

# CAPCOM-NL

D2: Proof Of Concept

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# 1 Introduction

In this document, the Proof of Concept of production of CAPCOM's (Clean Agro Pellet COMmodities) will be investigated. The commodities will be produced from agro residues and ligno cellulosic crops using a combination of Counter Current Simulated Moving Bed (CC SMB) Extraction and pretreatment. Chapter 2 will focus on CC SMB extraction and chapter 3 will focus on steam explosion pretreatment. Chapter 4 discusses the properties of the resulting CAPCOM's in relation to its intended applications.



# 2 Counter Current Simulated Moving Bed (CC SMB) extraction

In this chapter, Counter Current Simulated Moving Bed Extraction (CC SMB extraction) will be investigated. Several materials were prepared (see D1) and tested in small and medium scale preliminary experiments (paragraph 2.4). These experiments were used to test models and find values for important model parameters. Based on these preliminary experiments, 2 large scale trials were performed (paragraph 2.5).

# 2.1 Introduction to CC SMB extraction

In CC SMB extraction, a series of columns is applied to efficiently extract the target components from the biomass (Figure 1). The extraction liquid runs from top to bottom through each column. After a certain period (the switch time), valves are actuated to shift the liquid flow to the next column. This way, it seems as if the solids are moving from right to left.



Figure 1 Counter Current Simulated Moving Bed Extraction

In this project, the target components are monovalent ions such as  $K^+$ ,  $Na^+$  and  $Cl^-$ . All of these are highly soluble in water and therefore water was chosen as the elution liquid.

### 2.2 Theory

According to Kremser [1], the extraction efficiency in counter current processes without mass transfer limitations is determined by the extraction factor (E).

### **Equation 1** $E = \frac{\Phi_1}{\Phi_2} \cdot m$

Where:

- E is the dimensionless extraction factor
- $\Phi_1$  is the flow rate of phase 1 (the extraction liquid) in kg/hr
- $\Phi_2$  is the flow rate of phase 2 (the extracted material) in kg/hr
- m is the dimensionless distribution quotient of the target component over phase 1 and 2

In this case, phase 1 and phase 2 are both water (free flowing water and water absorbed in the biomass respectively). Therefore, we may presume that m is equal to one.

Kremser [1] showed that if E > 1, it is possible to (almost) fully recover all of the target component within a finite amount of equilibrium stages. In our case m = 1, so the extraction liquid flow rate should be slightly larger than the biomass adsorbed water flow rate.

### 2.3 Method

#### 2.3.1 Flow direction

Columns can be extracted with extraction liquid flowing from bottom to top (column fully filled with biomass and extraction liquid) or from top to bottom (column mainly filled with air, extraction liquid trickling down the biomass). As our biomasses have very low stacking densities (typically 100 kg/m<sup>3</sup> - 500 kg/m<sup>3</sup> (wet)), the void volume is very large.

Let us take a column of 1 m<sup>3</sup> that is filled with 100 kg dry biomass. In this biomass, 300 kg of water is absorbed. The extraction liquid runs from bottom to top. In order to fully replace all the extraction liquid once, at least 1500 kg of water is needed (600 kg to fill the void volume and then another 900 kg to replace all liquid in the column). So the extraction factor will be at least 5. If, however, the extraction liquid flows from top to bottom, the extraction liquid flow rate can be chosen much smaller (just above 300 kg). Therefore top down flow was chosen as the best option.

#### 2.3.2 Conductivity as a proxy for Potassium concentration

Conductivity should be a good proxy for the concentration of soluble monovalent ions (Figure 2). Measurement of conductivity is easy and cheap and therefore, many measurements can be done to produce a time series. The concentration of potassium was measured with LCK228 and was directly proportional to the conductivity measurements (Figure 3). This confirms that conductivity measurement can indeed be used as a proxy for the presence of monovalent salts.



*Figure 2 Conductivity of KCI solutions as a function of concentration according to literature* 



Figure 3 Measured conductivity and potassium concentration

# 2.4 One column trial experiments

The trial experiments were performed in a glass column with a diameter of 8 cm and a height of 0.5 m. The column was packed with biomass material. A layer of plastic balls (normally used to cover heating baths (diameter approx. 2 cm)) or special plastic Pall cylinders were added to reach even liquid distribution over the column. Then the column was closed. The extraction liquid was added at the top and collected at the bottom. The conductivity was measured and plotted on a log scale. The slope of the curve was derived.

Experiment	E13
Date	11/6/2019
Operator	WD
Material type	Miscanthus
Preparation	As received
Starting material	VIR 0001
Produced material	FBR 0005

#### 2.4.1 Miscanthus

This experiment was carried out with *Miscanthus* delivered by Viride. Viride has received this material from Cradle Crops before the start of the project. From the elution profile (Figure 4), a mass transfer rate of 0.4 /hr was derived.



Figure 4 Effluent conductivity during extraction of Miscanthus

COD measurements (with LCK 514) indicated that 1.85% of the dry matter was lost with the effluent. The dry matter loss according to dry matter measurements of starting material and final material showed a dry matter loss of 5.6%. The COD measurements do not include the loss of minerals. This may partially explain the difference.

Experiment	E14
Date	7/6/2019
Operator	WD
Material type	Miscanthus
Preparation	Pretreated
Starting material	VIR 0002
Produced material	FBR 0006

#### 2.4.2 Pretreated Miscanthus (VIR 0002)

This experiment was carried out with steam pretreated Miscanthus delivered by Viride. The starting material was the same as used in the experiment described in paragraph 2.4.1. From the elution profile (Figure 5) a mass transfer rate of 4 /hr at the start and 1.0 /hr in later stages was derived. This shows that steam explosion has increased the mass transfer rate.



Figure 5 Conductivity of effluent during extraction of pretreated Miscanthus

The COD measurements showed a 13% loss of COD in the extract, which is in accordance with a 12% loss of dry matter (dry matter of starting material minus dry matter of treated material). It is clear that dry matter losses are higher with pretreated material than with native material.

Experiment	E22
Date	16/10/2019
Operator	WD
Material type	Miscanthus
Preparations	As received
Starting material	CC 0002
Produced material	

2.4.3 Miscanthus as delivered by Cradle Crops (CC 0002)

This experiment was carried out with Miscanthus delivered by Cradle Crops. The starting material was harvested, chopped, dried and baled by Cradle Crops. From the elution profile (Figure 6), it is seen that in the beginning the mass transfer is dominated by the dilution rate (no mass transfer limitation), but after 1 hour, the mass transfer rate is significantly reduced (0.5 /hr).



Figure 6 Conductivity during extraction of Miscanthus

After the extraction experiment, the column was split in two parts and left to drip dry. The water that dripped out was collected and the conductivity was measured. Water drained from the top half of the column had a higher conductivity (47.9  $\mu$ S/cm) than water drained from the bottom half (21.7  $\mu$ S/cm). Probably the liquid had not been evenly distributed over the top half of the column. The conductivity was close to the values measured at the end of the experiment proving that indeed most of the salts had been removed by then.

At the end of the experiment, the Miscanthus had a dry matter content of 22%. This shows that Miscanthus has a very high water holding capacity.

Experiment	E6	
Date	5/12/2019	
Operator	WD	
Material type	Miscanthus	
Preparations	Hammer mill	
	Cutting 6.25 mm	
	Cutting mill < 8 mm	
	Cutting mill < 2 mm	
Starting material	FBR 0007	
Produced material	FBR 0011	

#### 2.4.4 Milled Miscanthus (FBR 0007)

For this experiment the Miscanthus delivered by Cradle Crops was hammer milled and then milled twice in the cutting mill with a 8 mm and a 2 mm sieve. This resulted in a very fine material. From the elution profile (Figure 7), it is seen that the mass transfer rate was 1.5 /hr. This is faster than the original material, but lower than expected as the material size had significantly been reduced. Miscanthus has channels that run in the direction of growth (to transport water). After milling it was observed that the material is mostly split along the direction of growth. Therefore, the particles do get smaller, but the length of the channels does not decrease significantly. This might explain the disappointing results obtained after milling.



Figure 7 Conductivity during extraction of milled Miscanthus

Experiment	E18
Date	15/4/2020
Operator	WD
Material type	Sugar Cane Trash
Preparation	Cutted 6.25 mm
Starting material	FBR 0013
Produced material	FBR 0014

#### 2.4.5 Sugar Cane Trash, cutted (FBR 0013)

For this experiment, the Sugar Cane Trash delivered by Raizen was chopped at 6.25 mm. From the elution profile (Figure 8), it is seen that the mass transfer is 1.1 /hr in the beginning, but reduced to 0.25 /hr later in the experiment.



