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Summary

A process has been developed for the production of 100 kton/yr levulinic acid with a purity of 98% from bagasse. Levulinic acid can be used as a platform chemical for the production of a wide range of value-added products. An amount of 1000 kton wet bagasse is needed as feedstock. The plant will be built in Brazil where the residue of sugar cane is abundantly available. The by-product of the process are furfural and formic acid. The amounts of these products are respectively 65 and 40 kton/yr both 98% pure. Furfural and formic acid with this purity can be sold at respectively

1 INTRODUCTION

The Bio-Fuels group from Shell Global Solutions is interested in producing biomass based fuels, fuel components and chemical building blocks. Levulinic acid might be such a component. The objective of this CPD-project is to design a plant for the production of 100 kton/yr levulinic acid (LA, 4-oxopentanoic acid, $C_5H_8O_3$) from bagasse. Another important product will then be furfural (2-furancarboxaldehyde, $C_5H_4O_2$). A purity of 98% is desired. Important boundary condition is that no or minimal energy should be imported into the plant. The approach of design should be as if the plant were on an island; e.g. all waste streams should be dealt with in situ. It should be assumed that the plant will be built close to a sugar factory, where bagasse will be sufficiently available.

Bagasse is the fibrous remaining after the extraction of juice from the crushed stalks of sugar cane. It consists mainly of cellulose, hemi-cellulose and lignin. Bagasse is in the chosen region (Sao Paulo, Brazil) only available for four months a year and will have to be stored in storage tanks. Incineration of bagasse can be used to generate energy. Compared to hemicellulose, cellulose has a well-ordered crystalline structure. Its hydrolysis requires strong acids, heat, and pressure. Hydrolysis will yield the formation of hydroxymethylfurfurole (HMF, 5-Hydroxymethyl-2-furancarboxaldehyde, $C_6H_6O_3$). Further hydrolysis will yield LA and formic acid.
Hydrolysis of the C5-sugars from hemi-cellulose will yield furfural (2-furancarboxaldehyde, $C_5H_4O_2$). The purity of furfural should also be 98%.

LA has never been produced on a large scale yet and therefore has the status as an expensive and relatively small market specialty chemical. Two processes have now been claimed to be feasible. The first process is developed by Biofine [1] and consists of a tubular reactor and a CSTR in series. LA is claimed to be recovered at 70% of the theoretical yield based on the hexose content of the carbohydrate material. The second process [15] is characterized by the use of a twin-screw extruder having a plurality of temperature zones where the reaction takes place. Both processes are patented. The process chosen is a combination of the two, where an extruder is used both as pump and as reactor and a second reactor is used to form the levulinic acid. Bagasse can be used without drying, thereby saving energy. The kinetics for the reaction steps are not well described in literature and should be derived from available process conditions.

Low cost LA can be used as a platform chemical for the production of a wide range of value-added products, such as the fuel additive methyltetrahydrofuran (MTHF). Derivatives are the key to marketability and markets for such LA derivatives as tetrahydrofuran, 1,4-butanediol, γ-butyrolactone, succinic acid, and diphenolic acid exist.
LA's worldwide market is about 500 tons per year at a price of €10-15/kg [2]. Full-scale commercial plants are feasible at 100 dry ton/day of feedstock. At this scale LA could be produced at €0.80/kg. Larger plants to convert 1000 dry ton/day of feedstock into LA at €0.13/kg allow economical production of fuel additives, since the diesel oil manufacturing costs are about €0.28/kg. The worldwide commercial market for LA and its derivatives could reach 500 Mton/yr.

2 PROCESS OPTIONS AND SELECTION

2.1 PROCESS CONCEPT CHOSEN

Process options

Levulinic acid is a major product of the controlled degradation of sugars by acid hydrolysis. Although levulinic acid has been known since the 1870's, it has never attained much commercial significance. One of the reasons for its slow development is the cost of the raw materials for synthesis. The direct use of cheap and abundantly available waste products cuts costs.
According to conventional methods of producing levulinic acid, carbohydrate material is digested with aqueous hydrochloric acid. By this procedure, an exceedingly troublesome amount of an insoluble resin product, known as humin, is formed which greatly complicates the problem of separating the resultant LA from the reaction mixture. [62] Also, the residues formed are insoluble in practically all of the conventional solvents [48] and, consequently, are very difficult to remove from the reactor [47]. Another reason is the low yields of levulinic acid obtained from most synthetic methods. Values from 22% [36], 35%[46] to 61% [53] are not atypical in literature. These low yields are largely due to the inherent physical properties of levulinic acid, which do not allow for its facile recovery. [48] Various methods have been proposed for recovering levulinic acid in a pure state. Generally the insoluble materials are first removed by filtration and then the levulinic acid is recovered in a more or less pure state from the filtrate by extraction with a solvent. Specific solvents employed in the prior art include diethyl ether, normal butyl alcohol and methylene chloride. Each of these solvents possesses disadvantages [48]. Furthermore, water forms an azeotrope with furfural and formic acid.

There have been a lot of processes described in the past to produce levulinic acid from cellulosic material. [50-52].
Relatively long reaction times (several hours [49,53] to 22-24 hours [16, 36, 46]), coupled with problems arising from the necessity of treatment of large volumes of corrosive and dilute solutions, have kept the known processes for manufacturing levulinic acid from becoming economically attractive. Under optimum conditions, these methods yield product solutions containing from about 1.0 to 2.0% levulinic acid. The requirement of large equipment, which should also be resistant to strong mineral acids, together with the high cost of evaporating (or extracting) and refining the dilute product solutions to recover the pure levulinic acid makes the process expensive.

The two most promising processes found in literature are:

Process 1, Process from the Corn Chem International Center:

- Continuous
- One reactor
- Twin screw extruder
- Plurality of temperature zones
- Yield ± 70%
- Temp. range: 120-150°C
- Process time 80-100 s
- Uses starch

The extrusion takes place in a twin-screw extruder having a plurality of temperature zones wherein the (starch) slurry is preconditioned, extruded, filter pressed, reboiled and vacuum distilled, before it is condensed and centrifuged, whereby the waste effluent from the centrifugation is reprocessed to the precondition stage. This process gives yields of about 48%, which is about 70% of the theoretical yield based on the hexose content of the carbohydrate material.

Process 2, Biofine process:

- Continuous
- Two reactors: PFR and CSTR
- Yield minimal 70%
- Temp. range: 205-220°C
- Process time: several minutes
- Uses all kinds off biomass

The material is continuously supplied to a tubular reactor and hydrolysed at approximately 220°C for several seconds in the presence of acid. The hereby-produced hydroxymethylfurfural is continuously removed from the first reactor and supplied to the second reactor, where it is further hydrolysed at approximately 205°C for several minutes to produce levulinic acid. The latter is continuously removed from the reactor. This levulinic acid is claimed to be produced in at least 70% of the theoretical yield based on the hexose content of the carbohydrate material.

Using a continuous two-stage reactor system in which the products are continuously collected provides an efficient use of equipment and space since large quantities of the sample can be run through a relatively small system and conditions in each stage of reaction can be precisely controlled. The lack of axial mixing in the tubular reactor ensures that a given portion of the sample does not spend too much time in that reactor.

The yield for both processes is approximately the same. The first process has only been described for the use of starch, the latter for the use of bagasse. By-products are expected to be the same for both processes.

In order to control the conversion of cellulose to HMF, and HMF to levulinic acid a two-stage reactor is preferred to minimize tar formation. The choice of reactors is made to prevent the formation of tar. This is formed (see chapter kinetics) by the oligomerisation

of 3 to 5 HMF molecules [40], or of HMF and furfural molecules. Both formations can be considered as 2nd order reactions, and low concentrations of HMF and Furfural prevent fast formation of tar. Also, C_6 sugars can, at longer residence times, form aromatics, which is the basis of tar formation. To prevent tar formation, a short residence time of possible tar 'formers' is necessary; hence a plug flow reactor is used with a short residence time. Another method to prevent tar formation is the insurance of low concentrations tar 'formers'. A longer residence is needed to form LA and furfural. In the CSTR it is possible to remove the formed furfural, making sure the furfural concentration is low.

This is the main reason a two-stage process like that of the Biofine-process is preferred. However since the bagasse, manifested as slurry, has to be transported by a pump to the PFR anyway, it would be easier to combine the pump and PFR into an extruder where the bagasse can react.
Therefore the process chosen is a combination of the processes or actually the second process with an extruder instead of a PFR (with pump).

Process Chosen, Combined process:

- Continuous
- Two reactors: Reactive Extruder and CSTR
- Yield minimal 70%
- Temp. range: 205-220°C
- Process time: several minutes
- Uses bagasse

3 BASIS OF DESIGN

3.1 BOUNDARY CONDITIONS

The plant will be approached as an 'island unit'. This means, there will be no energy resources from the outside, everything needed for the process must be inside the battery limits. The plant must be at least self-sufficient. The island approach has a few exceptions: possible produced electricity can be delivered to the net, this net also delivers the energy needed for the start up of the plant.

3.2 Continuous, batch, combination

The plant has to produce 100 kton LA per year. A factory producing less than 5×10^3 ton/year is usually batch-wise processed. An argument for choosing batch operation can be the demand for different grades or the difficultness of transporting the material. By using an extruder the process can be carried out continuously. Another option could be a process where the first part is processed batch-wise and the second continuously [57].

3.3 STOICHIOMETRY, CATALYST

The bagasse consists of lignocellulose, a combination of (hemi-)cellulose and lignin. Its composition, as it comes from a sugar mill is shown table 2.1 [9].

Table 2.1 Bagasse composition

Name	Mass fraction (%)
Cellulose	16-24
Hemi Cellulose	9-12
Lignin	12-16
Water	46-52
Sulphur	0.05-0.08
Potassium	0.37-0.48
Ash (mainly SiO_2)	3.8-4.2

Treatment at elevated temperature with acid will split the lignocellulose and hydrolyse the cellulose and hemicellulose to pentoses and hexoses respectively. Further treatment with acid makes the formation of HMF and furfural possible. HMF will react to LA. This is shown in figure 2.1

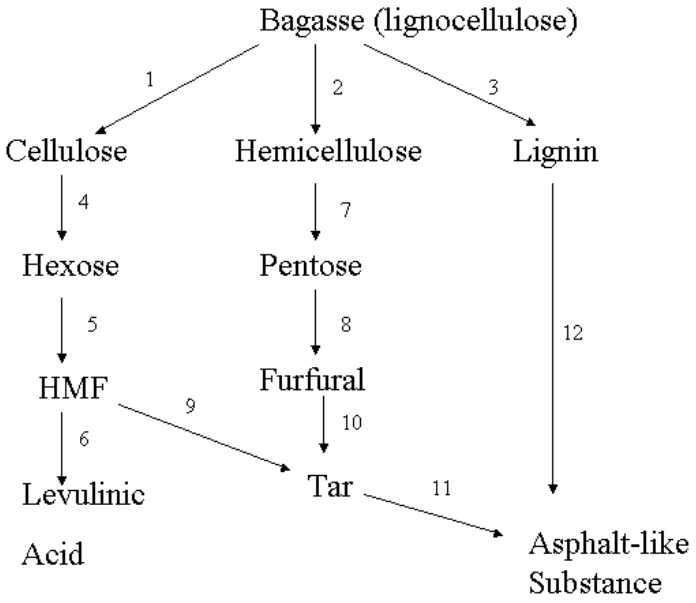

Figure 2.1 schematic reaction scheme of Levulinic acid

Step 1 to 3 is the split up from lignocellulose to its components. The overall reactions per step are shown below (number between brackets corresponds with the numbers in figure 2.1):

$(C_6H_{10}O_5)_n$ (s) + n H_2O (g) → n $C_6H_{12}O_6$ (l) (4)

$C_6H_{12}O_6$ (l) → $C_5H_8O_3$ (l) + CO_2H_2 (g) + 3 H_2O (g) (5/6)

The mechanism for these steps is shown in appendix 2 and 3 [25].

$(C_5H_8O_4)$n (s) + H_2O (g) → n $C_5H_{10}O_5$ (l) (7)

$C_5H_{10}O_5$ (l) → $C_5H_4O_2$ (g) + 3 H_2O (g) (8)

The mechanism for step 8 [25] is shown in appendix 1.

Too long heating of the mixture will cause tar formation (steps 9, 10). This will form an asphaltic-like substance with the lignin (steps 11, 12).

The catalyst chosen is sulphuric acid. Several mineral acids are tested in the literature, like HBr and HCl and H_2SO_4. The efficiency of these acids is as follows: HBr>HCl>H_2SO_4 [40]. But the double bonds in several products will cause the formation of halogenated hydrocarbons, which are damaging to the environment. Organic acids were less efficient. A recycle of formic acid may reduce the amount of sulphuric acid needed.

3.4 REACTION KINETICS

LA formation

Neglecting the formation of intermediates, the formation of LA can be described as (see also figure 2.1)

$$\text{Cellulose} \xrightarrow{k_{glu}} \text{Glucose} \xrightarrow{k_{HMF}} \text{HMF} \xrightarrow{k_{LA}} \text{LA}$$

Each of these reactions can be considered as a 'pseudo' first order reaction [66, 67, 68]. The rate constants of these reactions are dependant on temperature and acid concentration according to equation 2.1 [22, 66,67,68]:

$$k_i = k_0 \exp(-E_A / RT) \tag{2.1}$$

$$k_0 = k_0' A^n = k_0' \cdot 10^{n \cdot -pH} \tag{2.1a}$$

or

$$k_0 = k_0'' \cdot 10^{-pH} \tag{2.1b}$$

Equation 2.1a is used in reference [22], where A is the acid concentration. This equation is used in the cellulose hydrolysis. Equation 2.1b is used in references [66-68]. This is used in the second and third reaction, the HMF formation and the LA formation respectively.

The rate constant of first reaction is surprisingly not very dependant on the kind of lignocellulose used [22]. Because there is not enough information about bagasse, average values of E_A, k_0' and n are taken from this reference. These values are compared with the results in the examples from references [18] and [4]. The comparisons are shown in appendix 5. The rate constant is than calculated with equation 2.2.

$$k_{glu} = 1.25 \cdot 10^{19} \cdot 10^{-1.2 \cdot pH} \cdot \exp(-170{,}000 / RT) \tag{2.2}$$

References [22, 66] give values for E_A, k_0''. These are also compared with the examples in the US patents [4, 18]. The rate constant for the HMF formation can now be calculated with equation 2.3 [66].

$$k_{HMF} = \left[4.9 \cdot 10^{11} + 1.5 \cdot 10^{13} \cdot (10^{-pH}) + 4.7 \cdot 10^{22} \cdot (10^{pH-14}\right] \exp(-121{,}000 / RT) \tag{2.3}$$

The rate constant for the LA formation can be calculated with equation 2.4 [66].

$$k_{LA} = \left[1300 + 4.1 \cdot 10^{6} \cdot (10^{-pH})\right] \exp(-55{,}900 / RT) \tag{2.4}$$

Furfural formation

Neglecting the formation of intermediates, the formation of furfural can be described as (see also figure 2.1):

$$\text{Hemicellulose} \xrightarrow{k_{xyl}} \text{Xylose} \xrightarrow{k_{Fur}} \text{Furfural}$$

These reactions can also be considered as 'pseudo' first order reactions, with the same kind of dependency of the rate constants on temperature and pH as for the LA formation. Assumed is an approximately same rate constant of the hydrolysis of hemi cellulose. This assumption is made because of the lack literature references. The examples given in reference [4], seem to confirm this (also see appendix 5).

