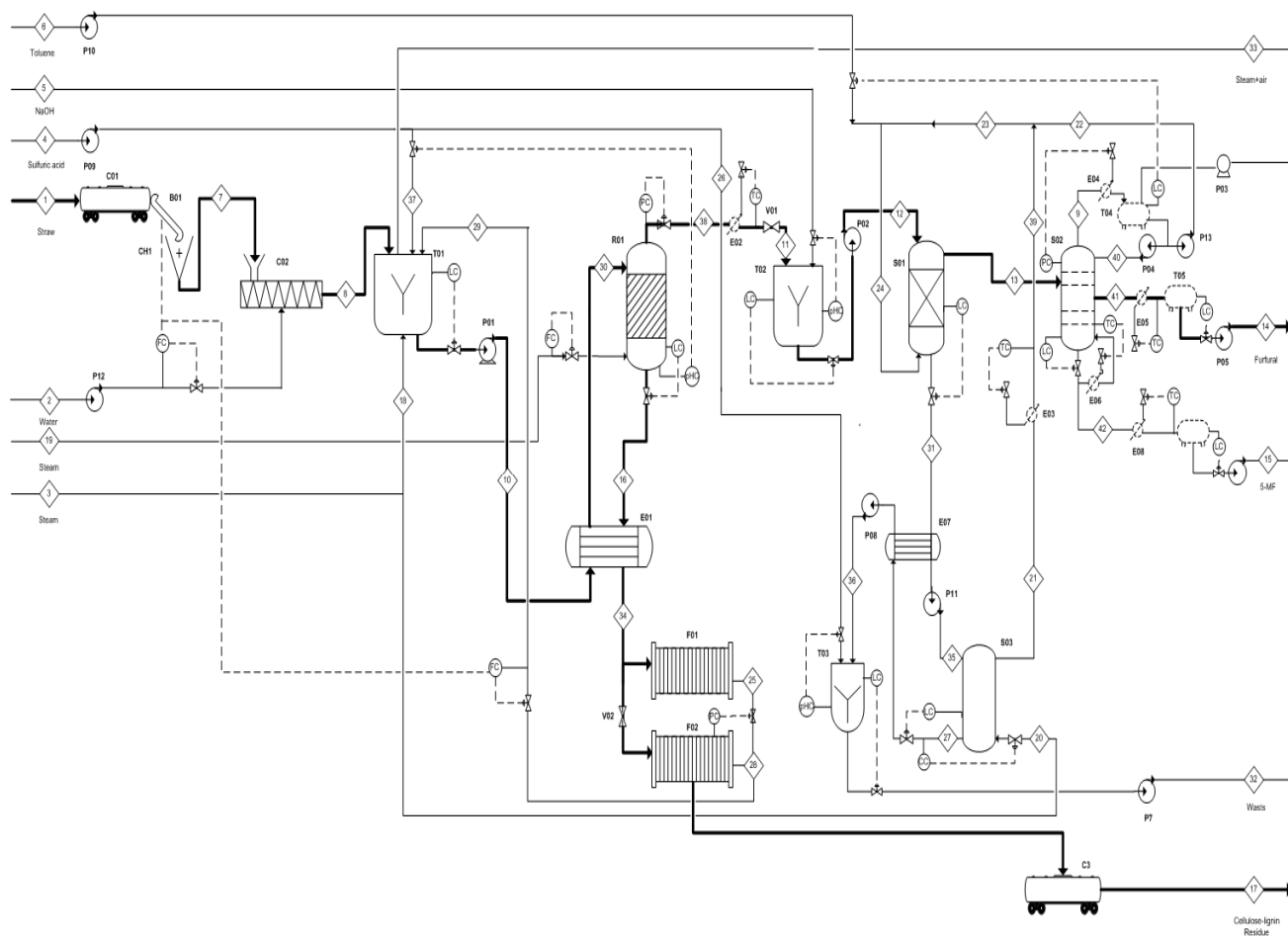
Figure 11. P&ID of the MTC process (Table 2 presents the equipment list).

Table 3. Mass Balance of the MTC process for approximately 10 kton/yr furfural production[+].