Figure 8 Conductivity during extraction of sugar cane trash

After standing for a while, a high concentration of potassium in the drainage water was observed (231 mg/liter). This is considerably higher than the concentration in the extraction liquid (29.8 mg/liter) and proves that the effluent from the column was not at equilibrium with the biomass in the column. This is also apparent from the low mass transfer rate (0.25 /hr) as compared to the applied dilution rate (6.6 /hr)

#### 2.4.6 Sugar Cane Trash, cutted, sieved and milled

Experiment	E16	
Date	23/4/2020	
Operator	WD	
Material type	Sugar Cane Trash	
Preparation	Cutted 6.25 mm	
	Sieved < 10 mm	
	Cutting Mill < 8 mm	
Raw material	FBR 0015	
Produced material	FBR 0016	

Sucar cane was further treated with a cutting mill (sieve 8mm) to increase the mass transfer rate. The elution profile indeed shows improved mass transfer (Figure 9).



Figure 9 Conductivity during extraction of sugar cane trash treated with cutting mill

Experiment	E27
Date	11/3/2020
Operator	WD
Material type	EFB
Preparation	
Starting material	FBR 0008
Produced material	FBR 0014

2.4.7	Empty	fruit	bunch	(FBR	0008)
2.1.7	Linpey	nuic	bunch		0000)

Mass transfer during extraction of EFB was much faster than with Miscanthus and Sugar Cane Trash (Figure 10). After shredding of EFB, a spaghetti like structure is observed with a diameter smaller than 1mm. These long and thin fibres are a natural property of EFB. This ensures short diffusion distance and fast mass transfer.



Figure 10 Conductivity during extraction of EFB

# 2.5 Counter Current Simulated Moving Bed Extraction pilot experiments

The situation in the pilot installation is different from a situation in practice. Therefore, it was not possible to apply the ideal settings for counter current extraction at the pilot scale. It was chosen to have a higher liquid over solids ratio than the factor 1.1 explained in paragraph 2.6. Three reasons for this are given here:

- 1. to ensure sufficient extraction in limited time and space
- 2. to compensate for the lower number of columns in the pilot compared to a full scale installation (our main goal is to prepare material for further experiments, not to minimize water usage)
- 3. to allow sufficient liquid flow for even liquid distribution (a full scale installation will be higher and therefore, the superficial liquid flow will be higher at large scale, also recirculation could be applied at larger scale and not in the current pilot facility)

The experiments were conducted with 3 counter current columns with a diameter of 25 cm and a height of 1 m.

Experiment	E1	
Date	16/3/2020	
Operator	WD	
Material type	EFB	
Preparation	Shredded	
	Cutted 6.25 mm 2x	
Starting material	FBR 0008	
Produced material	FBR 0009	

#### 2.5.1 CC SMB extraction of Empty Fruit Bunch (FBR 0008)

Empty Fruit Bunches were prepared and soaked in water. After soaking, the biomass was put in columns. The flow rate was set at 27 liter/hr, L/S ratio = 24). Air is added to push the liquid from the bottom of one column to the next column. The switch time was set at 2 hours. Table 1 shows the active columns during the procedure. During start up, column 1, 2 and 3 are extracted. After 6 hours, the first switch is made. After 12 hours, the active columns are phased out.

Table 1	Active col	umns during CC SM	B extraction of
From (hr)	Till (hr)	Active columns	Remark
0	2	1,2,3	Start up
2	4	1,2,3	Start up
4	6	1,2,3	Start up
6	8	2,3,4	
8	10	3,4,5	
10	12	4,5,6	Ending
12	14	5,6	Ending
14	16	6	Ending

During start up, columns 1 till 3 behave like one very large column. The reduction of conductivity is very good. On a log scale the slope of the curve is around 0.6 /hr, the same value we found in paragraph 2.4.7.



Figure 11 Conductivity of effluent during start up of EFB CCE

At the end of the procedure, column 4, 5 and 6 act as one column. It is clearly seen that after passage of the liquid with high conductivity from the last newly added column 6 (at 11 hours), the conductivity drops to even lower values.



Figure 12 Conductivity of effluent at end of EFB CCE

After soaking of the biomass at the start of the experiment, the conductivity was 10 mS/cm. At the end of the experiment (Table 2) the conductivity was reduced by more than a factor 40 (>98% reduction).

Table 2	Cond	uctivity of drain water from columns after experiments
Column	μS/cm	
1	252	
2	229	
3	91	
4	224	
5	98	
6	112	

From Table 3 it is seen that the Potassium concentration is highly reduced. Other components such as Sodium, Magnesium, Phosphorous, Manganese and Zinc are also reduced. Relative abundance of iron is slightly increased due to the removal of other components.

Table 3	Results of CCE SI	MB for EFB (E	urofins)
Label	Unit	FBR 0008	FBR 0010
Description	Unit	EFB	EFB extracted
Dry Matter	g/kg	899	795
Moisture	g/kg	44	51
ADL	g/kg DM	76	84
NDF	g/kg DM	816	907
ADF	g/kg DM	536	600
Sodium	g/kg DM	0.3	0.1
Potassium	g/kg DM	20.7	1.3
Magnesium	g/kg DM	1.4	0.5
Calcium	g/kg DM	2	1.9
Phosphorous	g/kg DM	1.2	0.3
Sulphur	g/kg DM	0.8	0.5
Manganese	mg/kg DM	21	15
Zinc	mg/kg DM	22	11
Iron	mg/kg DM	473	680
Copper	mg/kg DM	10.5	8
Hemi Cellulose*	g/kg DM	280	307
Cellulose*	g/kg DM	460	516
Acid Detergent	g/kg DM	76	84

\*Hemi Cellulose, Cellulose and Acid Detergent Lignin were calculated from ADL, NDF and ADF (Hemi cellulose = NDF- ADF, Cellulose = ADF - ADL, Lignin = ADL)

Ultimate analysis by SGS revealed that Chlorine is reduced from 0.36% to below the detection limit of 0.01% (Table 4). Ash was reduced from 5% to 2% and Potassium in the ashes was reduced from 47% to 6%, so a 95% reduction was achieved. The Shrinking Starting Temperature (SST) was reduced from 910 to 890 °C. The flow temperature (FT) was increased from 1180 to 1410 °C.

Table 4         Results of CCE SMB for EFB (SGS)					
Label		EFB	EFB		
Description	Unit	FBR 0008	FBR 0010		
Ash (550°C)	w%	5.13	2.06		
Ash (815°C)	w%	4.2	2.01		
Chlorine	w%	0.36	0.01		
Shrinkage starting temperature SST	°C	910	740		
Deformation temperature DT	°C	1040	1150		
Hemisphere temperature HT	°C	1150	1360		
Flow temperature FT	°C	1180	1410		
SiO2	w% of ash	24.48	59.5		
AI2O3	w% of ash	0.29	1.41		
TiO2	w% of ash	0.03	0.17		
P2O5	w% of ash	3.93	5.27		
SO3	w% of ash	3.44	6.19		
Fe2O3	w% of ash	0.38	1.9		
CaO	w% of ash	5.68	13.48		
MgO	w% of ash	5.71	5.05		
Na2O	w% of ash	0.79	0.5		
К2О	w% of ash	46.92	5.92		
MnO	w% of ash	0.04	0.05		

### 2.5.2 CC SMB extraction of Sugar Cane Trash

Experiment	E4
Date	11/5/2020
Operator	WD
Raw material	FBR 0023
Preparation	
Produced material	FBR 0017

A liquid flow rate of 12.5 liter/hr was applied (L/S ratio = 15.6). Nine columns were extracted according to the scheme in Table 5.

Table 5	Active columns durin	g large scale extrac	ction experiment
From (hr)	)	Active columns	Remark
0	2	1,2,3	Start up
2	4	1,2,3	Start up
4	6	1,2,3	Start up
6	8	2,3,4	
8	10	3,4,5	
10	12	4,5,6	
12	14	5,6,7	
14	18.5	6,7,8	Troubles with flow
18.5	20.5	7,8,9	Ending
20.5	22.5	8,9	Ending
22.5	25	9	Ending

The conductivity of the effluent reduces in time. After 4 hours a plateau is reached.



Figure 13 Conductivity of effluent during start up of SCT CCE

At the end of the experiment the conductivity drops to around 40  $\mu$ S/cm (very comparable to the one column trial results (paragraph 0).



Figure 14 Conductivity of effluent during ending

After soaking of the biomass at the start of the experiment, the conductivity was 1.9 mS/cm. At the end of the experiment (Table 6) the conductivity was reduced by more than a factor 10 (>90% reduction).