Xylose decomposition to furfural has an activation energy of 121 kJ/mol and a $\ln(k_{0,xyl})$ of 29.2 [69]. Unfortunately no acid concentration was given. In reference [43] a dependency on the pH is given, unfortunately no temperature was given. Appendix 5 shows the calculation of this rate constant, given in equation 2.5.

$$k_{fur} = 0.00102 \cdot 10^{-pH} \tag{2.5}$$

Tar formation

From furfural and HMF tar can be formed. According to ref [22] only small amounts of tar formed during the reaction of HMF to LA, accounting for only up to 7% of the initial carbon content. This tar has a molecular weight of about 500 g/mol.

The tar is formed by ketalformation of HMF and furfural. The aldehyde group of the HMF can react with the alcohol group of other molecules, in the presence of an acid. The mechanism is given in Appendix [7].The tar formation can be considered as a 'pseudo' second order reaction. The rate constant is heavily dependant on the temperature [22]. The reactionrate can be described as:

$$r_{tar} = k_{tar}[HMF] \cdot \{[HMF] + [furfural]\} \tag{2.6}$$

The dependency of k_{tar} on the temperature and the pH is yet unknown.

3.5 FORMATION OF SIDE PRODUCTS

During the production of LA, furfural and formic acid, several by products can be formed. The following byproducts are assumed to be formed.

1. HMF → furfuralalcohol + CO
2. HMF → Furan + CO_2 + methanal
3. HMF + 2 H_2O → 2-hydroxy pentoic acid + CO_2

These components represent all possible formed by products.

3.6 PLANT CAPACITY

The plant will run for 8000 hours per year, the average running time for a continuously streaming plant [57]. The plant must produce 100 kton/annum LA, according to the process description. The total lifespan of the plant will be 12 years [58]. This is below the average life span of a chemical plant. This value is taken because the plant is the first of its kind.

Feedstocks:

Bagasse

Bagasse is obtained after processing sugar cane in a sugar mill. Sugarcane is harvested 4 months a year. The sugar mill will process the sugarcane these 4 months, therefore the bagasse will be supplied during these months. A storage tank of bagasse will be needed or other solutions (e.g. subsidized harvesting of sugar cane, which ensures a prolonged availability of bagasse) are needed. The sugar mill uses the bagasse for heat and electricity generation with an efficiency of 35% [64]. The calorific value of dry bagasse is about 18500kJ/kg. In Brazil sugar mill owners receive $ 8/MWh delivered to the electricity net. This gives an approximate value of bagasse of € 15/ton.

High Pressure steam

High-pressure steam is used to maintain the temperature in the reactor at an elevated level. The asphalt is gasified for steam generation.

Sulphuric acid

Sulphuric acid (98%) is used in the process as a catalyst to hydrolyse the cellulose and hemi-cellulose, and as a catalyst for the LA and furfural formation. Sulphuric acid is separated and recycled to first reactor. A make-up stream is added to compensate for the loss of acid.

Product:

Levulinic acid

Levulinic acid is the main product of this process. The acid will be transformed to a fuel additive. The value of diesel is approximately US$ 250/ton. This will be the maximum value of LA, when it will not be subsidized.

By-Products:

Furfural

The hemi-cellulose in bagasse is converted to furfural. Furfural can be used as a solvent or in the manufacture of pesticides, phenol furfural resins, and tetrahydrofuran. Furfural is a valuable side product. The purity of commercial Furfural is 98 %.

Formic acid

Formic acid and levulinic acid are produced from HMF in equimolar quantities. Formic acid is used primarily in dyeing, in the textile and leather industries; in rubber production; and as an intermediate in the chemical and pharmaceutical industries.
This acid can possibly be used as organic catalyst in the process, decreasing the amount of sulphuric acid needed. This will be sought out in a later stadium. In the margin calculation is assumed that all the formic acid will be sold, with a purity of 98% (commercial value).

Waste:

Lignin

The lignin in the bagasse forms with the tar, an asphaltic waste product. The asphalt can be burned to generate HP steam

3.7 BASIC ASUMPTIONS

3.7.1 LOCATION

The plant will be constructed in Brazil, in the Sao Paulo region close to a sugar mill plant for the following reasons.

1. Brazil is the world largest producer of bagasse. The sugar mills in Brazil in the Sao Paulo region produce enough bagasse (averagely 1,25 Mton) to assure a 100 kton production of levulinic acid.
2. There is a good infrastructure in the Sao Paulo region.
3. Plenty of water (used as process water) is available.

3.7.2 BATTERY LIMIT

Equipment inside battery limit

1. Reactive extruder for decomposing bagasse into HMF and furfural.
2. CSTR for converting HMF into levulinic acid and formic acid
3. Separator for separating furfural from formic acid and water
4. Filtration unit for filtering the tar
5. Acid catalyst separator for recovering sulphuric acid
6. Separator for separating formic acid and water
7. Bagasse storage tank
8. Sulphuric acid storage tank
9. Product storage facilities
10. Lignin combustion for steam generation
11. Heat integration equipment

Facilities outside battery limit

1. Electricity net (mains supply)

3.8 DEFINITION OF STREAMS PASSING THE BATTERY LIMITS

To define the streams typical yields are used (ref. 3,4,5,50-55). These yields are given in table 3.1.

Table 3.1 Yield in Levulinic acid process

Yield (kg/kg)	Theoretical maximum	Obtainable	Theoretical max◦obtainable
LA on hexose	0.64	0.70	0.45
Furfural on pentose	0.64	0.80	0.51
Celluse.hemicellulose and lignin etc on lignocellulose	1.00	1.00	1.00

The outgoing streams are calculated with a product stream of 100 kton LA per annum and the given yields (also see the block scheme).
The stream definitions are given in the tables below.

Table 3.2 Stream definitions

Streams in	t/a	Streams out	t/a	Catalyst	t/a
Bagasse	991000	Levulinic acid	100,000		
Lime	445	Furfural	65,000	sulfuric acid	600
		Asphalt	241,000		
		Water	460,000		
		Formic acid	40,000		
		Gypsum	6,600		

Table 3.3 Feed streams

Stream Name :		**Bagasse**				
Comp.	Units	Specification		Notes		Additional Information (also ref. note numbers)
		Available	Design			
Cellulose	%wt	16-24	21.5	(1)	(1)	avarage value of cellulose,
Hemicellulose	%wt	9-12	12.0	(1)		hemi-cellulose and lignin
Lignin	%wt	12-16	16.0	(1)	(2)	no influence on process
Sulphur	%wt	0.05-0.08	0.1	(2)	(3)	Bagasse is diluted with water in
Potassium	%wt	0.37-0.48	0.4	(2)		sugar mill
Water	%wt	46-52	48.0	(3)		
ash	%wt	1.8-2.2	2.0	(4)		
					(4)	ash consists of SiO2
Total			100.0			
Process Conditions and Price						
Temp.	°C		25			
Press.	Bara		1			
Phase	V/L/S		S/L		(5)	Explained in the paragraph
Price	€/ton		15	(5)		feedstock'

Table 3.4: Stream 9, Levulinic acid

Stream Name		**Levulinic Acid**			
Comp.	Units	Specification	Notes		Additional Information (also ref. note numbers)
		Design			
Levulinic Acid	%mol	98.0	(1)	(1)	Commercial LA is 98% pure
water	%mol	1.0			
2-hydroxy pen.	%mol	1.0			
total		100.0			
Process conditions and price					
Temp.	°C	40			
Press.	Bara	1			
Phase	V/L/S	L		(3)	Value of diesel ($ 250/ton, with a
Price	€/ton	280.9	(3)		value of $ 25/barrel)

Table 3.5: Stream 6, Furfural

Stream Name		**Furfural**			
Comp.	Units	Specification Design	Notes		Additional Information (also ref. note numbers)
Furfural	%mol	97.5	(1)	(1)	Commercial Furfural is 98% pure
Furan	%mol	0.4	(2)		
Water	%mol	0.4			
Methanal	%mol	0.4			
CO	%mol	0.9			
CO2	%mol	0.4			
total		100.0			
Process conditions and price					
Temp.	°C	25			
Press.	Bara	1			
Phase	V/L/S	L			
Price	€/ton	791.96	(3)	(3)	ref. 44

Table 3.6. Water

Stream Name		**Water**			
Comp.	Units	Specification Design	Notes		Additional Information (also ref. note numbers)
Water	%mol	99.9			
formic acid	%mol	0.02			
furfural	%mol	0.05			
furfuralalcohol	%mol	0.01			
methanal		trace			
CO2		trace			
CO		trace			
total		100			
Process conditions and price					
Temp.	°C	25	(2)	(2)	When used to preheat feed, the temperature may change
Press.	Bara	1			
Phase	V/L/S	L			
Price	€/ton	1.187	(3)	(3)	wastewater value

Table 3.7: Formic acid

Formic acid					
Comp.	Units	Specification Design	Notes		Additional Information (also ref. note numbers)
Formic acid	%wt	98	(1)	(1)	industrial formic acid is 98 % pure
water	%wt	2			
total		100			
Process conditions and price					
Temp.	°C	25			
Press.	Bara	1			
Phase	V/L/S	L			
Price	€/ton	525	(3)	(3)	[61]

Table 3.8 Catalyst

Catalyst Name		Sulfuric Acid			
Comp.	Units	Specification Available	Design	Notes	Additional Information (also ref. note numbers)
Sulfuric acid	%wt	95-97	95	(1)	(1) Other products in commercial sulfuric acid are negligible
Water	%wt	2-5	5	(1)	(2) Ref 55, gives world trade value of sulfuric acid
total			100		
Process conditions and price					
Temp.	°C		195-230		
Press.	Bara		16-32		
Phase	V/L/S		L		
Price	€/ton		58.43	(2)	

4 THERMODYNAMIC PROPERTIES

In this chapter T-x-y and P-T diagrams and heat capacity and enthalpy values for the pure components will be shown. These graphs are derived from the Aspen^{+} database. The heat capacities and enthalpies are used to calculate reaction heats. From the T-x-y diagrams it can be seen how easy/difficult it is to separate specific components e.g. if there is an azeotrope there could be problems with the separation. P-T diagrams of pure components show the state (V/L) the component is in at given pressure and temperature.
The Peng-Robinson model is used to calculate vapour/liquid equilibria for furfural and formic acid since this model is valid for systems containing hydrocarbons at high/moderate pressure and temperature conditions [59]. Wilson-Hayden O'Connell is used to calculate vapour/liquid equilibria for the other components because it gives good results according to literature [79]. The following graphs are T-x-y plots at 16 bars.

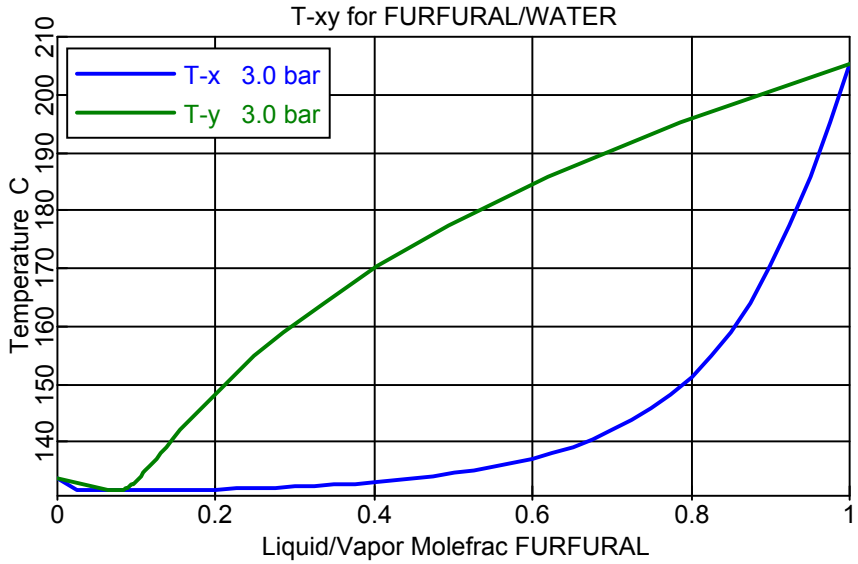

Figure 4.1: T-x-y diagram for furfural and water at 3 bar.

Thermodynamic model used: Wilson – Hayden O'Connell

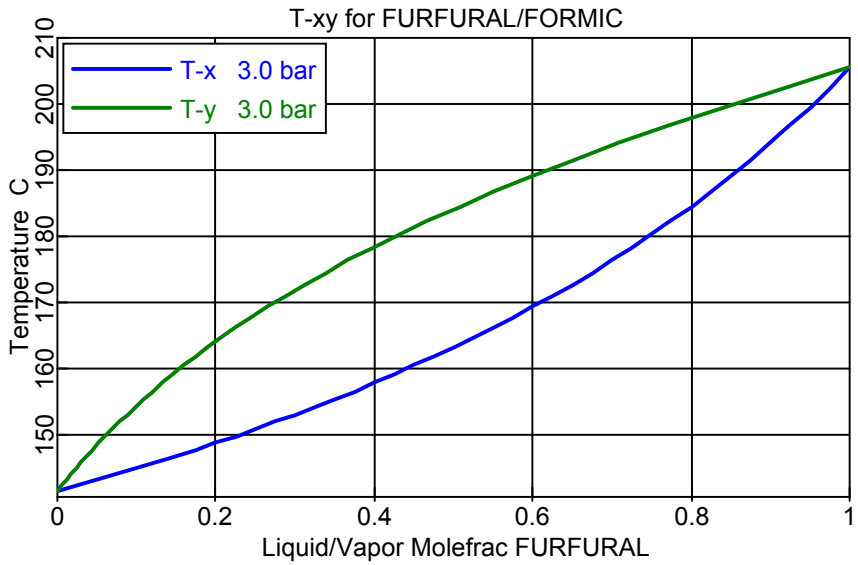

Figure 4.2: T-x-y diagram for furfural and formic acid at 3 bar.

Thermodynamic model used: Peng – Robinson.