Mass flows in (stream nr.)	(kg/h)	Mass flows out (stream nr.)	(kg/h)
Straw (1)	8152	Furfural (14)	1243
Water (2)	4947	5-MF (15)	7
Steam (3)	138	Waste water (32)	11863
Sulphuric Acid (4)	68	Ligno-cellulosic residue	17282
Sodium Hydroxide (5)	317		
Steam (19)	16773		
TOTAL	30395		30395

[+] excluding small make up stream of toluene

Concerning the heat balance of the process, the most important added heat is that of steam to the MTC ($1,3.10^4$ kW) and the reboiler of the distillation column E06 ($4,2.10^3$ kW). The heat extracted from the system is by heat exchanger E02 ($1,3.10^4$ kW) cooling down the gaseous raw furfural stream; the balance is made by removal of heat in the cooler of the distillation column ($4,2.10^3$ kW). The heat of reaction in the MTC has been neglected due to the dilute system considered and also heats of mixing of solutions have been discarded.

The flowsheeting calculations form the basis of dimensioning equipment; the details of which have been described elsewhere (Ma 2006). The purchased investment cost estimation figures are presented in Figure 12, differentiated to the different types of equipment. Based on the purchased equipment costs of 3.8 MEuro, the total fixed capital investment has been calculated as 14.7 MEuro, following the approach applied in (Sinnott 2003).

Purchased equipment costs
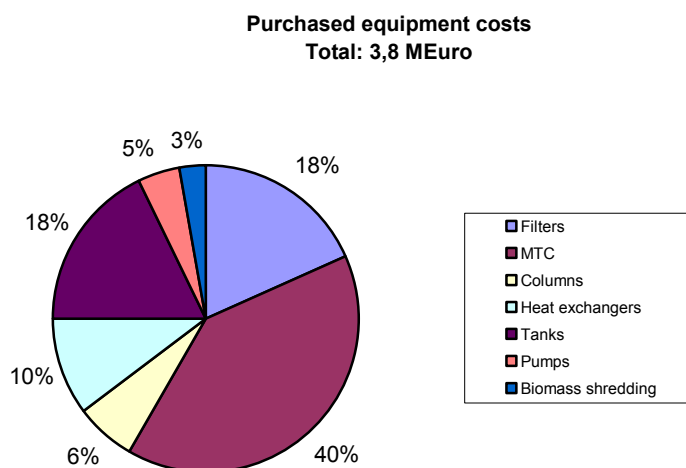**Total: 3,8 MEuro**

Figure 12. Purchased equipment cost estimation.

A simple economic analysis shows that the process has the potential to be further developed, depending on the economy of the processing of the cellulose-lignin residue. In case of a relatively conservative price of about 46 euro/ton for the residue, which corresponds to approximately 4,5 euro/GJ (as received fuel basis), an analysis has been made showing the influence of the furfural selling price and the biomass price on the economic margin and pay-out-time (POT) for a 10 kton/yr furfural production plant.

The economic margin is the money earned with sales of products minus the costs of consumables in the process. The POT has been defined as Investment in production installation (fixed capital investment and additional working capital) dived by the cash flow (taking into account a tax of 19%). Table 4 gives an example of the calculation of the economic margin.

Table 4. Example calculation of the expected economic margin.

| Raw material costs		kg/hr	ton/yr	€/ton	M€/yr
	Straw	8152	65217	40	2.61
	Sulphuric Acid	68	540	75.2	0.04
	Toluene	2	16	347.6	0.01
	Sodium hydroxide	318	2540	88.8	0.23
	water	4947	39579	0.2	0.01
	Total costs				**2.88**
Sales					
	5-MF	7	53	1000	0.05
	Furfural	1.243	9.944	750	7.46
	Residues	11.863	94.904	46	4.34
	Revenue				**11.85**
Utilities costs					
	10 bar (180°C) steam (for MTC)	16773	134184	11.02	1.48
	10 bar (180°C) steam (for distillation)	5652	45217	11.02	0.50
	1 bar (180°C) steam	138	1104	10.36	0.01
	cooling water	390665	3125322	0.02	0.07
	Electricity	1186[**]	9053760[*]	0.05[+]	0.45
	Total costs				**2.51**
Economic Margin					**6.46**