Table 6	Conductivity of drain water from columns after expe	
Column	μS/cm	
1	208	-
2	76	
3	79	
4	180	
5	204	
6	126	
7	61	
8	145	
9	126	

From Table 7Table 3 it is seen that Potassium is reduced by almost a factor 10. Other components are also reduced. Again, iron is increased.

Table 7 R	esults of CCL	SMB for S	SCT (Eurofins)
Label		FBR 0015	FBR 0018
Description	Unit	SCT	SCT extracted
Dry Matter	g/kg	900	888
Moisture	g/kg	35	47
ADL	g/kg DM	60	58
NDF	g/kg DM	780	782
ADF	g/kg DM	471	466
Sodium	g/kg DM	0.1	0.1
Potassium	g/kg DM	4.6	0.5
Magnesium	g/kg DM	1.4	1
Calcium	g/kg DM	2.9	2.8
Phosphorous	g/kg DM	0.5	0.2
Sulphur	g/kg DM	1.1	0.5
Manganese	mg/kg DM	132	121
Zinc	mg/kg DM	11	12
Iron	mg/kg DM	1971	2972
Copper	mg/kg DM	4.4	5.2
Hemi Cellulose*	g/kg DM	309	316
Cellulose*	g/kg DM	411	408
Acid Detergent Ligni	n* g/kg DM	60	58

\*Hemi Cellulose, Cellulose and Acid Detergent Lignin were calculated from ADL, NDF and ADF (Hemi cellulose = NDF- ADF, Cellulose = ADF – ADL, Lignin = ADL)

Ultimate analysis by SGS has revealed that Chlorine is removed below the detection limit. Ash increased from 5.4% to 7.9%. The reported increase of the ash content is highly unlikely. If it is assumed that SiO<sub>2</sub> is fully retained in the ashes during extraction, the ash content would drop to 3.9% (as shown in Table 8). Potassium in the ashes was reduced from 10.4% to 1.6%. If the ash content after extraction is presumed to be 3.9% after extraction, the potassium content of the sample is in accordance with the value measured by Eurofins. The Shrinking Starting Temperature (SST) was reduced from 890 to 840 °C. Flow temperature (FT) decreased from 1320 to 1290 °C.

Table 8 Results of CCE SME	B for SCT (SGS	5)	
Label		FBR 0015	FBR 0018
Description	Unit	SCT	SCT extracted
Ash (550°C)	w%	5.41	3.9
Ash (815°C)	w%	5.31	7.6
Chlorine	w%	0.089	0.01
Shrinkage starting temperature SST	°C	890	840
Deformation temperature DT	°C	1280	1180
Hemisphere temperature HT	°C	1300	1250
Flow temperature FT	°C	1320	1290
SiO2	w% of ash	41.21	56.52
AI2O3	w% of ash	8.89	11.75
TiO2	w% of ash	1.7	2.4
P2O5	w% of ash	3.74	1.77
SO3	w% of ash	6.13	3.07
Fe2O3	w% of ash	6.33	7.37
CaO	w% of ash	12.81	10.3
MgO	w% of ash	7.33	4.63
Na2O	w% of ash	0.43	0.13
K2O	w% of ash	10.43	1.59
MnO	w% of ash	0.37	0.28

### 2.6 Modelling

#### 2.6.1 Mass transfer

The mass transfer rate is the most important factor for the extraction process. It will determine the size of the equipment needed.

The mass transfer rate can be described with the following formula:

#### **Equation 2** $\phi = k \cdot a \cdot \Delta C$

Where:

 $\phi$  is the specific mass transfer rate in kg/(m<sup>3</sup>·hr)

k is the mass transfer coefficient in m/hr

a is the specific surface in  $m^2/m^3$ 

 $\Delta C$  \$ is the concentration difference in kg/m  $^3$ 

As described above, the shape and dimensions of biomass is highly irregular and not easily measured. Therefore, it is not possible to determine the specific surface (square meter of surface per cubic meter of column) of the biomass. At the same time, the mass transfer coefficient is a function of transport inside and outside the biomass. These are also not easily measured. Therefore, it was decided to determine k·a as one (lumpsum) parameter. This factor will be referred to as the volumetric mass transfer coefficient, in analogy to the transfer of oxygen in bioreactors, where a similar situation occurs.

#### 2.6.2 Elution profile of one column

Important information can be retrieved from the elution profile of one column. If the concentration in the liquid leaving the column is plotted on a logarithmic scale , it will follow a linear curve. The slope of this curve will be determined by three factors:

- 1. dilution rate
- 2. mass transfer limitation
- 3. column quality

The dilution rate can be calculated as follows:

# **Equation 3** $D = \frac{\Phi}{m_{ads}}$

Where:

- D is the dilution rate in /hr
- $\Phi$  is the liquid flow rate in kg/hr
- $m_{\text{ads}}$   $% m_{\text{ads}}$  is the mass of the liquid adsorbed in the biomass in kg

For a single equilibrium stage, the following equation will hold:

**Equation 4** 
$$\frac{dCH}{dt} = \frac{CH-C_{in}}{\frac{1}{k\cdot a}+\frac{1}{p}}$$

Where:

CH concentration in liquid adsorbed to the biomass (heap concentration) in kg/m<sup>3</sup>

C<sub>in</sub> liquid feed concentration in kg/m<sup>3</sup>

 $k \cdot a$  mass transfer coefficient in /hr

If the mass transfer rate  $(k \cdot a)$  is high, dilution will determine the slope of the line. If the mass transfer rate is low, mass transfer will determine the slope of the line. So: if the slope is less than the dilution rate, mass transfer limitation is apparent.

If mass transfer is highly limiting, the slope will get equal to the mass transfer rate. In an ideal system, mass transfer is not highly limiting, as this will lead to less efficient extraction (more extraction liquid needed to reach the same target component recovery).

If the slope is steeper than the dilution rate, the column quality is good and mass transfer limitation is absent. In this case, multiple equilibrium stages may be reached inside one column. In our experiments, this was never the case. Not only mass transfer limitation, but also uneven liquid distribution and back mixing may play a role here.



Figure 15 Effluent concentration (k·A=1 /hr, D=5 /hr)



Figure 16 Effluent concentration (k·A=5 /hr, D=1 /hr)



Figure 17 Effluent concentration (k·A = 5 /hr, D=5 /hr)

#### 2.6.3 Counter current SMB extraction

It was decided to model each column as a fully mixed extractor (i.e. one single equilibrium stage). This approach describes the results sufficiently well and makes modelling much easier. In practice it should be possible to reach more than one equilibrium stage. This model will then give a conservative estimate for the results at full scale.

Three important parameters should be chosen:

- 1. extraction liquid flow rate
- 2. column shift time
- 3. number of columns in series

The extraction liquid flow and the column shift time will determine the extraction factor E as well as the influence of mass transfer limitation.

Each parameter comes with its own considerations also in coherence with the other parameters.

1. extraction liquid flow rate

The larger the extraction liquid flow, the better the extraction, but the more diluted the extract. The extraction liquid flow should be chosen slightly higher than the flow of water adsorbed to the solids (see also column shift time).

#### 2. column shift time

The column shift time will determine the biomass throughput (flow of water absorbed in the solids). The lower the throughput, the better the extraction, but the larger the installation will be. If the column shift time is chosen is too fast, mass transfer limitation will kick in and extraction efficiency will be reduced. The column shift time should be a bit longer than the mass transfer characteristic time.

3. number of columns

In potential, an increase of the number of columns will improve the recovery without increasing the extraction liquid flow. This is especially true if the columns are operated close to equilibrium. The more columns, the larger the installation, the more space and capital is needed to process the biomass. This is the price we pay for high recovery with low extraction liquid flow.

Based on preliminary experiments, it was assumed that the characteristic time for mass transfer is around 0.5 /hr. Based on the experimental setup with 3 active columns at a time, a simulation with the following parameters was performed.

Extraction factor:	2.5
Number of heaps:	3
Number of switches:	6
Switch time:	2 hours

During start-up of a simulated moving bed, it will take some time for the concentration profile to develop. In Figure 18, this development is clearly seen. At the start of the run (nS = 0), the concentration in all heaps is 1. Heap 2 is fed with fresh biomass after each switch and therefore its concentration is highest. Heap 0 is always washed with fresh elution liquid and fed with biomass from heap 1 that was already washed before, therefore the concentration in heap 0 will quickly drop. After 6 switches, the profile is already well developed and a 85% reduction of salts is reached.





nS

Figure 18 Development of heap concentration profiles over time (nS)



*Figure 19 Development of concentration heap concentration profiles over time (nS)* 

After around 6 switches, the profile is fully developed. A salt removal of 85% is reached.