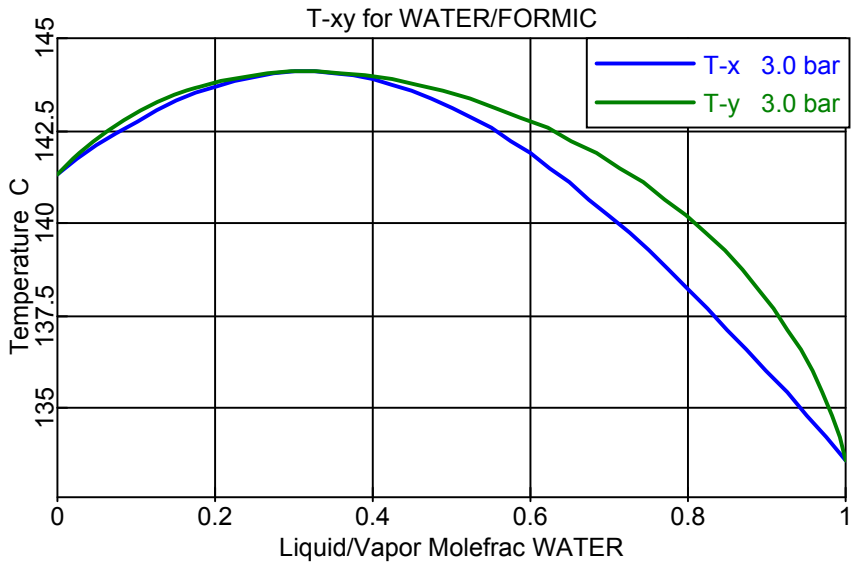

Figure 4.3: T-x-y diagram for water and formic acid at 3 bar.

Thermodynamic model used: Wilson – Hayden O'Connell

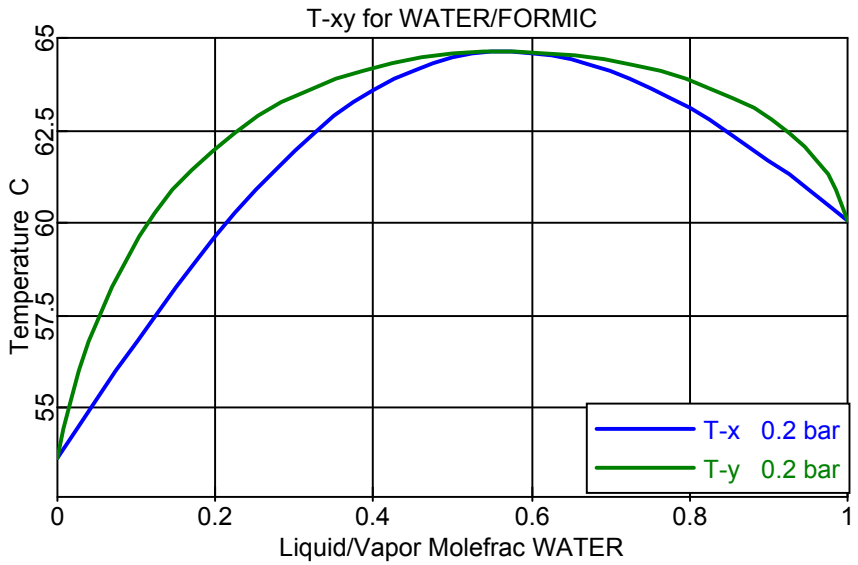

Figure 4.4: T-x-y diagram for water and formic acid at 0.2 bar.

Thermodynamic model used: Wilson – Hayden O'Connell

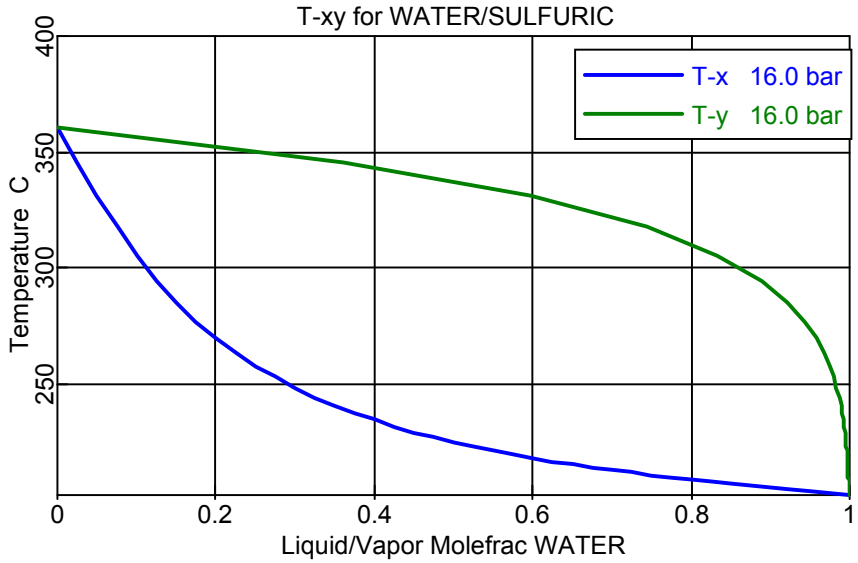

Figure 4.5: T-x-y diagram for water and sulfuric acid at 16 bar.

Thermodynamic model used: Wilson – Hayden O'Connell

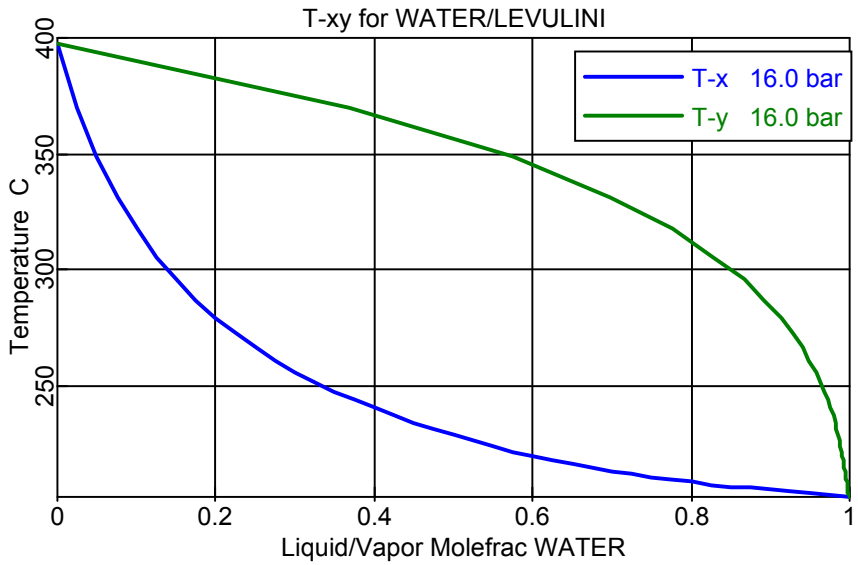

Figure 4.6: T-x-y diagram for water and levulinic acid at 16 bar.

Thermodynamic model used: Wilson – Hayden O'Connell

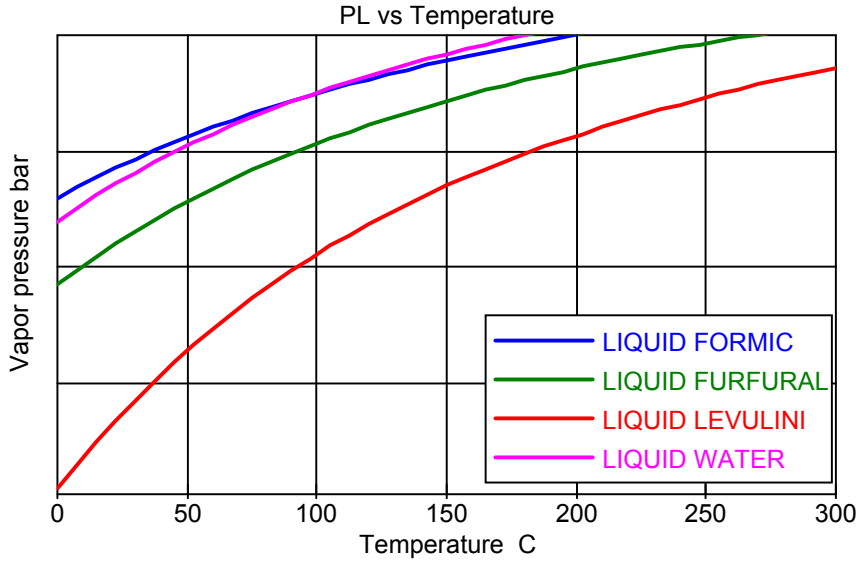

Figure 4.7: Vapor pressure diagram for formic acid, furfural, levulinic acid and water at 16 bar.

4.1 PURE COMPONENT PROPERTIES

PURE COMPONENT PROPERTIES

Component Name			Technological Data					Medical Data							
								MAC		LD50 [mg/kg Body Wt]					Remarks
										Oral			Skin		
Trivial	System	Design	Structural Formula	MW	BP	MP	Dens. Liquid	ppm	mg/ m3	Rat	Mouse	Gn. Pig	Rabbit	Rabbit	
				g/mole	°C	°C	kg/m3	vol.							
Sulfuric acid	Sulfuric acid	SA	H_2SO_4	98.08	279.6	10.4	1841.00		1	2140 [1]					
Levulinic acid	4-oxo-Pentanoic acid	LA	$C_5H_8O_3$	116.12	245-246	37.2	1139.00			1850					
Furfurylalcohol	2-Furanmethanol		$C_5H_6O_2$	98.10	171.0		1130.00								
Furfural	2-Furancarboxaldehyde	FUR	$C_5H_4O_2$	96.08	161.6	-36.5	1160.00	2	8	127	400	541			
5-hydroxymethylfurfural	5-(hydroxymethyl)-2-Furancarboxaldehyde	HMF	$C_6H_6O_3$	126.11	114-116	35.0	1110.00			3100	1910				
Formic acid	Formic acid	FA	$HCOOH$	46.03	100.8	8.3	1220.00	5	9	1830	1076				
Water	Water		H_2O	18.02	100.0	0.0	1000.00	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	
Furan	1,4-Bioxa-1,3-butadiene		C_4H_4O	68.07	32.0		940.00			5200	7				
Methanol	Methanol	Methanol	CH_3O	30.03	-19.1		735.0								
Carbonmonoxide	Carbonmonoxide	CO	CO	28.01	-264.5		297.0								
Glucose	D-Glucose	Glucose	$C_6H_{12}O_6$	180.16		146.0									
Xylose	D-Xylose	Xylose	$C_5H_{10}O_5$	150.13		144.0	1530.00								
Lignin	Lignin		$(C_{10}H_{10}O_3)_n$	~20000											
Hemicellulose	Hemicellulose		$(C_5H_8O_4)_n$	~22500											
Cellulose	Cellulose	Cellulose	$(C_6H_{10}O_5)_n$	~240000		n.a. [2]	1590.00								Tg = 160 °C Tg = 190 °C
Carbondioxide	Carbondioxide	CO2	CO_2	44.01			712.0								
2H-dihydropentanoic acid	2H-dihydropentanoic acid 2-Hyd-01		$C_5H_{10}O_3$	118.13			900.0								
Lime	Lime	Lime	$Ca(OH)_2$	74.09			247.0								
Gypsum	Gypsum	Gypsum	$CaSO_4$	136.14			499.0								

Notes:
[1] 25% solution
[2] Thermal decomposition at 180 °C

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5 PROCESS STRUCTURE AND DESCRIPTION

5.1 CRITERIA AND SELECTIONS

In the process wet bagasse (± 50% water) is used, because storage and handling of dry bagasse is laborious (see also appendix 8). A transporter belt is used to convey the bagasse to the reactor.

The process chosen is the two stage process as proposed in the BOD: a reactive extruder (RE) followed by a CSTR.

Because kinetics of the tar formation are missing and the furfural kinetics are incomplete, residence times chosen in reference [4]. The reactor conditions are set as shown in table 5.1. The pressure is set on 21 bar to make sure all of the steam condensates. The pressure in the CSTR is chosen to make sure all of the formed furfural and formic acid is gaseous. The temperatures are set according to reference [4].

Table 5.1. Reactor conditions

Reactor	Pressure (bar)	Temperature (°C)	Residence time (s)	Acid concentration ($\%_{weight}$)
Reactive extruder	21	210	14	5
CSTR	16	195	1800	5

The temperature in the RE is controlled by adding high-pressure steam of 250°C and 21 bar. Adding sulphuric acid controls the acid concentration.
Gaseous furfural, formic acid, water and side products are removed from the top of the CSTR. These are then separated in a several distillation columns.

Furfural is separated from the formic acid – water mixture using a distillation column C01. Both furfural and formic acid form an azeotrope with water. In this case formic acid acts as an entrainer to make the separation feasible. Formic acid and water leave the column at the bottom and furfural leaves at the top. The column is operated at 3 bar because there is no need for a high pressure and the second column also operates at 3 bar so no compressors or expanders are needed.
The second (C02) and third (C03) column separates formic acid and water. Formic acid and water form an azeotropic mixture which cannot be separated using simple distillation. Azeotropic mixtures can be separated by azeotropic and extractive distillation. The disadvantage of these separation methods is the presence of an entrainer or extractor in the mixture which has to be removed to obtain pure formic acid and water. Pressure shift distillation is chosen to separate formic acid and water. Formic acid and water form maximum boiling azeotropes containing 77.5 % acid at 101.3 kPa and 83.2 % acid at 2.4 MPa. At the 101.3 kPa, the azeotropic mixture boils at 380.3 K, and at 2.4

MPa it boils at 407.8 K. This dependence upon pressure makes it possible to produce concentrated formic acid using pressure shift distillation. The feed liquor is pumped to a column operated at 300 kPa producing nearly pure water as distillate. The bottom product is fed to a vacuum (20 kPa) column producing nearly pure formic acid as distillate. The bottom product from the vacuum column is circulated to the pressurized column [79]. The temperatures of all feeds entering the column are at the bubble point temperature of the feed. This results in an optimal separation.
In Table 5.2 the operating temperature and pressure for the 3 columns are given.

Table 5.2: Distillation column operating temperature and pressure

	Temperature (°C)	Pressure (bar)
C01	120	3
C02	125	3
C03	147	0.2

The bottom stream leaving the RE, contains LA, sulphuric acid, water, tar and lignin. The tar and lignin form an asphaltic like substance (see BOD). This is removed in a centrifuge. This unit is not specified. A diameter of 1 meter is chosen, because of the guidance given in reference [47].

Sulphuric acid has the tendency to attract water. About 10% in weight of the sulphuric acid is water [80]. LA and water separate, only 10% of the sulphuric acid mixture will be dissolved in LA. This makes the use of a decanter possible. The LA will decant from the water. The bottom stream, the sulphuric acid, will be recycled to the RE. The decanter conditions are shown in table 5.2.

Table 5.3. Decanter conditions

Unit	Pressure (bar)	Temperature (°C)	Residence time (s)
Decanter	16.2	195	239

The remaining sulphuric acid is removed by adding lime in a short residence time CSTR. The reaction time needed for the lime and sulphuric acid to form gypsum is set on 10 seconds. The conditions in the reactor are the same as the stream entering the reactor. The gypsum reactor conditions are given in table 5.3.