[**] kW; [*] kWh; [+] euro/kWh
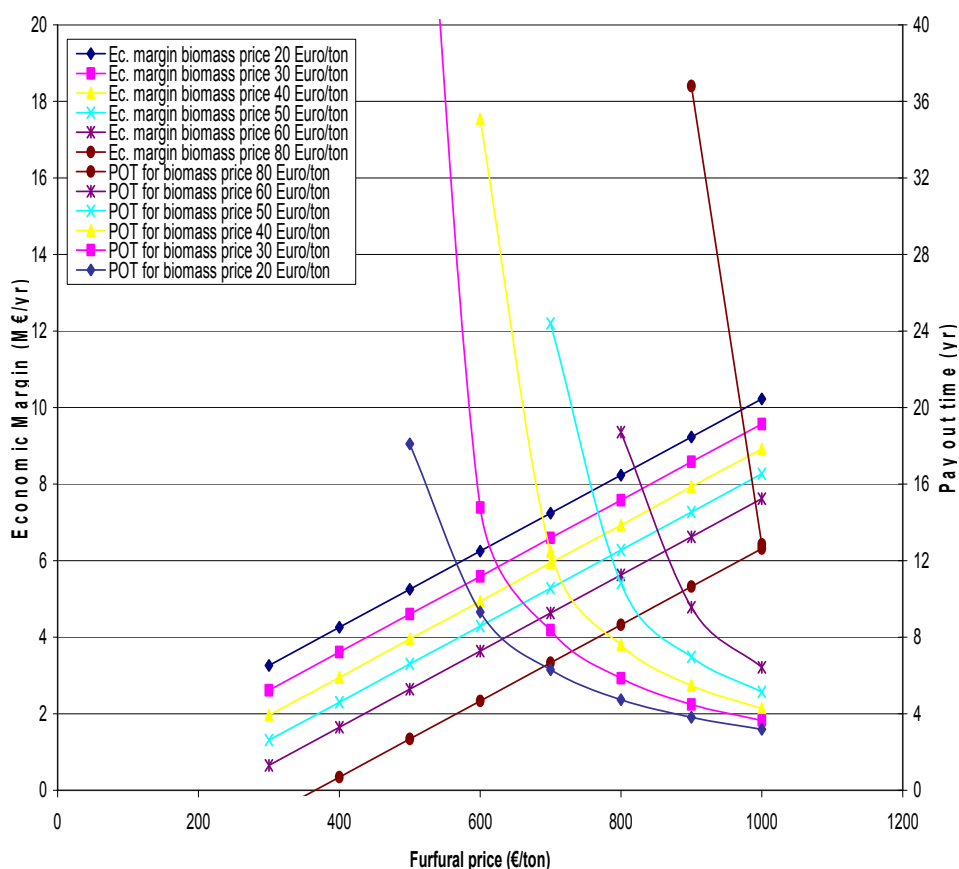
Figure 13. Simple economic analysis for the MTC process.

Without going into details of further economic analysis (taking into account the time value of money), it can be concluded that only with relatively low biomass prices of the order of 20 euro/ton (cheap residues, e.g. bagasse) and reasonable prices for furfural that are in range of nowadays values, the process can be reasonably attractive. However, further effort must be put in finding higher added value processes for the ligno-cellulosic residue in order to realize POT's of less than 3 years.

What would improve the economic performance is of course the scale-up of the process as investment costs scale less than linear. The authors have not done so, as with new technology one cannot expect immediate scale-up to huge values; a choice has been made for an approximate market entry at a few percent of the current world market, which seems most realistic.

As the literature concerning current furfural production processes is still very scarce, and in particular reliable economic figures are practically impossible to obtain, a comparison with the other mentioned process is not yet possible.

CONCLUSIONS & RECOMMENDATIONS

In this paper, a conceptual overview of some novel biorefineries with co-production of furfural has been given, with an emphasis on new developments. The emphasis was put on acid hydrolysis based production systems. Continuous processes based on dilute acid hydrolysis have as a major advantage over batch processes the scale-up possibility to large input capacities needed for expected large-scale applications of furfural and derived products. A large-scale process profits from economies of scale.

A comparatively simple economic analysis was made for a newly developed process concept based on continuous dilute acid hydrolysis of biomass. This concept appears to be promising at a scale of 10 kton/yr furfural production and prices of biomass input of about 20 Euro/ton, given furfural prices which are in the range of current market prices. The furfural prices, however, strongly fluctuate mostly depending on the supply side (Chinese production market). Improvements are realized in economic terms when use can be made of no to low cost residues as input and when the ligno-cellulosic residue of the hydrolysis/dehydration reaction step can be further valorized to high added value products with prices higher than 4,5 Euro/GJ. Critical techno-economic evaluations must be made for such integrated concepts.

For the near future, research is also needed concerning the basics of the process. Improved kinetics and thermodynamic phase behavior studies are needed to validate chemical reaction paths and gain enhanced basic knowledge concerning the integration of reaction and product separation to improve product yields significantly.

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