# 3 Pretreatment

In this chapter, Steam Explosion (SE) pretreatment will be investigated. SCB, EFB, and SCT were tested in a medium scale (kg) setup. Process conditions, expressed as severity factor variated from 3.6 to 4.6. Moisture content of the biomasses before and after steam explosion was registered during the experiments. Mass yields of steam explosion, drying, pelleting, and the total process are also presented. Appearance, bulk density, and water uptake of the pellets were analyzed as a preliminary evaluation of the CAPCOMs. A full evaluation of the CAPCOMs is shown in chapter 4.

### 3.1 Introduction to Steam Explosion Pretreatment

In SE pretreatment, the material is submitted to high-pressure saturated steam for a short period of time. An explosive decompression is created once the vessel is rapidly depressurized to atmospheric pressure. The initial material is converted into a fibrous dispersed solid and the lignocellulosic matrix is disrupted providing access to its polymeric sugars.

#### **Biomass**



Figure 20 Scheme steam explosion unit at bench scale, batch system

In this project, the type of material, temperature, and time will be studied. Their effect will be reflected on the handling properties of the pellets (durability, bulk density, hydrophobicity) and on the application in ethanol and energy production.

### 3.2 Theory

Temperature and residence time are essential to the SE pretreatment. Since both parameters are interrelated variables, their performance can be described through a single parameter. Overend and Chomet [2] developed a model that related temperature and residence time, known as the severity factor. This factor can be calculated as follow:

$$\log R_0 = \log \left( t * \exp^{((T-100)/14.75)} \right)$$

Where t is minutes and T is degrees Celsius, 100 is the reference temperature and 14.75 is the arbitrary constant  $\omega$  which is the activation energy from first-order kinetics.

As in this project, the severity factor allows for comparing between pretreatments carried out at different conditions and it correlates with the recovery yield after SE, the handling properties, EH yield and fuel properties.

### 3.3 Method

#### 3.3.1 Raw material

Sugar cane trash (SCT) and empty fruit bunches (EFB) were submitted to counter-current extraction and delivered by WUR for steam treatment, drying, and pelleting trials by Viride. Sugar cane bagasse (SCB) was used in its original state. No counter current extraction was required for SCB due to the low K and Cl content. EFB and SCT without counter-current extraction treatment were also selected for the trials to test the effect of K and Cl removal on combustion and ethanol applications.

#### 3.3.2 Steam explosion trials

A bench scale reactor was used for the steam explosion trials. It consisted of three parts: pressure reactor, cyclone and collection vessel. The reactor was filled with equal proportions of biomass up to 85 - 90 % capacity. Saturated steam was used to reach the desired conditions of temperature and time. Once the set time was accomplished, a sudden reduction of the pressure was promoted allowing the pretreated biomass to automatically transfer to the cyclone. The pretreated biomass was collected and taken for drying and pelleting.



*Figure 21* Steam explosion system at bench scale. Batch system. This picture was kindly provided by Bioprocess Pilot Facility for use exclusively in the CAPCOM project.

#### 3.3.3 Drying and pelletizing

The steam exploded material was first dried in a ventilation dryer cabinet until reaching approximately 30% moisture content. Biomass was spread out on trays and temperature was settled at 60°C. Once 30% moisture content was reached, biomass was transferred to the double cone drier to finish drying and to homogenize the biomass.



*Figure 22* Drying equipment. Left: Ventilation dryer cabinet. Right: Double Cone Dryer. This picture was kindly provided by Bioprocess Pilot Facility for use exclusively in the CAPCOM project.

Pelleting of the steam exploded and dried biomass was performed in a Khal pelletizer 14-175, die plate AKN13 chrome steel. Biomass was fed manually to the pelleting system. It was transported to the pellet press via a screw. A water pump is installed just after the screw to regulate manually the moisture content. Pellets are made in the pellet press and collected in a mesh band. Air is circulated through the mesh band and fines are collected at the end of the band. The amount of material produced during the steam treatment allowed one run of pelleting.



*Figure 23 Pelleting system: Feeding, pelletizing and cooling.* 

### 3.4 Results

Data collected during the trials are presented in Table 9. Steam explosion conditions expressed as severity factor ranged from 3.6 to 4.6. Moisture content of the biomasses before and after steam explosion was registered during the experiments. Mass yields of steam explosion, drying, pelleting and of the total process are also presented.

#### Table 9 Steam explosion trials. LOD before and after steam explosion

Mass yield of steam explosion (SE), drying, pelleting and total process. Final pellets were named as CAPCOM A,B,C,D,E,F,G,I.

Biomass	Conditioning	CAPCOM	Severity factor	LOD (%)		Yield (d.b.)			
			SF	before SE	after SE	SE	Drying	Pelleting	Total
EFB	Wet	1	3.6	55	78	1.24*	0.55**	0.73	0.40
	CCE- Dried	G	3.9	20	57	0.94	0.92	0.94	0.74
SCB	Dried	С	4.6	9	73	0.73	0.97	0.91	0.64
	Dried	В	4.2	9	69	0.82	0.83	0.94	0.66
	Wet	А	3.9	58	70	1.31*	0.68	0.92	0.77
SCT	Dried	F	4.6	13	77	0.58*	1.36	0.89	0.71
	Dried	E	4.2	8	65	0.87	0.97	0.92	0.72
	CCE - Dried	D	4.2	13	70	0.97	0.94	0.93	0.79

CCE: Counter current extraction. LOD: Loss on drying. d.b: dry basis.

\*Inaccuracy on LOD measurement.

\*\*Issues during drying. Biomass after steam explosion was directly fed to DCD. Due to the high moisture content, biomass balls were observed during the process. The balls impeded the proper drying of the biomass. After this first batch, a combination of ventilation dryer cabinet and DCD was used. The rest of the biomasses were dried with a combination of ventilation cabinet and DCD.

A quick lookup table starting from CAPCOM label is given below (Table 10).

Table 10	Quick le	ookup table starting
CAPCOM	Biomass	Severity factor (SF)
А	SCB	3.9
В	SCB	4.2
С	SCB	4.6
D	SCT	4.2
E	SCT	4.2
F	SCT	4.6
G	EFB	3.9
1	EFB	3.6

#### 3.4.1 Steam explosion system

All the biomasses, independently of the LOD before steam explosion, reached LOD values higher than 60% after SE. Dried and wet biomass was fed to the steam treatment reactor. Biomasses with LOD of 8% and 9% reached values of 65% and 73% after steam explosion. EFB after CCE and drying reached the lowest moisture increase (from 20% to 57%). SCT after CCE and drying followed the trend of the rest of biomasses reaching a moisture content of 70% after steam explosion. The data suggest that independently of the biomass type, preconditioning and LOD, all the biomasses tend to reach a water holding capacity close to 70%. No extra water was observed on the biomass after steam explosion. To better understand these measurements, a consumption of steam will be required. Within this project, it was not possible to perform such measurements. The steam explosion system lacked the measurement equipment.

#### 3.4.2 Severity factor and steam explosion yield

Severity factor and mass yields of steam explosion are plotted in Figure 24. EFB treated at severity factor of 3.9 had a SE yield of 94%. SCB and SCT treated at SF=4.2 had a SE yield between 82 and 97%. SCB and SCT treated at SF=4.6 had SE yields between 58% and 72%. The data suggest that the higher the severity factor the lower the SE yield. Given the LOD inaccuracy of the data, only 5 out of 8 data points were analyzed. Using a secondary moisture analysis method could support this trend.



Figure 24 Yield of steam explosion in function of yield

#### 3.4.3 CAPCOMs, bulk density and water resistance

Due to the limited amounts of steam exploded biomasses, the pelleting trials were restricted to one run per biomass condition thus the main objective of the trial was to evaluate the suitability of the steam exploded material for pelleting. Pelleting of raw SCB resulted in shinny and well compacted pellets. Pelleting of SCT and EFB raw material delivered loose and dull pellets. These pellets were full of fissures and easy to manually disintegrate. Pellets from EFB and SCB pretreated at SF=3.9 (A and G) were dull with a surface free of fissures. Pellets from EFB pretreated at SF=3.6 (I) were shiny and free of fissures. Pellets from SCT and from SCB pretreated at SF=4.6 (C and F) were dull and with fissures. All the pellets made of steam exploded material were well compacted and showed high resistance to manual disintegration.



Figure 25 CAPCOMs from SCB, SCT and EFB



Figure 26Severity factor and bulk density of CAPCOMsSeverity factor zero means pellets made of raw material without pretreatment.