Table 5.4. Gypsum reactor conditions

Unit	Pressure (bar)	Temperature (°C)	Residence time (s)
Gypsum reactor	16	195	10

The formed gypsum is removed with a centrifuge, with a diameter of 0.5m, for the same reason as the previous centrifuge.

In order to have as much energy conservation as possible, energy integration of the total process has been taken into consideration. A heat exchanger analysis (shown in Appendix 6) has been done to determine which streams can be coupled. The outgoing water stream (nr. 25) is partially recycled and is heated by the product stream that contains the levulinic acid. It showed also feasible to couple the cool stream 33 with the hot stream 30. An extra cooler had to be used to further cool down stream 30. The part of the water that is not recycled is disposed of as wastewater and has to be cooled down to 30°C. The other outgoing streams do not have to be cooled.

Storage tanks are used for the LA, Furfural and formic to store a production of 1 month.

The asphaltic substance is used in plant to generate power and steam. This plant is not designed. A comparison is made with a coal processing plant [80]. This plant has an efficiency of 45%, processes about 60 million tons of coal. A plant processing 'asphaltic substances' will provide sufficient power and steam for this design.

A block scheme of the process is given in figure 5.1, shown in appendix 8.

5.2 PROCESS FLOW SCHEME

According to the previous decisions process flow scheme is made, shown in appendix 10. The stream summary is given in appendix 4.

5.3 UTILITIES

Because an abundance of (river) water is assumed, cooling will be done with water. The average temperature in the Sao Paulo region (see also BOD) is 25 °C, an average temperature of the river water is assumed to be 20°C. The asphalt processing plant has enough power to generate high-pressure steam; so heating will be done with this steam.

Electricity needed to work the pumps and the RE is also provided by this plant.

Lime is used to remove the sulphuric acid. The gypsum formed is easily removed. Whether the gypsum is sellable is not sure. The presence of the worldwide gypsum pile makes it uncertain. Table 5.4 provides the utilities.

Table 5.5. Utilities

Utility	Unit	Units/a
Steam	kton	61.5
Cooling water	Kton	140
Lime	Ton	445
Electricity	MWh/a	2300

5.4 YIELDS

Yields are given the block scheme presented in figure 5.2.

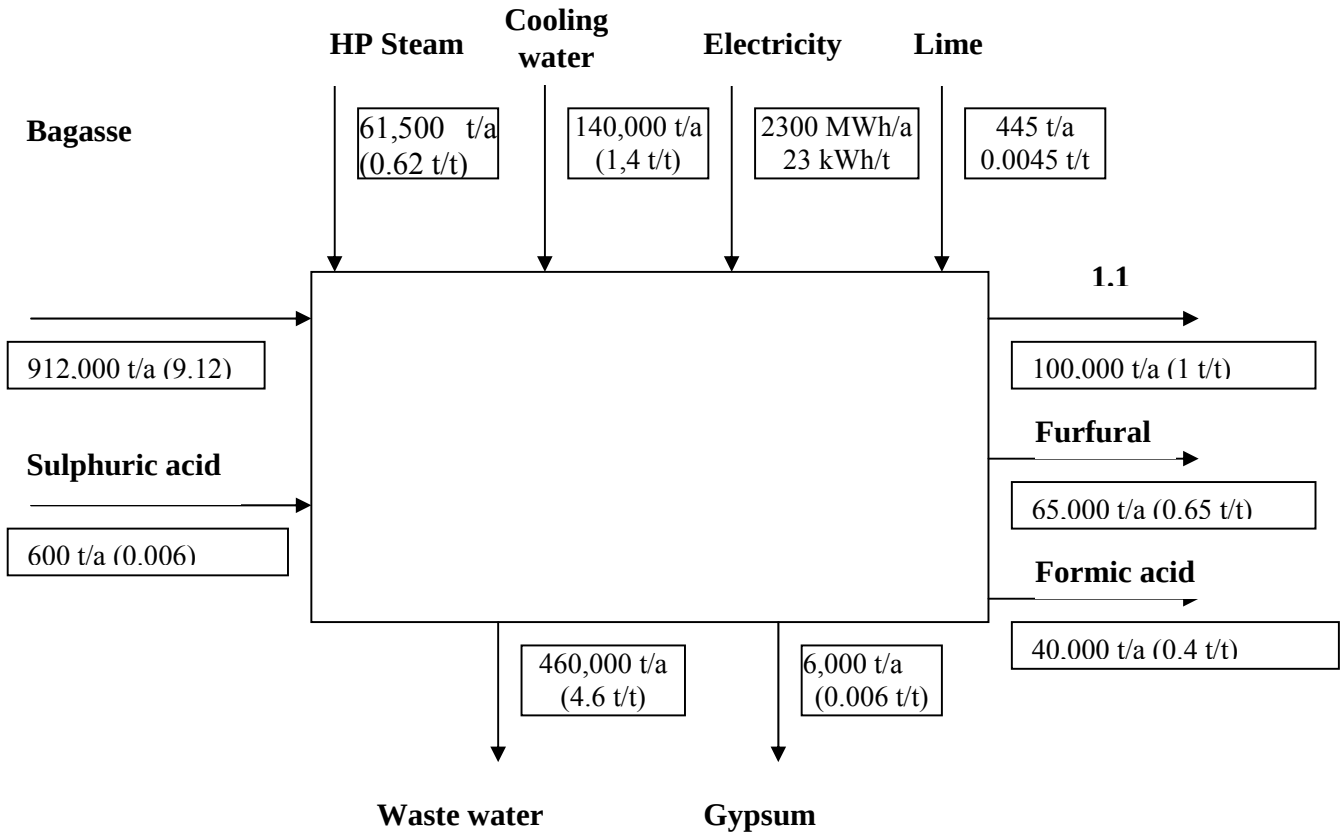

Figure 5.2. Block schema for utility and feedstock use

6 PROCESS CONTROL

The objectives when specifying instrumentation and control schemes are:

1. Safe plant operation:
   (a) To keep the process variables within known safe operating limits
   (b) To detect dangerous situations as they develop and to provide alarm and automatic shutdown systems.
   (c) To provide interlocks and alarms to prevent dangerous operating procedures.
2. Production rate:
   To achieve the design product output.
3. Product quality:
   To maintain the product composition within the specified quality standards.
4. Cost:
   To operate at the lowest production cost, commensurate with the other objectives.

The process control for the equipment is designed considering to objectives stated above.

6.1 DISTILLATION COLUMNS

To maintain the pressure in the top of the column a pressure controller and valve are installed. When the pressure reaches a maximum value, the valve open and the distillate rate increases. The result will be a pressure drop in the top stage of the column.
To maintain the temperature of the reflux stream a temperature controller and valve are installed. When the temperature of the reflux stream is too high more cooling water is pumped through the condenser to cool down the reflux stream.
A level controller is installed to prevent the column from flooding or drying. The bottom stream can be adjusted by a valve to prevent flooding or drying. The temperature of the bottom of the column is controlled by the steam flow rate through the reboiler. When the temperature in the column is too low more steam is pumped through the reboiler.

6.2 REACTORS, DECANTER AND MIXER

Both reactors are equipped with pressure controllers to prevent pressure built up in the reactors. If the pressure in the reactor is to high, the outlet flow of the reactor is increased.

Reactor R01

The temperature in the reactor is controlled by the steam flow rate into the reactor. When the reactor is too hot less steam is inserted into the reactor and vice versa. The pH in the reactor is regulated by the sulfuric acid stream.

Reactor R02

To prevent the CSTR from flooding or drying up a level controller measures the amount of liquid in the reactor. When the amount of liquid in the reactor decreases the flow rate of the liquid bottom stream is decreased to stabilize the liquid level.

Decanter

To prevent the decanter from flooding or drying up a level controller measures the amount of liquid in the reactor. When the amount of liquid in the reactor decreases the flow rate of the liquid bottom stream is decreased to stabilize the liquid level.

Mixer

The liquid level in the mixer is controlled by a valve in the outlet stream of the mixer.

6.3 PROCESS STREAMS

The flow of the feed streams is measured and controlled with a flow controller so the amount of feedstock in can be regulated if necessary.

7 MASS AND HEAT BALANCES

The heat and mass balances for the several equipment are shown in table 7.1

Table 7.1 Heat and mass balance

HEAT & MASS BALANCE FOR STREAMS TOTAL										
IN						OUT				
Plant		EQUIPMENT			EQUIPM.	EQUIPMENT			Plant	
Mass kg/s	Heat kW	Mass kg/s	Heat kW	Stream Nr.	IDENTIF.	Stream Nr.	Mass kg/s	Heat kW	Mass kg/s	Heat kW
29.67	279120	29.67	279120	**<1>**	**R01**	**<4>**	39.4	394152		
0.20	1500	0.20	1500	**<2>**						
		7.57	98759	**<3>**						
		2.02	98759	**<9>**						
		39.46	478138.00		Total		39.40	394152.00		
		39.40	394152	**<4>**	**R02**	**<17>**	25.56	324582		
						<5>	13.88	48526		
		39.40	394152.00		Total		39.44	373108.00		
		25.56	324582	**<30>**		**<31>**	25.56	324582		
					E08					
		25.56	324582		Total		25.56	324582		
		25.56	324582	**<31>**		**<18>**	25.56	324582		
					E09					
		25.56	324582		Total		25.56	324582		
		25.56	356064	**<18>**	**C01**	**<24>**	2.69	5587	**2.69**	**5587**
						<19>	22.95	353436		
					E01					**55570**
52389					**E04**					
		25.56	356064		Total		25.64	359023		
		25.65	364949	**<20>**	**C02**	**<25>**	21.61	341259		
						<21>	3.38	30399		
					E02					**109057**
102261					**E05**					
		25.65	364949		Total		24.99	371658		
		3.38	30399	**<21>**	**C03**	**<26>**	1.35	12402	**1.35**	**12402**
						<22>	2.07	18621		
					E03					**15864**
15864					**E06**					
		3.38	30399		Total		3.42	31023		
		21.61	341259	**<25>**	Splitter	**<28>**	13.95	215852	**13.95**	**215852**
						<29>	7.57	98759		
		21.61	341259.00		Total		21.52	314611.00		
		13.88	48526	**<5>**	**V01**	**<6>**	8.28	11614	**8.28**	**11614**
						<7>	5.60	37320		
		13.88	48526.00		Total		13.88	48934		
		5.60	37320	**<7>**	**V02**	**<8>**	2.02	16356		
						<11>	3.58	37320		
		5.60	37320		Total		5.60	53676		

IN							OUT			
Plant		EQUIPMENT		Plant	Equipm	Equipment			Plant	
Mass	Heat	Mass	Heat	Stream	IDENTIF.	Stream	Mass	Heat	Mass	Heat
kg/s	kW	kg/s	kW	Nr.		Nr.	kg/s	kW	kg/s	kW
		0.02	188	**<10>**	**V03**	**<12>**	3.60	20600		
		3.58	37320	**<11>**						
		3.60	37508.00		Total		3.60	20600		
		3.60	20600	**<12>**	**V04**	**<13>**	3.39	19130	**3.39**	**19130**
						<14>	0.22	132	**0.22**	**132**
		3.60	20600		Total		3.61	19262.00		
					E07					
					E07					
					E09					**3140**
					E10					**7800**
29.87	**451134**				Total				**29.88**	**456148**
OUT - IN :									0.01	**5014**

8 EQUIPMENT DESIGN

8.1 DISTILLATION COLUMS

8.1.1 DISTILLATION COLUMN C01

This column separates furfural from water and formic acid. Both furfural and formic acid form an azeotrope with water. In this case formic acid acts as an entrainer to make the separation feasible. The specifications of the column can be found in the appendices. Aspen was used to simulate the column. The input variables for Aspen are:

Table 8.1: Input variables C01

Reflux ratio	44
Condenser pressure (bar)	3
Reboiler pressure (bar)	3
Furfural recovery in distillate	0.98
Water recovery in distillate	0.0001
Condenser specification	Total condenser

The reflux ratio is quite high because the mixture is difficult to separate. Lower reflux ratios give unrealistic column heights.

The column height of all columns is calculated with the following equation given in reference [57]:

$H = 2.3*N_{actual}*0.030$

H = column height [m]
N_{actual} = actual number of stages [-]
The diameter of all columns is calculated with the following equation given in Douglas:

Dt = (4*At/pi)^0.5

At = V*(Mg/ρm)^0.5/(1.5*3600)

Dt = column diameter [ft]
At = column area [ft^2]
V = molar flow rate of vapor [mol/hr]
Mg = molecular mass of vapor
Pm = density of vapor [mol/ft^3]

Other column specifications are calculated with Aspen.
The column and the sieve trays are made of stainless steel 304 because of the presence of a diluted acid mixture in the column. Due to the presence of acid carbon steel cannot be used as it is sensitive to corrosion.

8.1.2 DISTILLATION COLUMNS C02 AND C03

These columns are used to separate formic acid from water. Formic acid and water form an azeotropic mixture, which cannot be separated using simple distillation. Azeotropic mixtures can be separated by azeotropic and extractive distillation. The disadvantage of these separation methods is the presence of an entrainer or extractor in the mixture, which has to be removed to obtain pure formic acid and water. Pressure shift distillation is chosen to separate formic acid and water. Formic acid and water form maximum boiling azeotropes containing 77.5 % acid at 101.3 kPa and 83.2 % acid at 2.4 MPa. At the 101.3 kPa, the azeotropic mixture boils at 380.3 K, and at 2.4 MPa it boils at 407.8 K. This dependence upon pressure makes it possible to produce concentrated formic acid using pressure shift distillation. The feed liquor is pumped to a column operated at 300 kPa producing nearly pure water as distillate. The bottom product is fed to a vacuum (20 kPa) column producing nearly pure formic acid as distillate. The bottom product from the vacuum column is circulated to the pressurized column [79]. The input variables for simulation in Aspen for the two distillation columns are given in Table 8.2 and 8.3.

Table 8.2: Input variables C02

Number of stages	28
Condenser pressure (bar)	3
Reboiler pressure (bar)	3
Formic acid recovery in distillate	0.005
Water recovery in distillate	0.98
Condenser specification	Total condenser

Table 8.3: Input variables C03

Number of stages	22
Feed stage	19
Condenser pressure (bar)	0.2
Distillate rate (kmol/hr)	106.1
Reflux ratio	24
Condenser specification	Total condenser

Column heights and diameter are calculated using equations given under distillation column C01.

The columns and the sieve trays are made of stainless steel 316 because of the presence of acid in the mixture. SS 316 is more expensive than SS 304 but is more resistant to corrosion [58]. Due to the presence of acid carbon steel cannot be used as it is sensitive to corrosion.

All the specifications for the distillation columns are listed in the equipment specification sheet.

8.2 REBOILERS AND CONDERSERS

8.2.1 CONDENSERS E01, E02 AND E03

For designing the condensers mathematical equations from references [57] and [58].