Figure 26 summarizes the results within this project. Results obtained by Viride in previous trials were also included for better analysis. Bulk densities of raw material pellets are seen on the left side of the figure, at severity factor 0.0. Pellets from steam treated biomasses are seen on the right side of the figure at severity factors between 3.6 and 4.6. Pretreated EFB and SCT showed a high improvement of bulk densities, from 400kg/m3 to 550-800kg/m3. SCB pretreated at 3.6 increased bulk density from 620kg/m3 to up to 860kg/m3. SCB pretreated at SF=4.6 resulted in similar and lower bulk densities (640kg/m3 and 550kg/m3) than raw material SCB. In general, steam treatment seems to improve the bulk density of the pellets until certain severity factor (3.6 for SCB and all the values for EFB and SCT). The data suggests there is an optimum severity factor at which a maximum bulk density of SCB and EFB can be achieved. More trials at severity factor lower than 3.6 must be perform for SCB and EFB. SCT must be evaluated at lower severity factors to identified its trend.

CAPCOMs and raw material pellets were fully submerged in tap water. LOD was measured after 89 hours of submersion. Raw material pellets made of SCT and SCB disintegrated after few hours (1h SCB, 5h SCT) and no LOD measurement was possible. EFB treated at severity factor 3.9 showed the highest LOD value (49%). LOD of SCB registered values between 26% and 38%. SCT had the lowest set of LOD between 19% and 31%. The data suggest that the higher the severity factor the lower the water intake of the pellets.



*Figure 27* Severity factor and moisture intake after 89h of CAPCOMs being submerged in water

# 4 Properties and application of pellets

The pellets were tested for logistical properties (bulk density, durability, hydrophobicity, biological stability) (Paragraph 4.1), properties in combustion applications (grindability, ash melting behavior, heat exchanger fouling, NO<sub>x</sub> emission, fines emission) (Paragraph 4.2) and application in fermentation (Paragraph 4.3). A quick reference for the applied severity factors starting from CAPCOM labels can be found in Table 10.

### 4.1 Test analysis for logistics

#### 4.1.1 Bulk density and durability

Viride has produced several pellets of biomass materials based on SCB, SCT and EFB. Part of these materials – 12 samples – were sent to TNO for logistical and storage testing: four material based on SCB – raw SCB, CAPCOM A, CAPCOM B and CAPCOM C; four materials based on SCT – raw SCT, CAPCOM D, CAPCOM E and CAPCOM F and 3 materials based on EFB: raw EFB, CAPCOM G and CAPCOM I. The pictures of the pellets received by TNO are presented in Figure 28. Visually, the raw SCB, CAPCOM A, CAPCOM G and CAPCOM I appeared to be of reasonable quality, looking shinny and presenting no fissures, or cracks. All the other materials presented a significant number of cracks and no glossy finishing at all.



*Figure 28 Pelletized materials produced by Viride for logistical and storage testing at TNO* 

The pellets samples were tested for moisture content, bulk density and durability. The results are presented in Table 10. The samples had moisture contents between 9 and 20% as received. Before testing the samples were dried at 60 °C till a moisture below 5%. The pellets that looked of better quality were the ones that presented higher bulk densities as well (> 600 kg/m<sup>3</sup>) – CAPCOM I < raw SCB < CAPCOM A < CAPCOM G.

The production of pellets is one of the most common ways to process a solid biomass, since both the transport and handling becomes more efficient. When these pellets display insufficient mechanical strength, partial degradation during transport and handling can lead to dust formation. The extent of the mechanical strength is quantified by a standardized durability test (EN15210-1, 2009). This standard test consists in the tumbling of 500 grams pellets from which the native fines (particles with

diameter below 3.15 mm) is removed prior to the experiment. Tumbling occurs during 10 minutes in a standard revolving machine at 50 rotations per minute. After tumbling, the pellets are collected and the produced fines (fraction below 3.15 mm) is separated by sieving and quantified. The fraction of the remaining pellets is known as the Pellet Durability Index (PDI) and is usually presented as a weight fraction of the initial mass of the pellets tested. The durability values did no correlate completely with the bulk densities, and despite the "bad" appearance of some of the pellets its durability presented reasonable results (> 95%) and some of the pellets very good results (> 97%), as was the case of CAPCOM B, CAPCOM I, CAPCOM G and CAPCOM A, presenting increasing durability values from 97.9 to 99.13%, respectively. Analyzing the data obtained with the SCB based materials, the steam explosion process seems to improve the durability of the pellets significantly. However, from the results it is not clear how the steam explosion process conditions (e.g. material wetness, temperature, residence time) influence the final durability.

#	Description	Background	Moisture (%)	Density (kg/m3) db	Native dust (%)	Durability (%)
1	SCB_Raw	SCB RAI 001_pelleted	9.0	609	0.35	95.58
2	CAPCOM A (SCB_wet_SF=3.9)	SCB RAI 001_soaked in water_ steam treated_dried_pelleted	12.0	619	0.16	99.13
3	CAPCOM B (SCB_dry_SF=4.2)	SCB RAI 001_steam treated_dried_pelleted	11.6	565	0.25	97.94
4	CAPCOM C (SCB_dry_SF=4.6)	SCB RAI 001_steam treated_dried_pelleted	11.5	527	0.63	96.29
5	CAPCOM C (SCB_dry_SF=4.6)	SCB RAI 001_steam treated_dried_pelleted	14.0	540	0.77	96.36
6	SCT_Raw	SCT_FBR 0015>10mm_pelleted	n.a.	n.a.	n.a.	n.a.
7	CAPCOM D (SCT_W+SE_SF= 4.2)	SCT_FBR 0018_steam ) treated_dried_pelleted	19.7	496	0.78	95.11
8	CAPCOM E (SCT_SE_SF=4.2)	SCT_FBR 0015steam treated_dried_pelleted	12.2	550	0.59	95.70
9	CAPCOM F (SCT_SF=4.6)	SCT_FBR 0015steam treated_dried_pelleted	19.5	524	0.46	96.55
10	EFB_Raw	EFB_FBR 008_pelleted	n.a.	n.a.	n.a.	n.a.
11	CAPCOM G (EFB_W+SE_SF=3.9)	EFB_FBR 0010_steam treated_dried_pelleted	10.8	653	0.13	99.03
12	CAPCOM I (EFB_SE_SF=3.6)	EFB_FBR 008_soaked in water_steam treated_dried_pelleted	11.5	602	0.49	98.10

#### Table 11Results of the pellets physical properties (Moisture, Bulk density; Durability)

n.a. - Data not available due to low amount of sample delivered to TNO

#### 4.1.2 Biological Stability

The moisture absorption tendency and biological degradation of the pelletized material was evaluated using a climate chamber, which is depicted in Figure 29. The test conditions were selected to simulate tropical climate conditions typical from South American countries like Colombia and Brazil – 28 °C and 90% of relative humidity. The materials were pre-dried and several samples of known masses of each material were introduced in the climate chamber at the selected conditions. One sample of each material was collected periodically (after 1, 3, 7, 14, 28 and 56 days) and the moisture content determined. The dry mass loss was quantified and assumed to be due to biological degradation.



*Figure 29 Climate chamber used for the moisture absorption and biological degradation tests of the pelletized materials produced by Viride – T= 28 °C, RH = 90%.* 

The results of the moisture uptake and biological degradation are presented in Figure 30. All the pelletized material absorbed moisture at a fast rate. The raw materials are more hygroscopic and after one day the EFB, SCT and SCB had a moisture content of 20.7, 17,5 and 12,9% respectively. The steam exploded materials had absorbed significantly less water, e.g. CAPCOM D and G had a moisture content of 10.2 and 11.6 after one day. The steam exploded SCB materials presented also a lower amount of moisture when compared to the raw SCB and a decreasing moisture content absorption was observed with an increase of the SE temperature from 12.4 to 6.8% for the CAPCOM A and CAPCOM C, respectively.

After the third day, the moisture contents changed only slightly for all the materials. After 56 days, the CAPCOM C, CAPCOM D and CAPCOM B were the materials with lower moisture content presenting a moisture level between 12-13%. On the other extreme was the EFB and SCT raw materials followed close by the CAPCOM A presenting a moisture contents of 20.4, 18,7 and 18,1 % respectively. The SE process proved to be useful to reduce the water absorption, except when mild conditions were used (CAPCOM A).



Figure 30 Results of the moisture absorption and biological degradation tests of the pelletized materials produced by Viride – T = 28 °C, RH = 90%.

The biological degradation process only started after one week testing. The significant loss of dry weight was accompanied with the appearance of mold/fungi (Figure 31). After only seven days, the EFB raw material clearly presented evidences of mold/fungi development.