$Q = U*A*dT_{lm}$

$Q = \phi_m*C_p*(Tin-Tout)$

$$dT_{lm} = \frac{(T1-t2)-(T2-t1)}{\ln\frac{(T1-t2)}{(T2-t1)}}$$

Q = Condenser cooling required [kW]
U = Overall heat transfer coefficient [kW/m^2°C]
A = heat-transfer area [m^2]
dT_{lm} = log mean temperature difference [°C]
ϕ_m = coolant flow rate [kg/s]
C_p = Specific heat capacity [kJ/kg°C]
T1 = Inlet temperature reflux stream [°C]
T2 = Outlet temperature reflux stream [°C]
t1 = Inlet temperature cooling water [°C]
t2 = Outlet temperature cooling water [°C]

The condenser cooling required is calculated with Aspen. An estimation of the overall heat transfer coefficient is taken reference [57]. The overall heat transfer coefficient is estimated at 1.0 kW/m^2°C.

The cooling water has an inlet temperature of 20 °C and an outlet temperature of 40°C, which is the highest outlet temperature possible. For the specific heat capacity of cooling water is taken 4.18 kJ/kg°C. The inlet and outlet temperature of the reflux stream are equal because this stream is condensing at constant temperature.

The cooling water is flowing through the shell side of all the condensers because it's the cleanest stream. Tubes are easier to clean than shells so the cleanest stream must flow through the shell. The shell side is made of carbon steel because it is cheap and water is not a harmful component.

The calculated heat-transfer area and the coolant flow rate are very high as can be seen in the specification sheets. This is due to the very high value that Aspen calculates for the condenser cooling required. The duty is high because the reflux rates are very high due to high reflux ratios (condenser E01 and E03).
All the specifications for the condensers are listed in the equipment specification sheet.

8.2.2 REBOILERS E04, E05 AND E06

For designing the reboilers mathematical equations from references [57] and [58].

$Q = U*A*dT_{lm}$

$Q = \phi_m*C_p*(Tin-Tout)$

$$dT_{lm} = \frac{(T1-t2)-(T2-t1)}{\ln\frac{(T1-t2)}{(T2-t1)}}$$

Q = Reboiler heating required [kW]
U = Overall heat transfer coefficient [kW/m^2°C]
A = heat-transfer area [m^2]
dT_{lm} = log mean temperature difference [°C]
ϕ_m = steam flow rate [kg/s]
C_p = Specific heat capacity [kJ/kg°C]
T1 = Inlet temperature boilup stream [°C]
T2 = Outlet temperature boilup stream [°C]
t1 = Inlet temperature steam [°C]
t2 = Outlet temperature steam [°C]

The reboiler heating required is calculated with Aspen. An estimation of the overall heat transfer coefficient is taken from reference [57]. The overall heat transfer coefficient is estimated at 1.0 kW/m^2°C.

For reboilers E04 and E05 medium pressure steam is used because the temperature of the boilup streams are respectively 134.2 °C and 146.5 °C. These temperatures are above 133.5 °C, the outlet temperature of low pressure steam. For reboiler E06 low-pressure steam is used because the temperature of the boil up stream is 66.7 °C.
Medium pressure (MP) steam has an inlet and outlet temperature of respectively 220 °C and 180°C at a pressure of 10 bar. Low pressure (LP) steam has an inlet and outlet temperature of respectively 190 °C and 133.5 °C at a pressure of 3 bar. The inlet and outlet temperature of the boil up stream are equal because this stream is vaporizing at constant temperature.

The heating steam is flowing through the shell side of all the condensers because it's the cleanest stream. Tubes are easier to clean than shells so the cleanest stream must flow through the shell. The shell side is made of carbon steel because it is cheap and steam is not a harmful component.

The calculated heat-transfer area and the steam flow rate are very high as can be seen in the specification sheets. This is due to the very high value that Aspen calculates for the condenser cooling required. All the specifications for the reboilers are listed in the equipment specification sheet.

8.3 PUMPS

The specifications of the pumps are calculated with Aspen. The only input variable in Aspen is the pressure change. The specifications are listed in the equipment specification sheets.

8.4 REACTORS

8.4.1 REACTOR R01

Reactor R01 is a reactive extruder and converts cellulose to hexoses and hemi-cellulose to pentoses. The reactor operates under plug flow conditions. The volume of the reactor was calculated from the inlet flow and the residence time inside the reactor according to the following equation:

$V_r = \phi_v * \tau$

V_r = volume of the reactor [m^3]
ϕ_v = inlet flow reactor [m^3/s]
τ = residence time [s]

It is assumed that the screw fills half of the reactor so the total volume two times V_3.
The reactor is made of stainless steel because it contains corrosive components such as sulfuric acid and stainless steel is corrosion resistant.

8.4.2 REACTOR R02

Reactor R02 is a CSTR and is used to convert hexoses to HMF and HMF to furfural. It also converts pentoses to furfural. A vapor products stream leaves the reactor at the top and levulinic acid, sulfuric acid and solids leaves at the bottom.
The volume of the reactor is calculated the same way as R01.
The reactor is made of stainless steel because it contains corrosive components such as sulfuric acid and stainless steel is corrosion resistant.

8.5 EQUIPMENT SPECIFICATIONS

All equipment are specified in appendix 9.

9 WASTES

The production of levulinic acid from bagasse produces three streams that cannot be sold or used in another way and are therefore defined as waste streams. The three streams are:

- a waste water stream
- gypsum
- stream containing ashes from burned tar

The wastewater stream is almost pure and contains only traces of other component. Therefore it can be disposed into the water outside the plant. The stream is cooled to 30°C so it is allowed to be disposed into the water outside the plant.

The gypsum is formed in the reaction of sulfur with lime. Sulfur is a harmful component and therefore has to be removed from all products stream. The cheapest way to purify to levulinic acid is to remove the sulfur with lime. The disadvantage is the formation of gypsum. The gypsum that is formed during the removal of sulfur from the levulinic acid can be sold. It can be used for different purposes but it remains uncertain if all of the gypsum can be sold. Therefore a part of the gypsum has to be disposed.

The tar formed in the CSTR can only be used as fuel and is combusted to generate high-pressure steam. The ashes that are formed during the combustion are waste and have to be disposed.

10 HEALTH SAFETY AND ENVIRONMENT

10.1 HAZOP OF THE REACTIVE EXTRUDER

A HAZOP study of the reactive extruder has been made. This is shown in table 10.1.

Table 10.1 HAZOP study of an extruder where hydrolysis of bagasse takes place to form pentoses and hexoses with the use of sulfuric acid and high-pressure steam.

Guide Word	Deviation	Possible Causes	Consequences	Action Required
NOT, NO	No flow of sulfuric acid stream, or	1) storage tank is empty 2) pump defect	pH rise, no reaction	back-up tank or sufficient capacity Ensure good communications with storage operator
	No flow of bagasse	See (1) 3) impurities cause congestion 4) transporter belt defect	no reaction	Monitoring by personnel or automatic, regular maintenance and check-ups
	No flow of high pressure steam	See (2) 5) tar processing plant down 6) water recycle not functioning properly	reaction slows down obstruction of next reactor through increased viscosity (slurry)	Install flow controller
LESS	Less flow of sulfuric acid	7) Corrosion pipelines, See (2)	Decrease in the acid-catalyzed reaction	PH-controller
	Less pressure	8) Leak	Phase change, vapours are not wanted in extruders	Pressure-controller
	Decrease in temperature	9) No steam	Less conversion of bagasse	Temperature controller

MORE	More flow of sulfuric acid	10) Pump not working properly	Deterioration of reactor strength by higher acid concentration	
	Increase in residence time	11) Reactor is not working (fouling or a screw stopped/broke)	Tar formation	Flow controller
	Increase in pressure	12) Blocking in reactor, 13) pressure controller defect	Possible damage to reactor (not designed for higher pressures)	Press red button
	Increase in temperature	14) Valve steam supply defect	More tar formation	Temperature controller
AS WELL AS	Formation of tar	15) Temperature too high, 16) residence time too long	Less product	See MORE (increase in residence time & increase in temperature)
	Formation of aromatics (out of hexoses)	See (15) and (16) 17) pH too low	Less product	Decrease residence time
PART OF	Bagasse conversion not complete	18) pH too high 19) residence time too short 20)	Increase in viscosity, complete shutdown	Increase sulfuric acid stream, extend residence time
OTHER THAN	No conversion at all			
	All HMF and furfural turn into tar			

11 ECONOMY

11.1 PURCHASE COSTS

To estimate the costs for the LA plant, calculations are made with the use of the Lang method [57]. The total costs of the plant ready for start-up, the fixed capital costs (FC), are calculated with formula 11.1.

$$C_f = f_L C_e \tag{11.1}$$

where C_f = fixed capital costs
C_e = the total delivered costs of all major equipment
f_L = Lang factor

The Lang factor depends on the process type. In this case, a mixed fluids-solids processing plant, f_L is set on 3.6. This factor is used to estimate all other costs, such as equipment erection, piping, instruments etc. The total delivered cost of the equipment are estimated using figures 6.3 to 6.6 and table 6.2 of reference [57]. These calculations are shown in Appendix 7.

For these calculations an average inflation of 3 % is used. The UK pound to euro exchange is set on 1.6 €/£.

The costs of the reactors are calculated as vessels, with an extra factor of 1.2 to estimate extra piping and controlling [57]. The extruder is calculated a vessel with 2 extra smaller vessel used as the actual extruding parts. To calculate the rotating parts and the 'pumpfunction' of the extruder, a pump-estimation is used, as if a pump was attached to the reactor.

The decanter specifactions are shown in appendix 6. The presence of highly concentrated sulphuric acid at high temperatures makes a extra coating to protect the equipment against corrosion necessary. This coating will be a 'nodular ferritic graphite' as presented in ref. [76], used in a sulphuric acid plant. This is estimated to have a material cost factor of 4 [76].

Al other equipment is specified in chapter 8. These specifications are used to calculate the total equipment costs, as shown in table 11.1.

The value of the 'asphalt' gasifier and the steam/power generator is estimated at k€ 10,000. A coal processing plant with a 30 times higher coal throughput costs approximately 500 million [77].

Table 11.1 purchase costs of equipment

purchase cost of item:	value (k€)
columns	805.04
reactors	240.17
heatexchangers	754.31
compressors/pump and expander	1.69
costs of decanter	42.09
costs centrifuges	75.60
costs of storage tanks	1,870.91
power/steam generator	10,000.00
Total delivered costs of major equipment (Ce)	13,789.81
Fixed capital costs (Cf)	55,159.22

11.2 TOTAL PRODUCTION COSTS

The total productions costs are shown in tables below.

Table 11.2. The total investment costs

Capital					
Description				%	IN k€
- Fixed Capital (FC)	89%of Total Invest.,			89	55,159
- Working Capital	11%of Total Invest.,	Factor FC:	0.125	11	6,817
Total Investment				100	**61,977**

Table 11.3. Gross income calculation

Products				
Description		OUT t/a	Sales €/t	IN k€/a
- Product	LA	100,000	181.00	18,100
-	Furfural	65,000	792.00	51,480
- By product	Formic acid	40,000	525.00	21,000
Sub-total		165,000		90,580
- Waste	Gypsum	7,000	-10.00	-70
-	Wastes from 'aphalt' processing plant	241,000	-100.00	-24,100
-	Waste water	460,000	-0.05	-23
Total / Gross Income		913,000		**66,387**

Table 11.4. Raw material costs

Raw Materials				
Description		IN t/a	Purchase €/t	OUT k€/a
- Feedstock	bagasse	912,000	15.00	13,680
- Sweetener	Lime	445	5.50	2
Total		912,000		**13,682**

Table 11.5. Utility costs

Utilities				
Description	Units	IN Units/a	Purchase €/Unit	OUT k€/a
- Cooling water, dutch value	kt	7140	0.50	8
- Electrical Power	MWh/a	2300	0.00	0
Total				**5**

Table 11.6. Catalyst costs

Catalyst			
Description	IN t/a	Purchase €/t	OUT k€/a
- Continues refreshment of new catalyst	581	58.4	34
Total			**34**

In table 11.7 the total annual production costs are calculated according to reference 57. There are a few exceptions. The economical lifetime of the plant is 10 years. The interest rate is set on 7%. The royalties and license fee is set on 2 % of the sales of the products, which is done because of the 2 patents used in this design (1% per patent).

Table 11.7. Annual production costs estimation

Summary of Annual Production (Manufacturing) Costs (k€/a)				
Cost Type	k€/a	%		Remarks
Direct				
Variable				(A)
1.Raw materials	13,682	96%	36%	
2.Miscellaneous materials	552	4%	1%	(5): k€ 5.52 10%
3.Utilities	0	0%	0%	
4.Shipping & packaging		0%	0%	
Sub-total	*14,234*	*100%*		
Fixed				(B)
Catalyst	34	0%	0%	
5.Maintenance	5,516	29%	14%	10% of Fixed Cap.: k€ 55,159
6.Operating labour	2,350	12%	6%	3 oper. x 5 shifts=15 oper.'s
7.Laboratory	470	2%	1%	20% of (6): k€ 2.35
8.Supervision	470	2%	1%	20% of (6): k€ 2.35
9.Plant overhead	1,175	6%	3%	50% of (6): k€ 2.35
10.Capital charges	5,516	29%	14%	10% of Fixed Cap.: k€ 55,159
11.Insurance	552	3%	1%	1% of Fixed Cap.: k€ 55,159
12.Local taxes	1,103	6%	3%	2% of Fixed Cap.: k€ 55,159
13.Royalties	1,812	10%	5%	2% of LA/Fur revenue k€ 90,580
Sub-total	18,997	*100%*		
Total	*33,231*			(A)+(B)
Other			0%	(C)
14.Sales expenses			0%	
15.General overhead	*4,985*		13%	(A)+(B): k€ 33.23 15%
16.Research & Dev.			0%	
Total Production Costs				
Annual [k€/a]	**38,216**		*100%*	(A)+(B)+(C)
Per ton LA [€/t]	382.16			100000 t/a

11.3 GROSS INCOME, NET CASH FLOW AND ECONOMIC CRITERIA

The net cash flow and the economic criteria are presented in table 11.8 and are calculated as shown in ref 57. The pay out time is the number of years needed to pay back the investments. Afters this period all of the plant sales is profit. The rate of return is the reciprocal value of the pay out time.

Table 11.8. Net cash flow and economic criteria estimations

GROSS INCOME, NET CASH FLOW, ECONOMIC CRITERIA				
Item	Unit	Value	k€/a	Remarks
Gross Income			66,391	
Production Costs			38,216	
Net Cash Flow, *Before Tax*			**28,175**	= (A)
Economical Plant Life & Depreciation				Excl. 13th year salvage.
- **Total Investment**	k€	**61,977**		= (B)
- Econ. Plant Life, years:	Years	10		Incl. 2 yrs Des.& Con.
- Annual Depreciation over 10 years			6,198	
Net Cash Flow, *After Depreciation*			**21,977**	
Pay-Out Time, *Before Tax*	Years	**2.2**		= (B) / (A)
Rate of Return, *Before Tax*	%	**45.5%**		= (A) / (B)
DCF Rate of Return, *Before Tax*	%	**18.6%**	**nil**	DCFRoR, IRR, EP
Net Present Value, *Before Tax*	%	**7.0%**	**171**	From DCF Calc.
Net Future Value, *Before Tax*			**336**	Interest = 0

11.4 NET PRESENT AND NET FUTURE VALUES

The building time of the plant is assumed to be 2 years. After this period the plant starts to produce LA, furfural and formic acid.It will be doing so for 15 years. The net present value and net future values are shown in table 11.9 and schematically in figure 11.1. The present value is calculated with a depreciation of 7%.