The pellets needed to absorb a minimum water content of 15-20%, depending on the pellet type, prior to significant signs of degradation start to occur. The EFB raw material start to degrade faster (2% dry mass loss after 14 days) followed by the SE EFB (CAPCOM G), the SE SCB (CAPCOM C), the SCT raw, the SE SCT (CAPCOM D) and the SE SCB (CAPCOM B), all between 0.5-1% dry mass loss. From Figure 31 is possible to see that all the raw materials had developed evident signs of mold/fungi together with the CAPCOM G. The other CAPCOM pellets exhibited still few signs of mold/fungi after 14 days testing.

After approximately one month, the degradation of the SE EFB (CAPCOM G) surpassed significantly the raw EFB (4% vs 3% of dry mass loss). The degradation of the SE SCT (CAPCOM D) was at the same level of the raw material (approx. 1% of dry mass loss). The degradation of the raw SCB was slightly higher than the SE SCB materials (1.4% vs 0.6-1.3%). With the exception of the CAPCOM B, all the other pellets presented significant levels of developed mold/fungi (Figure 31).

After two months (56 days), the biological degradation of the CAPCOM G reached 7.2% of dry mass loss, thus twice the degradation of the raw EFB. Moreover, also the SE SCT and the SE SCB pellets presented higher dry mass losses than the raw SCT and raw SCB. This indicates that the SE process can be beneficial for storing the pellets in a short term below 14 days, however for longer storage periods in tropical climate conditions the SE process seems to promote the biological degradation faster, although the moisture absorption is decreased.

Most probably the SE process makes the "chemical food" more accessible for biological activity development, by converting most part of the hemicellulose content of the raw materials.



Figure 31 Pictures of the biological degradation tests of the pelletized materials produced by Viride – T= 28 °C, RH = 90%.

# 4.2 Application as fuel

A selection of the pellets was tested for fuel applications. The key parameters to be tested which are relevant for application as a fuel are grindability and combustion characteristics. Detailed results can be found in [3].

#### 4.2.1 Grindability tests

The pellets grindability was evaluated with the SCB based materials, following an internal method developed by TNO. The grindability tests consisted in 3 steps. First, about 250 g of a pelletized material (pre-dried) was grinded using a cutter mill with several bottom sieves (0.25 -1.5 mm) and the milling net energy consumption was recorded. Second, the particle size distribution (PSD) of the milled material resultant of each bottom sieve was measured and the characteristic D80 (undersize correspondent to 80% mass faction) was calculated.

Finally, for each material the characteristic D80, obtained for each bottom sieve milling experience, was plotted in function of the measured specific milling energy. The results are presented in Figure 32. The steam explosion process seemed to increase the grinding energy required to reduce the particle size, when comparing to the raw SCB. However, if the steam explosion/pelletization process is optimized it seems to be possible to obtain a similar milling power consumption as the raw material (see SCB raw vs CAPCOM B in Figure 32).



*Figure 32 Grinding tests of the pelletized materials produced by Viride (SCB based materials)* 



Figure 33 Crushability tests of the pelletized CAPCOM A material produced by Viride

A crushability test was performed with the CAPCOM A material, following an internal procedure developed by TNO. The crushability test consisted in milling about 10g of pelletized material using several residence times and determining the PSD of the milled material. The results are presented in Figure 33, where is possible to see that the milled steam exploded material, instead of disintegrating completely, seemed to form some pressed agglomerates (up to 20 mm length) which might explain why the steam exploded materials presented significant higher specific energy consumption during the grinding tests.

#### 4.2.2 Combustion tests results

Among the 12 materials presented in Table 10, 6 biomass fuels were selected for a combustion study under pulverized fuel combustion conditions: two samples of sugar cane bagasse (raw and steam exploded), two samples of trash (steam exploded and washed and steam exploded) and two samples of EFB (steam exploded and washed and steam exploded). The biomass samples were prepared by Viride and delivered to TNO in pelleted form. The biomasses were dried and milled under 1.0 mm for the combustion tests.

The TNO's Lab-Scale Combustion and Gasification Simulator (LCS) installation was selected to perform these tests. The combustion conditions were selected to simulate an generic supercritical steam boiler. This study focused on the NOx formation, the near-burner slagging propensity, the elemental release/aerosol formation and the fouling propensity of the fuels.

The tests described in this report were carried out in TNO's Lab-Scale Combustion and Gasification Simulator (LCS), depicted in Figure 34. The LCS consists basically of a drop tube reactor with an integrated, premixed and multi-stage flat flame gas burner. The staged gas burner accommodates high initial heating rates and temperatures and provides the possibility to simulate air staging as in low-NOx burners



*Figure 34* Staged flat flame gas burner and reactor (drop) tube in TNO combustion simulator.

Industrial low-NO<sub>x</sub> burner conditions are simulated based on the notion that, after entering a furnace, fuel particles are rapidly heated in an environment resulting from volatile matter combustion (gas containing CO, CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub> and little to no O<sub>2</sub>). To create a similar environment in the LCS, the primary inner burner is fed with a sub- or near-stoichiometric  $CH_4/O_2/N_2$  mixture. The secondary outer burner is then fired with an excess of oxygen to obtain a flue gas containing 3-4% vol. of oxygen. For slagging tests a specialised deposition probe is used. Different coupons can be attached to the probe head to simulate different deposition surfaces in terms of material and surface structure. The coupon was placed at a burner distance of 280 mm, corresponding to a residence time of approximately 200 ms. The local gas temperature was slightly above 1400°C. The gathered samples were subsequently analysed by means of SEM/EDX. The results are presented in Figure 35, where the slag deposit is shown on the left column part, the SEM pictogram of the morphology of the slag is shown in the middle column and the EDX analysis is presented on the right side column for the 6 biomass materials tested.





Figure 35 Slagging test results.

It can be concluded that both raw bagasse and steam exploded sugar cane trash form an almost fully molten slag, with a slag matrix based on K,Fe,Ca - (alumino-) silicates, while steam exploded bagasse and washed+steam exploded sugar cane trash form a heavily sintered and porous deposit. Therefore, the SE process and mainly the washing step reduces the melting tendency, by removing part of the K but doesn't avoid the slagging formation for these materials.

For sugar cane based materials, it was found that the molten particles matrix is predominantly made of iron-calcium (alumino-) silicates and that increasing potassium levels increase the amount of melt formed under high temperature near-burner conditions.

The EFB based fuels form deposits that are more commonly associated with herbaceous biomass combustion, namely potassium-silicate glasses based systems. The pre-washing step for EFB is essential (by removing the K) for suppressing a fully molten running slag, as found for the steam exploded EFB, which had by far the most severe slagging effects, among all biomasses tested. Fuel-NO<sub>x</sub> is the dominant NO<sub>x</sub> formation route in solid fuel-fired systems. For proper NO<sub>x</sub> control measures, it is important to know in which phase of the conversion the fuel-bound nitrogen is released and converted. Primary  $NO_x$  is mainly formed from pyrolytic N-containing species, while secondary  $NO_x$ is attributed to char-bond nitrogen or high char particle temperatures in the final burnout zone. This distinction was made experimentally in the evaluation by measuring the NO<sub>x</sub> formation during the different stages of conversion in the LCS. This approach was previously validated against full-scale measurement data and proved to be valid. The measured specific NO<sub>x</sub> formation of the investigated fuels is given in Figure 36, where the results are putted in perspective regarding a commercial bituminous coal. The total  $NO_x$  formation is dominated by the primary NOx formation for all of the investigated fuels. The primary  $NO_x$  can be further reduced by advanced air staging; a technique applied in most modern power plants. In conclusion, neither the sugar cane derived nor the EFB derived fuels are prone to cause any  $NO_{\boldsymbol{x}}$  related problems but can be used as an efficient means to reduce NO<sub>x</sub> emissions readily in the boiler.



Figure 36 Specific NOx formation rates of the investigated fuels.

Fine particulate matter is difficult to separate from the flue gases in electro-static precipitators (ESP) in power plants, especially the fraction of 1 micron and smaller. Biomass derived fuels often form significant amounts of super-fine particulates which are causing problems with the particulate emissions of a plant. Furthermore, alkali rich fuels, such as fast growing biomasses, release substantial amounts of the alkalis into the flue gases as vapours inside the boiler where temperatures are sufficiently high. In the course of flue gas cooling in and at heat exchanger surfaces these elements condense and form super-fine salt particle (most often sulphates and/or halides). Those particles are prone to be attracted by thermophoretic forces to the cooler heat exchanger surfaces. Once impacted there, these salts can cause severe corrosion. It is therefore very important to trace the fate of alkalis during biomass combustion. In order to study the fate of alkalis and to determine the amount of fine particulate matter a Pilat Mark V cascade impactor was coupled with the particle collection probe and particle formation were measured under combustion conditions at a residence time of 2000 ms.