Table 11.9. Net present- and net future values

NET PRESENT- @ FUTURE VALUES									
	NET FUTURE VALUES (1) No Discount					NET PRESENT VALUES Discounted, Accumulated			
END YEAR NO.	CAPIT. COSTS ANN.	CAPIT. COSTS ACCUM.	CASH FLOW ANN.	CASH FLOW ACCUM.	**NFV**	DISC. FACT. @ Interest	CAPIT. COSTS ACCUM.	CASH FLOW ACCUM.	**NPV**
	€ mill	€ mill	€ mill	€ mill	€ mill	**7.0%**	€ mill	€ mill	€ mill
0					0				0
1	30.988	30.988			-30.988	1.000	30.988		-30.988
2	30.988	**61.977**			-61.977	0.935	**59.949**		-59.949
3			28.175	28.175	-33.802	0.873		24.609	-35.340
4			28.175	56.350	-5.627	0.816		47.608	-12.341
5			28.175	84.525	22.548	0.763		69.103	9.154
6			28.175	112.700	50.724	0.713		89.191	29.242
7			28.175	140.875	78.899	0.666		107.966	48.016
8			28.175	169.050	107.074	0.623		125.512	65.562
9			28.175	197.225	135.249	0.582		141.910	81.960
10			28.175	225.400	163.424	0.544		157.235	97.286
11			28.175	253.575	191.599	0.508		171.558	111.609
12			28.175	281.751	219.774	0.475		184.944	124.994
13			28.175	309.926	247.949	0.444		197.454	137.504
14			28.175	338.101	276.124	0.415		209.145	149.196
15			28.175	366.276	304.299	0.388		220.072	160.123
16			28.175	394.451	332.474	0.362		230.284	170.335
17		*(3) :*	*3.099*	397.550	335.573	0.339		231.334	171.384
ACCUM.		**61.977**		**397.550**	**335.573**	10.447	**59.949**	**231.334**	**171.384**
RATIO		**:**	[Cash Flow / Capital] @ Disc.					**3.9**	
NET PRESENT VALUE :			[Cash Flow - Capital] @ Disc.					**171.4**	

N.B. :
1. Cash-Flows "Before Tax".
2. Earning Power = Interest, for which [Cash Flow - Capital]@Disc. = 0
   Disc. Factor = 1/(1 + r)^n with r = interest fraction
3. Rest Value = 5.0% of Capital Investment

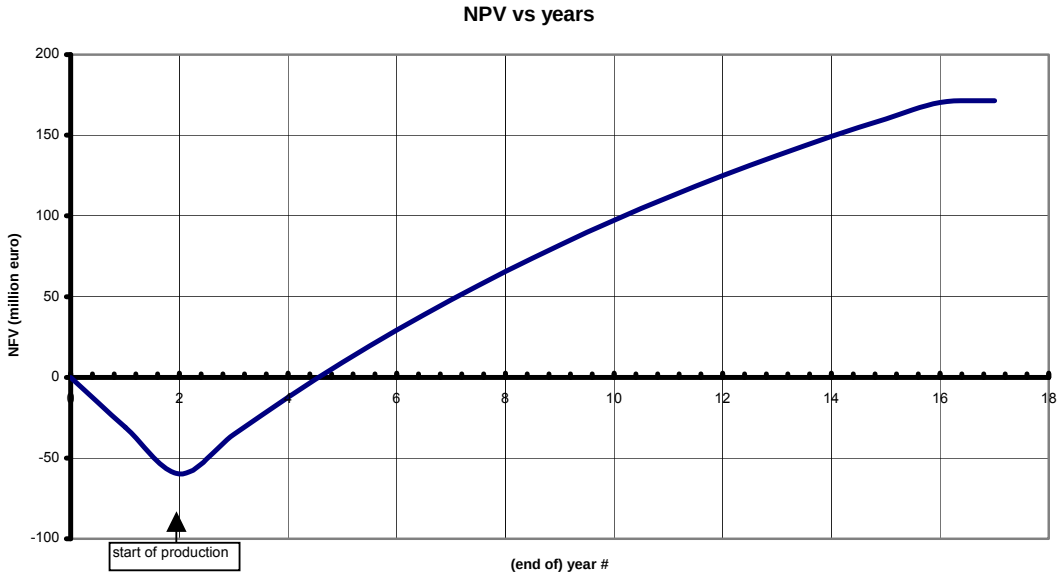

Figure 11.1. NVP over the years.

11.5 SENSITIVITIES

The furfural production is very important to the economics of this design. The production of LA is only feasible because of the furfural sales.

12 CONCLUSIONS AND RECOMMENDATIONS

12.1 CONCLUSIONS

The process as a whole is economically feasible. In particle the produced furfural makes it very profitable.
Burning the tar and asphalt-like substances will generate enough power to support the whole plant.

12.2 RECOMMENDATIONS

More research should be done on the removal of the sulfuric acid. New technologies where for example a chromatographic column is used seem interesting. The produced gypsum is not very valuable.

Better knowledge of the kinetics of tar formation will improve rector design.
It is also recommended that the market for electricity be further investigated as well as effects on prices of electricity and chemicals by increasing local and/or global production

LIST OF SYMBOLS

symbol	meaning	unit
Q	Condenser cooling required	[kW]
U	Overall heat transfer coefficient	[kW/m^2°C]
A	Heat-transfer area	[m^2]
dT_{lm}	Log mean temperature difference	[°C]
ϕ_m	Coolant flow rate	[kg/s]
C_p	Specific heat capacity	[kJ/kg°C]
T1	Inlet temperature reflux stream	[°C]
T2	Outlet temperature reflux stream	[°C]
t1	Inlet temperature cooling water	[°C]
t2	Outlet temperature cooling water	[°C]
V_r	Volume of the reactor	[m^3]
ϕ_v	Inlet flow reactor	[m^3/s]
τ	Residence time	[s]

τ	residence time	[min]
k_i	rate constant	[min]
r_i	reaction rate	[kg/(m^{3}min) or mol/(m^{3}min)]
c_i	concentration	[kg/m^3 or mol/m^3]
$c_{i,0}$	concentration in feedstream	[kg/m^3 or mol/m^3]

subscripts

glu	glucose
cel	cellulose
xyl	xylose
LA	levulinic acid
exp	experimental value from reference [4] or [18]
calc	calculated value with formula 2.1 - 2.4
CSTR	continued stirred tank reactor
PFR	plug flow reactor

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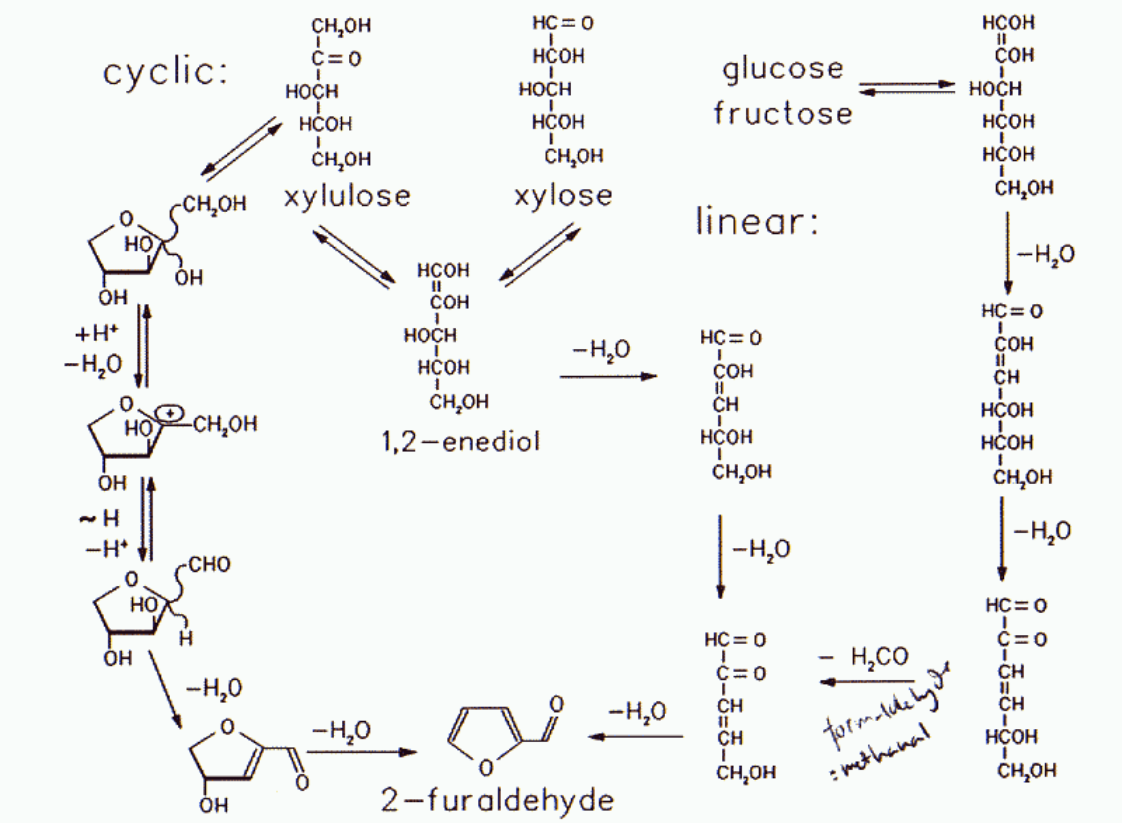
APPENDIX 1. MECHANISMS FOR THE CONVERSION OF PENTOSES FURFURAL

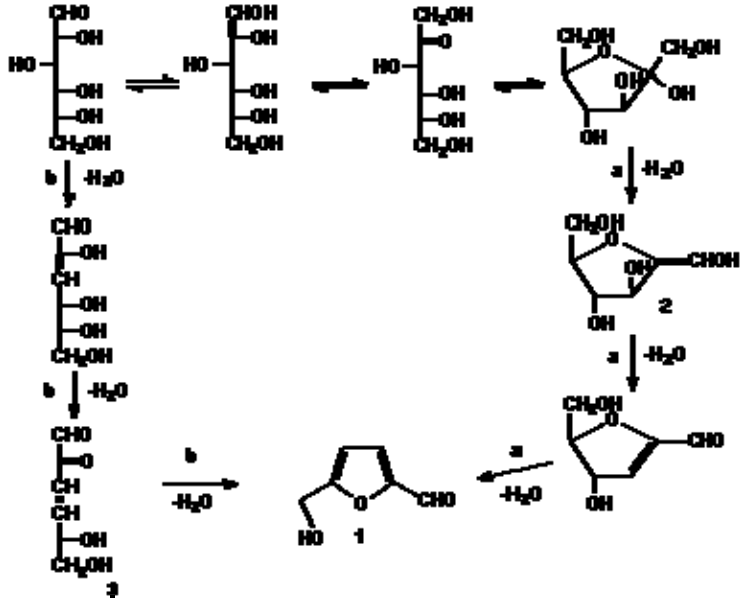
Figure A1.1. Mechanisms for the conversion of pentoses furfural.



Scheme 1. Linear[46] *and tentative cyclic pathway of 2-furaldehyde formation from* D*-xylose, and from* D*-fructose and* D*-glucose via a retro-aldol formaldehyde split-off*[49].

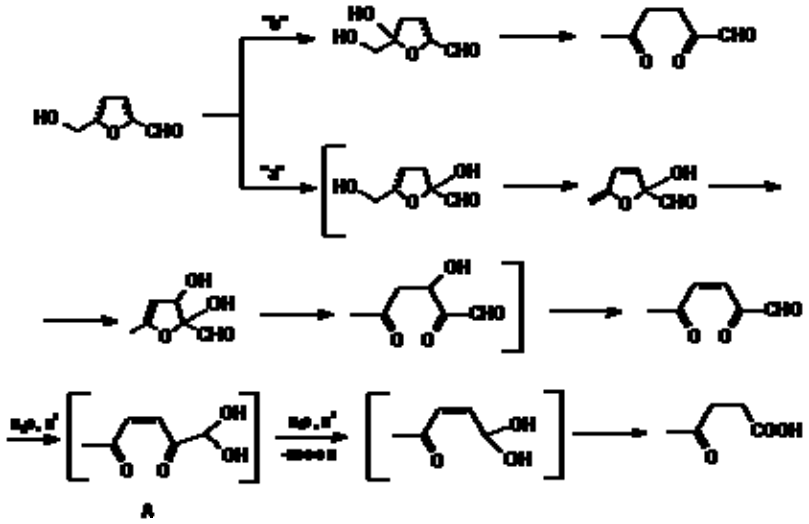
APPENDIX 2. MECHANISM FOR THE HMF FORMATION FROM HEXOSE

Figure A2.1. Mechanism for the HMF formation from hexose



APPENDIX 3. MECHANISM FOR THE FORMTION OF LA FROM MHF

Figure A3.1. Mechanism for the formation of LA from MHF.



APPENDIX 4. STREAM SUMMARIES

APPENDIX 5. RATE CONSTANT CALCULATIONS

LA formation

In the US patents 4,897,497 [18] and 5,608,105 [4] a few examples are given with a PFR followed by a CSTR to produce LA from cellulose. Herein, the acid concentration, temperature and yields, feed conditions and residence times are given. With the use of a mass balances (formula's A1 to A7) the rate constant could be determined.

$$\text{Cellulose} \xrightarrow{k_{glu}} \text{Glucose} \xrightarrow{k'_{LA}} \text{LA}$$

The second rate constant combines the formation of HMF and the formation of LA.

$$r_{cel} = -k_{glu} c_{cel} \tag{A1}$$

$$r_{glu} = k_{glu} c_{cel} - k_{LA} c_{glu} \tag{A2}$$

$$r_{LA} = k_{glu} c_{glu} \tag{A3}$$

The PFR:

$$\frac{dc_i}{d\tau} = -r_i \tag{A4}$$

The CSTR

$$\tau = \frac{c_{i,0} - c_i}{r_i} \tag{A5}$$

$$\tau = \frac{c_{cel,0} - c_{cel}}{k_{glu} c_{cel}} \rightarrow c_{cel} = \frac{c_{cel,0}}{1 + k_{glu}\tau} \tag{A6}$$

$$\tau = \frac{c_{glu}}{r_{glu}} = \frac{c_{glu}}{k_{glu} c_{cell} - k_{LA} c_{glu}} \tag{A7}$$

$$\tau = \frac{c_{LA}}{k_{LA} c_{glu}} \tag{A8}$$

A few assumptions are made:

- 99% of the cellulose is hydrolysed in de PFR
- $c_{glu,0} = c_{LA,0} = 0$

- HMF formation and decomposition is combined to one reaction
- The reactors behave ideally

With the values given in the examples 1 to 7 in reference [4] it is possible to calculate the rate constant for the hydrolysis and LA formation.
With a trial and error approach, the hydrolysis rate constant was changed until the residence time was equal to the given time, with a 99% conversion of the cellulose in the PFR.
With the calculated cellulose and glucose concentrations coming out of the PFR, the rate constant for the glucose decomposition was calculated. With a trial and error approach the rate constant was changed until the residence time was equal to the given time, with the LA yield given in the examples [4]. The found constant was then used again in the CSTR calculations to find a new rate constant for the hydrolysis. This iterative procedure had to be repeated twice, after which the constants did only change marginally.
These experimental values are compared with the calculated constants with formula 2.1 to 2.4. The results are presented in table A5.1.