The raw bagasse forms less sub-micron particles compared to the steam exploded bagasse (e.g., Figure 37), most likely due to the higher specific ash content per unit energy of the steam exploded bagasse, however also the steam explosion process may alter the fragmentation behaviour of the fuel. The formed aerosols are rich in NaCl and KCl (20-30% m/m in Cl), which are corrosive and hence pose an operational risk when deposited on hot heat exchanger surfaces.

The WSE trash and the SE trash produced similar total amount of aerosol particles (and comparable to the values obtained for steam exploded bagasse). However, in opposition to the WSE trash aerosols, the fine particulate matter of the SE trash is very rich in potassium chloride (> 35% m/m in Cl), demonstrating the advantages of the washing step (WSE trash aerosols had < 5% m/m in Cl). The measured fouling factors (given by the slope of the lines presented in Figure 38) for these biomass fuels (based on sugar cane biomass) were relatively low (compared to a reference coal sample) and no salt condensation on the deposition probe was observed, which indicates that with simple measures the corrosion can be controlled (see Figure 38).

In-depth fouling studies were carried out by means of a horizontal deposition probe, which can be placed at a fixed distance from the burner to mimic the gas/particle flow around a single boiler tube. It consists of a ring-shaped quadruple heat-flux sensor assembly and a detachable deposition substrate. For the EFB based materials the submicron particle formation can be reduced by more than 90% on a weight per energy basis after washing. Furthermore, compared to SE EFB, the aerosols formed by WSE EFB are depleted in chlorine and sulphur, indicating lower corrosive potential. Due to the high fouling factor and corrosion potential, the SE EFB cannot be burned in large quantities in combustion systems and it requires the use of significant quantities of additives



*Figure 37 Particle concentrations as function of particle diameter formed by sugar cane bagasse derived fuels.* 



Figure 38 Fouling factors for SCB and EFB derived fuels.

# 4.3 Application of pellets in fermentation

#### 4.3.1 Introduction

The various biomass samples have been subjected to enzymatic hydrolysis. This hydrolysis is a necessary step to start ethanol fermentations since the yeast is not able to convert polysaccharides but only monosaccharides and some disaccharides. In addition, the results of the enzymatic hydrolysis indicate the effect and success of the steam explosion treatment as a means to make ethanol production based on fermentation of SCT, SCB and EFB possible. The polysaccharides in our biomass types are part of a lignocellulose complex. Steam explosion should make cellulose and hemicellulose more accessible for enzymes.

The ethanol fermentations in this project have the nature of a proof of principle, without the opportunity to carry out process optimisation. Two types of fermentations were carried out: (1) dilute fermentations, to avoid inhibition by medium (hydrolysate) compounds and products, with the purpose to find the ethanol/glucose yield factors, and (2) concentrated fermentations to study the rate of the fermentation and to see possible inhibitions caused by compounds in the hydrolysates, compared to a clean and defined glucose medium.

We used a well-known strain of the baker's yeast (*Saccharomyces cerevisiae*). This yeast can only convert C6 sugars (such as glucose) into ethanol and not the C5 sugars. For conversion of both C6 and C5 sugars a different microbial species is required or a genetically modified strain of baker's yeast, but these were not used in study.

#### 4.3.2 Enzymatic hydrolysis

#### Materials and methods

The samples for hydrolysis are shown in Table 12.

tor chizymatic nyarorys	<i></i>	
EFB	Sugar Cane Trash	Bagasse
х		х
X CAPCOM I	X CAPCOM E	X CAPCOM A
		Х САРСОМ В
X CAPCOM G	X CAPCOM D	
	EFB X X CAPCOM I X CAPCOM G	EFBSugar Cane TrashxXX CAPCOM IX CAPCOM EX CAPCOM GX CAPCOM D

Tahla 12	Samples for	onzymatic H	vdrolvsis
I able 12	Samples for	enzymatic i	iyaroiysis

Two different enzymatic hydrolysis procedures were use: diluted and concentrated, in preparation of diluted and concentrated fermentations. In dilute hydrolysis 50 grams biomass dry matter/L was used and in the concentrated hydrolysis 230 g/L. All eight biomass types were subjected to dilute enzymatic hydrolysis, but for the concentrated enzymatic hydrolysis the two untreated biomass samples were omitted, as we were not intending to carry out fermentations with these.

The dilute enzymatic hydrolysis was carried out using the eight biomass types. For each biomass types the procedure started by adding biomass representing 15 grams dry matter and 200 g demineralized water to a plastic vessel of 500 mL. Ten mL pen-strep mixture (3.6 mg penicillin and 6 mg streptomycin per mL) was added to avoid the growth of bacteria. The pH of the mixture was adjusted to pH 5,0 using HCl or NaOH. Subsequently 540  $\mu$ L Cellic CTec2 (a cellulase and cellobiase) and 60  $\mu$ L NS22244 (a hemicellulase mixture), both a gift of Novozymes, were added and the total weight was adjusted to 300 g with water. The mixture was put in a thermostated shaker at 150 rpm and 50 °C for 72 hours. Samples were taken at 24 and 72 hours. After 72 hours incubation the whole content was centrifuged and the supernatant was taken and stored frozen. This supernatant was used in the fermentations. The concentrations of arabinose, galactose, glucose en xylose were analysed in all supernatants using HPLC.

The concentrated enzymatic hydrolysis was carried out using the same procedure, except 92 gram biomass was used, mixed with 350 g water and subsequently with 13 mL pen-strep, 3.31 mL Cellic CTec2 and 368  $\mu$ L NS22244 and adjusted to a total of 400 grams.

#### **Results and discussion**

To avoid an overload of information only the monosaccharide concentrations in the final supernatants (after 72 incubation) are given here. But the authors also have the concentrations of the monosaccharides after 24 hours hydrolysis. In samples A, B, D-diluted, E-diluted, I-diluted, EFB and bagasse it can been seen that most cellulose hydrolysis (glucose production) occurred in the first 24 hours, about <sup>3</sup>/<sub>4</sub> of the amount finally reached after 72 hours. That means that 72 hours indeed was a good time to reach a high monosaccharide concentration; it was also a compromise to avoid contamination with micro-organisms that may consume the sugars. The hydrolysis of the hemicellulose sugars was nearly complete already after 24 hours. This was in line with what we expected based on 20 years' experience with enzymatic biomass hydrolysis. A few deviations:

D-concentrated: 72 hours sample: almost all sugars lower than 24 h sample. Sample mix up? E-concentrated: hydrolysis already complete within 24 hours

I-concentrated: slow start, most activity in 24-72 h interval

CAPCOM A was also sampled at time zero from which it appeared that steam exploded bagasse contains low amount of monosaccharides. This means that most of the monosaccharides have been produced by enzymatic hydrolysis.

Table 12shows the monosaccharide composition of all eight hydrolysates.

	suspe	ensions						
nr	Biomass	Fucose (g/L)	Rhamnose (g/L)	Arabinose (g/L)	Galactose (g/L)	Glucose (g/L)	Mannose (g/L)	Xylose (g/L)
A	Bagasse steamed	0	0.02	0.38	0.14	4.89	0	7.08
В	Bagasse steamed	0	0	0.07	0.04	5.19	0	1.43
D	Trash steamed and washed	0	0	0.05	0.03	4.11	0	0.82
E	Trash steamed	0	0	0.05	0.03	3.35	0.05	0.78
G	EFB steamed and washed	0.03	0.04	0.15	0.10	13.16	0	6.86
I	EFB steamed	0.04	0.05	0.40	0.08	14.4	0	8.57
EFB	EFB	0.03	0.01	0.46	0.08	6.09	0.17	2.24
Bag	Bagasse	0	0	0.30	0.05	3.91	0	1.37

 Table 13
 Monosaccharide production after 72 hours enzymatic hydrolysis in dilute

We did not measure the original carbohydrate composition of EFB, trash and bagasse, instead we use data from other biomass batches.

The composition of EFB was measured by Van Groenestijn using EFB from Colombia in a previous project. Table 13 shows the composition.

 Table 14
 Saccharide composition EFB from Colombia

	Fucose (% of DM)	Rhamnose (% of DM)	Arabinose (% of DM)	Galactose (% of DM)	Glucose (% of DM)	Xylose (% of DM)
EFB	< 0.1	0.3	1.1	0.4	38.5	20.6

This means 385 g glucose and 224 g hemicellulose sugars per kg EFB dry matter.