Table A5. Comparison of the experimental and calculated rate constants at different temperatures and acid concentrations.

Example nr	T_{PFR} (°C)	τ_{PFR} (min)	T_{CSTR} (°C)	τ_{CSTR} (min)	pH (-)	$k_{glu,ecp}$ (min^{-1})	$k_{glu,\ calc}$ (min^{-1})	$k'_{LA,\ exp}$ (10^{-2} min^{-1})	$k_{hmf,\ calc}$ (min^{-1})	$k_{la,\ calc}$ (min^{-1})
1	232	14.0	196	1800	0.44	19.7	9.45	2.52	0.19	0.87
2	215	14.0	202	1200	0.71	19.7	1.11	3.15	0.17	0.57
3	230	23.3	208	1788	0.51	11.8	6.68	1.36	0.36	1.07
4	220	14.0	200	1200	0.93	19.7	9.27	3.91	0.10	0.32
5	215	14.0	200	1500	0.82	19.7	8.34	2.74	0.12	0.42
7	220	15.7	210	1200	0.29	17.6	5.41	2.81	0.67	1.88

The large differences between the experimental and calculated rate constants for La formation can be explained by the differences in temperature in the CSTR and the PFR, a 10° temperature increase gives a twice as high reaction rate. And the assumption of ideal reactors can be wrong. Also is the formation of tar not taken into account.
The difference between the rate constants for the cellulose hydrolysis can be explained by the assumption of 99% yield. Differences in temperature and pH have little or no effect on the experimental constants, so some assumptions must be wrong.

Because of the possible errors in the calculations of the experimental rate constants, the calculation of the constants described in the references [22,66-68] will be used in the simulation.

The dependency of the rate constants on the pH at constant temperature is shown in the figures A1 and A2:

Figure A1. Rate constant versus pH at 235°C

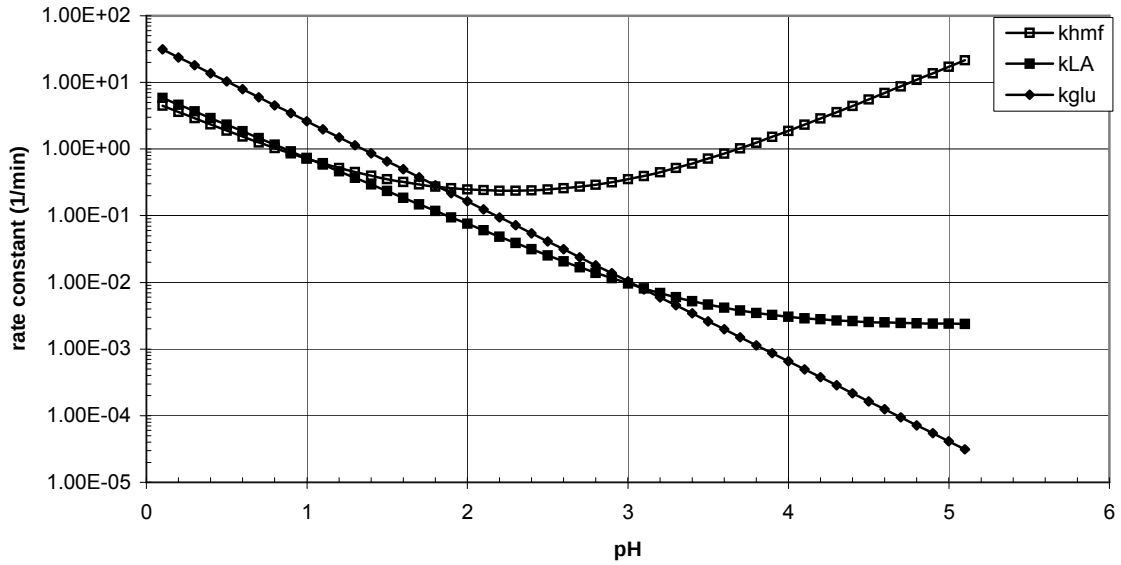
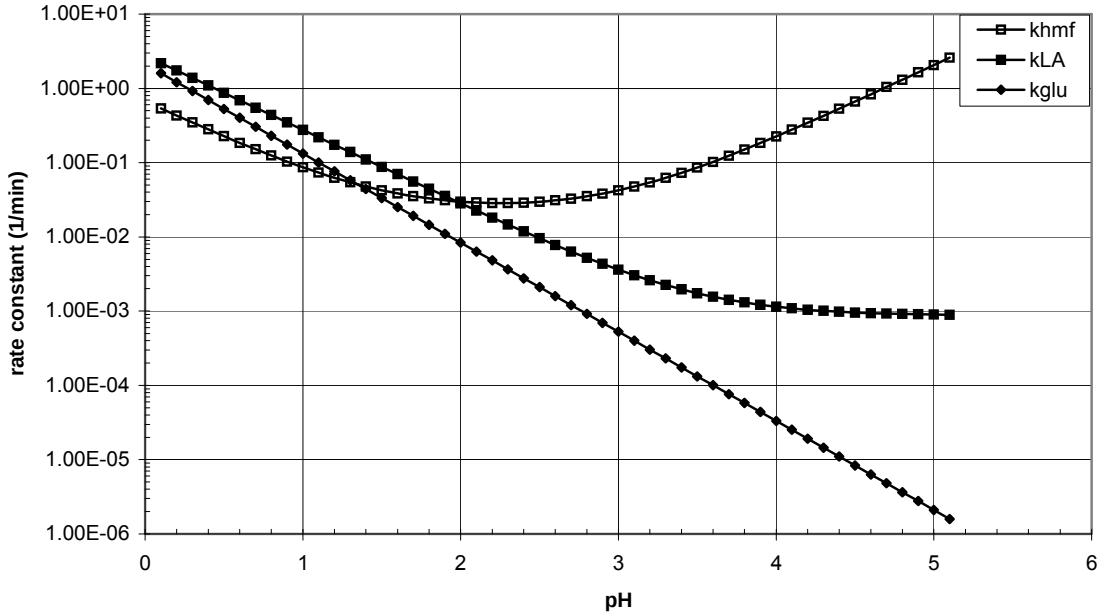


Figure A2. Rate constant versus pH at 200°C



The dependency of the rate constant on the temperature at constant pH is shown in figures A3 and A4.

Figure A3. Rate constant verus Temperature at pH=1

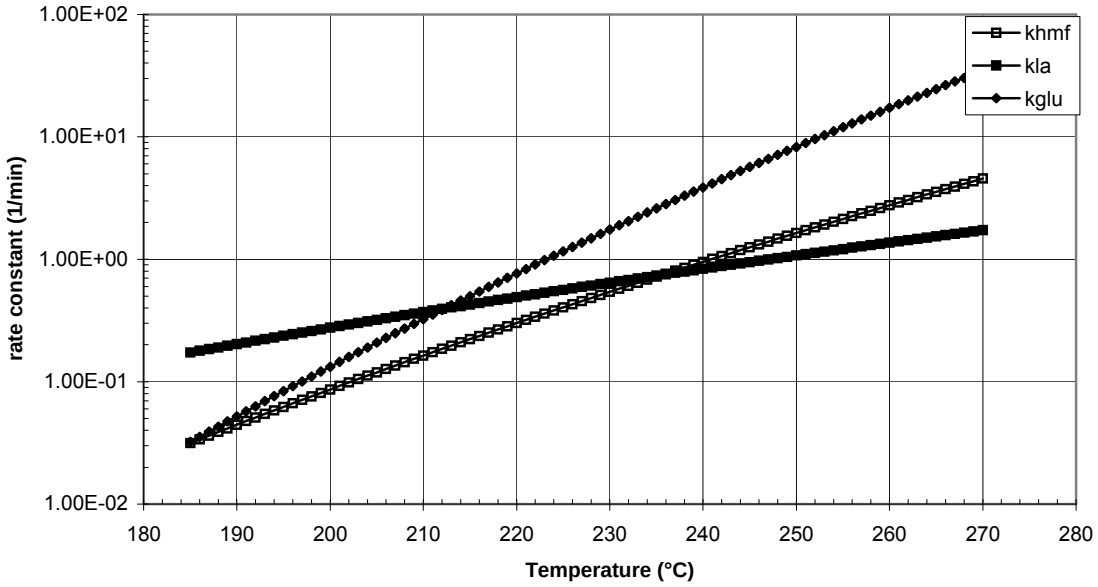
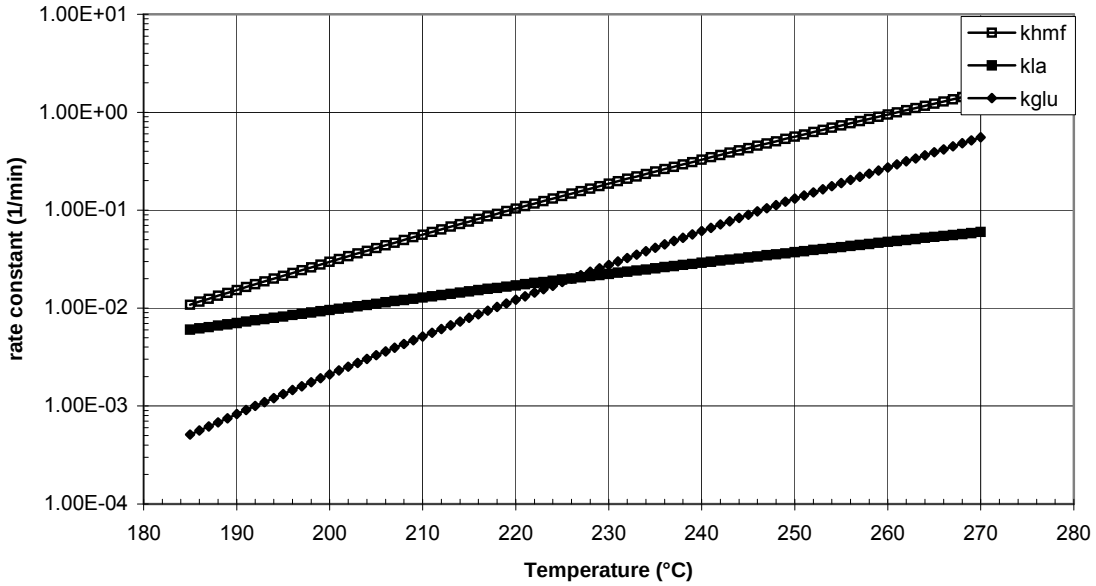


Figure A4. Rate constant verus Temperature at pH=2.5



Furfural formation

The furfural formation from hemicellulose can be described as:

$$\text{Hemicellulose} \xrightarrow{k_{xyl}} \text{Xylose} \xrightarrow{k_{Fur}} \text{Furfural}$$

The hydrolysis rate of hemicellulose is assumed to have the same rate constant as the hydrolysis of cellulose, because no literature references were found on this subject.

The furfural formation rate constant is dependant on pH and temperature. According to reference [69], the dependency of the rate constant on the temperature is the following:

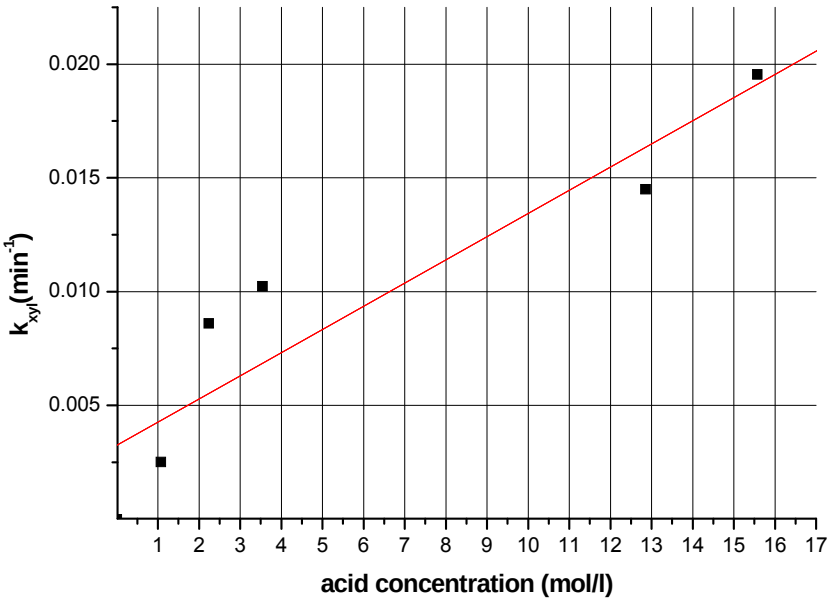
$$k_{xyl} = 4.80 \cdot 10^{12} \exp(-121,000 / RT) \qquad \text{(A9)}$$

Unfortunately no acid concentration was given for this relation. Reference [43] gives a dependency on the pH shown table A1 and figure A5.1. Unfortunately no temperature was given for this relation.

Table A5.1. The dependency of the rate constant on the acid concentration

Concentration of H_2SO_4 ($\%_{mass}$)	Concentration of H_2SO_4 (mol/l)	$k_{xyl} \cdot 10^2$ (min^{-1})
10	1.07	0.251
20	2.24	0.816
30	3.54	1.024
60	12.85	1.450
90	15.57	1.954

Figure A5. Rateconstant k_{xyl} versus the acid concentration



A linear dependency is assumed. This gives with the use of the program 'origin' the following equation:

$$k_{fur} = 0.00102 \cdot 10^{-pH} \qquad \text{(A10)}$$

Symbols and subscripts

symbol	meaning	unit
τ	residence time	min
k_i	rate constant	min
r_i	reaction rate	kg/(m^3min) or mol/(m^3min)
c_i	concentration	kg/m^3 or mol/m^3
$c_{i,0}$	concentration in feedstream	kg/m^3 or mol/m^3

subscripts

glu	glucose
cel	cellulose
xyl	xylose
LA	levulinic acid
exp	experimental value from reference [4] or [18]
calc	calculated value with formula 2.1 - 2.4
CSTR	continued stirred tank reactor
PFR	plug flow reactor

APPENDIX 6 EQUIPMENT DESIGN/SPECIFICATIONS

A6.1 DECANTER DESIGN

According to reference [57] a rough design of a decanter can be made by taking a hold-up time of 3 to 10 minutes. Here, the decanter vessel is sized on the basis that the velocity of the continues ('heavy') phase must be less thsn the settling velocity of the droplets of the discharged ('light') phase. Plug flow is assumed, and the velocity of the continues phase is calculated using the area of the interface:

$$u_c = L_c / A_i < u_d \tag{A6.1}$$

Stokes' Law is used to determine the settling velocity of the droplets:

$$u_d = \frac{d_d^2 g(\rho_d - \rho_c)}{18\mu_c} \tag{A6.2}$$

Than for a vertical, cylindrical decanter the area of interface is:

$$A_i = \pi r^2 \tag{A6.3}$$

Design parameters (at 195°C and 16 bar) to separate levulinic acid from water/sulphuric acid are (see also stream summary, stream # 7):

Flow rates:	densities	viscosities
Φ_{LA} = 12200 kg/hr	ρ_{LA} = 1000 kg/m^3	μ_{LA} = 0.28 mNs/m^2
Φ_{water} = 920 kg/hr	ρ_{water} = 920 kg/m^3	μ_{water} = 0.15 mNs/m^2
Φ_{sulph} = 7200 kg/hr	ρ_{sulph} = 7200 kg/m^3	μ_{sulph} = 1.76 mNs/m^2
Φ_c = 8120 kg/hr	ρ_c = 1570 kg/m^3	μ_c = 1.57 mNs/m^2

A droplet size of 75 μm is assumed [ref 57]. An average (by weight) density and viscosity of the water/sulphuric acid mixture are taken.
With formula A6.2, the rising velocity of the droplets is calculated, u_d = 1.11 x 10^{-3} m/s. Because this flowrate is low, a cylindrical, vertical vessel is used. The volumetric flowrate of the continues flow rate is calculated with:

$$L_c = \frac{\varphi_c}{\rho_c} \cdot \frac{1}{3600} \tag{A6.4}$$

This flow rate is L_c = 1.44 x 10^{-3} m^3/s. Then with A6.2, the interface area is calculated: A_i = 0.1.29 m^2. The radius will be (A6.3): 0.64 m so the diameter is 1.28 m. Taking the height as twice the diameter, it will be 2.56 m. The dispersion band is taken as 10 % of the height: 0.256 m.

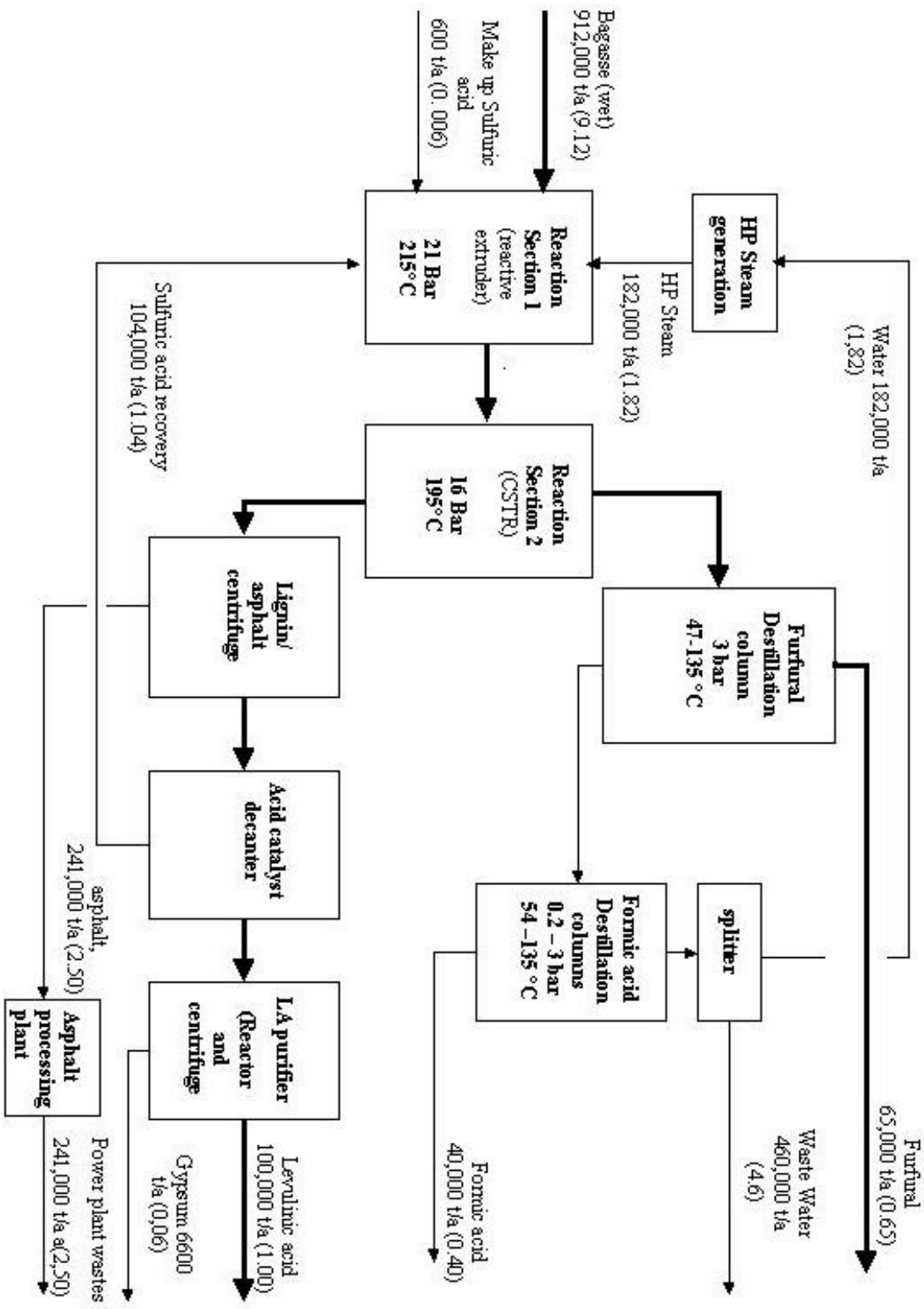
Checking the residence time of the droplets in the dispersion band:

$$t = \frac{h_d}{u_d} \tag{A6.5}$$

This residence time is 239 s, which is according to the reference satisfactory.

A6.2 CALCULATION OF THE HEAT EXCHANGE NETWORK AREA

APPENDIX 7. BLOCK SCHEME



APPENDIX 8: BAGASSE, HANDLING AND STORAGE

The residue remaining of sugar cane, after the juice cane has been removed, is called bagasse. The bagasse needed for the production of 100 kton/annum levulinic acid amounts 1.000 kton/annum of wet bagasse. Since the harvesting period lasts only for 4-6 months (the latter has been chosen for the warm region of Sao Paolo), half of this material will have to be stored.

In Louisiana/ Florida there was a storage place for 450 000 tons in 3 lots, 150 000 tons each. This worked properly and nearly automatic. Distribution was done with belt conveyors and bulldozers.

A problem with storage is losses due to fermentation. Approximately 20 to 30% during the first three months of storage can be lost; then the temperature inside the pile has increased (due to fermentation) to a temperature that stops the microorganisms and no further losses occur.

When bagasse is stored in bulk [A*] (see Figure A7.1) it will keep its wetness of 50%. Only the outer shelter (5 to 10 cm) will get wetter due to rain, but the rain will not penetrate to the inner part. It will dry if you produce bales (see Figure A7.2) and if you store the bales in a way that air can take off the water.

To avoid the loss you have 3 possibilities

1) Increase the moisture to more than 50% or
2) Decrease the moisture to less than 25%;
   In both cases microorganism are not active. Or
3) Add chemicals to kill the microorganisms.

Ad 1: This is utilized where a higher moisture content is no problem or even required, e.g. in wood factories.
Ad 2: This is utilized when bagasse is used as fuel for boilers for co-generation plants [A*] is utilized in case of fuel too. [3] too, in former times, but is too expensive.
Bagasse can be dried:

- Mechanically with hot flue gases (too expensive)
- By producing pellets/ briquettes etc. (both expensive too, but may be an alternative for the future) By producing large bales and store them properly. In this case there will still be some losses, but energy content will be higher due to less moisture. Therefore this is done in case of use as fuel only.

Baling is an advantage, for example, if the bagasse is used as fuel for co-generation and power plants. The advantage of baling is that the bagasse dries. This increases the energy content; in a power plant you can get more kW out of the same quantity of bagasse and

this will balance the costs for baling. When the bagasse has to be wet for processing anyway (tissue production for example) the bagasse is kept/increased in wetness.

Baling is cost intensive (personnel, equipment, maintenance). In cane sugar countries land is not very expensive and baling would save 10 to maximum 30% storage area only, because of a maximum storage height of approximately 12m. Bulk stores can be much higher.

Bulky stored bagasse with 50% wetness reaches a temperature of 60-65°C after 6-7 days, until then approximately 10% fibre is lost due to fermentation (and 10% water is evaporated, too; therefore the remaining bagasse has still 50% wetness). With the temperature of 60 to 65°C fermentation continues with 1% per month, only.

In sugar cane plants the bagasse is finally eluted with water of 90°C to extract the last sugar. Therefore the bagasse pile easily reaches a temperature of 50°C. And fermentation will not be too strong. Temperature will rise some and after that drop some but will be around the 50°C. This temperature is therefore chosen constant in the process, as well as the wetness of bagasse. [71, 72, 77, 78]

APPENDIX 9. EQUIPMENT SPECIFICATIONS

APPENDIX 10 PROCESS FLOW SHEET

APPENDIX 11 UNIT COSTS

Table A11.1 Column costs

#	height	diameter	material factor	SS extra factor	pressure factor	bare column costs (k£)	total costs @ 1992 (k£)
CO1	55	1.06	2	1	1	45	90
CO2	20	3.24	2	1.5	1	50	150
CO3	15	0.8	2	1.5	1	15	45

# of plates	diameter	material factor	extra ss factor	bare plate costs (£)	total plate costs @ 1992 (£)	total column costs (k£)	total costs @ 2002 (k€)
78	1	1.7	1	180	23868	113.868	249.5989
28	3	1.7	1.5	700	49980	199.98	438.3565
22	0.8	1.7	1.5	150	8415	53.415	117.0858
					total	367.263	805.0412

Table A11.2. Decanter costs

#	heigth	diameter	material	SS extra	pressure factor	bare vessel costs	total cost @ 1992 (k£)	total costs @ 2002 (k€)
1	2.56	1.28	4	1	1.2	4	19.2	42.08644

Table A11.3. Reactor costs.

Reactor	Height	Diameter	Material factor	Extra SS factor	Pressure factor	Bare vessel costs	total cost @ 1992 (k£)	total costs @ 2002 (k€)
CSTR	6.4	3.2	2	1.5	1.2	15	64.80	142.04
extruder	1.92	0.96	2	1.5	1.2	2	8.64	18.93
extruder mix	1.92	0.48	2	1.5	1.2	1.5	10.80	47.34
motor/pump	73	700	0.8				13.78	23.15
gypsum reactor	0.7	0.35	2	1.5	1	1.1	3.96	8.68
						total	101.98	240.16

Table A11.4. Pump costs

#	characteristic size parameter	cost constant	index	costs (£)	costs @ 2002 (€)
P01	1.6	700	0.8	302.13	507.57
P02	0.16	700	0.8	30.213	50.757
P03	0.13	700	0.8	24.548	41.24
P04	3.434	700	0.8	648.45	1089.39

Table A11.5. Boiler costs

#	characteristic size parameter	cost constant	index	costs (£)	costs @ 2002 (€)
1	50	30	0.8	759.7435	1276.359
2	50	30	0.8	759.7435	1276.359
3	50	30	0.8	759.7435	1276.359
			total	2279.231	3829.078

Table A11.6. Condensor costs

#	characteristic size parameter	cost constant	index	costs (k£)	costs @ 2002 (k€)
1	1000	6000	0.53	100.55	168.93
2	1000	6000	0.53	100.55	168.93
3	1000	6000	0.53	100.55	168.93
			total	301.67	506.81

Table A11.7. Centrifuge costs

#	characteristic size parameter	cost constant	index	costs (k£)	costs @ 2002 (k€)
1	1	30000	1	30000	50399.61
2	0.5	30000	1	15000	25199.8
			total	45000	75599.41

Table A11.8. Storage tank costs

product	characteristic size parameter	cost constant	index	costs (k£)	costs @ 2002 (k€)
LA	7500	3000	0.55	613024.7	1029873
Furfural	6000	1200	0.55	296279	497744.9
Formic	2500	3000	0.55	204341.6	343291.1
			total	1113645	1870910

HEAT EXCHANGER – SPECIFICATION SHEET

EQUIPMENT NUMBER	**:** **E-04**	**In Series**	**:** 1
NAME	**:** **C-01 Reboiler**	**In Parallel**	**:** none

General Data

Service	**:**	**- ~~Heat Exchanger~~**	**- ~~Vaporizer~~**
		- ~~Cooler~~	**- Reboiler**
		- ~~Condenser~~	
Type	**:**	**- ~~Fixed Tube Sheets~~**	**- ~~Plate Heat Exchanger~~**
		- ~~Floating Head~~	**- ~~Finned Tubes~~**
		- ~~Hair Pin~~	**- Thermosyphon**
		- ~~Double Tube~~	**-**
Position	**:**	**- ~~Horizontal~~**	
		- Vertical	

Capacity	**[kW]**	**:**	19787	**(Calc.)**
Heat Exchange Area	**[m^2]**	**:**	255	**(Calc.)**
Overall Heat Transfer Coefficient	**[$W/m^2.^oC$]**	**:**	1000	**(Approx.)**
Log. Mean Temperature Diff. (LMTD)	**[^oC]**	**:**	77.7	
Passes Tube Side		**:**	1	
Passes Shell Side		**:**	1	
Correction Factor LMTD (min. 0.75)		**:**	1.0	
Corrected LMTD	**[^oC]**	**:**	77.7	

Process Conditions

			Shell Side	**Tube Side**
Medium		**:**	HP steam	Furfural / Water
Mass Stream	**[kg/s]**	**:**	0.17	1.46
Mass Stream to				
- Evaporize	**[kg/s]**	**:**	-	1.46
- Condense	**[kg/s]**	**:**		-
Average Specific Heat	**[$kJ/kg.^oC$]**	**:**	1.94	
Heat of Evap. / Condensation	**[kJ/kg]**	**:**	2200	
Temperature IN	**[^oC]**	**:**	410.0	298.5
Temperature OUT	**[^oC]**	**:**	350.0	298.5
Pressure	**[bara]**	**:**	40.0	16
Material *(1)*		**:**	CS	CS

Remarks:
(1)CS = Carbon Steel

Designers : D. van Benthem, P. ten Holder, S. Smallegange	Project ID-Number : **CPD3271** Date : Februari 6 2002