Bagasse: In the Phyllis2 database (www.phyllis.nl)[4] an average was taken of samples 1049, 1050, 2567 and 2535. The result was 39.8% cellulose and 26.5% hemicellulose based on dry weight. Including the hydrolysis water this will yield 442 g glucose and 301 g hemicellulose sugars.

Sugar cane trash: analyses by Singh *et al.* (2008)[5]: 45% cellulose and 25% hemicellulose. Including hydrolysis water this will result in 500 g glucose and 284 g hemicellulose sugars.

Now the yield expressed in grams monosaccharides obtained after enzymatic hydrolysis per gram glucose or hemicellulose units in the original material can be calculated. The result is presented in Table 14.

	DM/L)							
nr	Biomass	Glucose in original (g/L)	Hemicellulose sugars in original (g/L)	Glucose in hydrolys ate (g/L)	Yield (%)	Hemicellulose sugars in hydrolysate (g/L)	Yield (%)	
A	Bagasse steamed	22.1	15.1	4.89	22	7.62	50	
В	Bagasse steamed	22.1	15.1	5.19	23	1.54	10	
D	Trash steamed and washed	25	14.2	4.11	16	0.90	6.3	
E	Trash steamed	25	14.2	3.35	13	0.91	6.4	
G	EFB steamed and washed	19.3	11.2	13.16	68	7.18	64	
I	EFB steamed	19.3	11.2	14.4	75	9.14	82	
EFB	EFB	19.3	11.2	6.09	32	2.29	20	
Bag	Bagasse	22.1	15.1	3.91	18	1.72	11	

Table 15Monosaccharide yields after enzymatic hydrolysis in dilute suspensions (50 gDM/L)

Steam treatment only worked well with EFB, and washing slightly decreased the monosaccharide yield. In addition, differences may be due to steam treatment severities: G at SF=3.9 and I at SF=3.6. Higher temperatures bear the risk of conversion of C5 sugars into furfural.

Accessibility of cellulose in bagasse for enzymes was hardly improved by steaming. For hemicellulose hydrolysis only improvements were seen in sample A. Steamed bagasse A and B got a different steam explosion treatment A at SF=3.9 and B at SF=4.2. In B C5 sugars may have been converted into furfural.

Steaming of sugar can trash followed by enzymatic hydrolysis yielded low amounts of monosaccharides. The monosaccharide production in the concentrated batches are presented in Table 15 and Table 16.

	<u>conc</u>	entrated	suspensions	5				
nr	Biomass	Fucose (g/L)	Rhamnose (g/L)	Arabinose (g/L)	Galactose (g/L)	Glucose (g/L)	Mannose (g/L)	Xylose (g/L)
A	Bagasse steamed	0	0.07	1.61	0.60	16.2	0	23.85
В	Bagasse steamed	0	0.01	0.29	0.19	13.88	0.18	5.45
D1	Trash steamed and washed	0 0.14	0.01 0.16	0.24 1.51	0.14 0.35	11.56 21.39	0.18 0	3.63 22.51
E	Trash steamed	0	0.01	0.22	0.14	10.47	0.21	3.28
G	EFB steamed and washed	0.14	0.17	0.65	0.49	19.36	0.41	22.22
I	EFB steamed	0.22	0.19	1.71	0.48	28.37	0.56	27.02

Table 16Monosaccharide production after 72 hours enzymatic hydrolysis in<br/>concentrated suspensions

1: two possible values (sample mix up suspected)

	suspensions (230 g DM/L)							
nr	Biomass	Glucose in original (g/L)	Hemicellulose sugars in original (g/L)	Glucose in hydrolysate (g/L)	Yield (%)	Hemicellulose sugars in hydrolysate (g/L)	Yield (%)	
A	Bagasse steamed	102	69.2	16.2	16	26.13	38	
В	Bagasse steamed	102	69.2	13.88	14	6.12	8.8	
D	Trash steamed and washed	115	65.3	11.56 21.39	10 19	4.20 24.67	6.4 38	
E	Trash steamed	115	65.3	10.47	9.1	3.86	5.9	
G	EFB steamed and washed	88.6	51.5	19.36	22	24.08	47	
Ι	EFB steamed	88.6	51.5	28.37	32	30.18	59	

# Table 17 Monosaccharide yields after enzymatic hydrolysis in concentrated suspensions (230 q DM/L)

Hydrolysis under higher concentration performed different.

EFB samples: as expected the yields are lower now. Concentrated suspensions are subjected to endproduct inhibition and mixing problems. It was observed visually that in all concentrated samples more pieces of pellets were found after 72 hours hydrolysis.

The other biomass samples: this effect is lower, the production already was poor because of other reasons.

Based on the results samples CAPCOM A, G and I were selected for fermentation experiments: the dilute and concentrated hydrolysates.

#### 4.3.3 Ethanol fermentations

#### **Materials and methods**

Because in the past we have discovered that sterilizing hydrolysates causes a production of furfural and other inhibiting substances, we did not sterilize (but work cleanly). The antibiotics present ensure that bacteria cannot develop and the slightly lower pH (4.5) also inhibits bacterial growth (but unfortunately not that of other yeasts and fungi). The incubations were anaerobic. Ergosterol was added since that is a necessary cell wall component for the yeast which cannot be made under anaerobic conditions. Dilute and concentrated fermentations were carried out using three biomass types (Capcom A, G and I) and we used a glucose medium for reference. All fermentation were carried out in duplicate.

[(3 Biomass types x 2 concentrations) + 1 glucose medium] x duplicate = 16 bottles

#### Preculture

Saccharomyces cerevisiae (Ethanol Red yeast, a kind gift from Lesaffre) was transferred from a glycerol stock to two YPD agar plates and these plates were placed at 30°C for 16 hours. After incubation, one colony of *S. cerevisiae* was transferred to two 500 mL shake flasks by using an inoculation loop. These flasks contained 20 g/L glucose, 5.0 g/L (NH4)2SO4, 3.0 g/L KH2PO4, 0.5 g/L MgSO4\*7H2O, 0.1 mL trace elements and 0.1 mL vitamins. Subsequently, the shake flasks were placed at 32°C 200 RPM for 24 hours.

Main medium Volume 100 mL per serum bottle. 98 mL hydrolysate 0.125 mL stock solution ergosterol/tween 80 0.1 mL trace element solution 0.1 mL vitamin solution 2 mL macronutrient solution 0.05 mL anti foam The pH was adjusted on pH 4.5. The yeast was added as a pellet from 10 mL centrifuged preculture (is about 0.1 g yeast dry matter).

For the glucose medium: same but hydrolysate was replaced by 98 mL glucose solution. This glucose solution had a concentration of 80 g/L.

Macronutrient solution In 40 mL demi-water: 10.8 g disodiumsulfate 4.6 g urea 6 g potasium dihydrogen phosphate 1 g magnesium sulphate heptahydrate

*Trace element concentrated solution* In 100 mL demi-water: 1500 mg EDTA 450 mg ZnSO4.7H20 30 mg CoCl2.6H20, 100 mg MnCl2.4H20, 30 mg CuSO4.5H,O, 450 mg CaCl2.2H20, 300 mg FeSO4.7H20, 400 mg NaMoO4.2H20 100 mg H3BO3, 10 mg KI

Vitamin concentrated solution In 20 mL demiwater: 1 mg biotin, 20 mg calcium pantothenate, 20 mg nicotinic acid, 500 mg inositol, 20 mg thiamin.HCl, 20 mg pyridoxine.HCl, 4 mg para-aminobenzoic acid

Ergosterol solution In 12.5 mL ethanol: 100 mg ergosterol

4200 mg Tween 80

The solution was made fresh before making a series of medium bottles. Because of this addition the medium already starts with 1.2 g ethanol/L. That amount was subtracted from the analysed amount in the fermentation bottles to calculate the produced amount.

#### Fermenting and sampling

Fermentation took place in serum bottles. Since  $CO_2$  gas will be produced during the fermentation, a needle was pricked and left in the septum of the serum bottle. It helped to let  $CO_2$  gas escape and prevented pressure increase, while the needle was sufficiently narrow to prevent introduction of ambient air (oxygen) into the bottle.

#### Removing head space air by flushing with nitrogen gas

The fermentation took place under anaerobic conditions. After filling the bottle with medium and yeast and closing the bottle with the screw cap with septum, and pricking the needle, a second needle was temporary pricked in the septum and connected to tubing with  $N_2$  gas. The head space was flushed with  $N_2$  gas for 5 minutes.

#### Incubation

Incubation in a shaker at 32°C.

#### Sampling

Samples were taken after 0, 3, 5.5, 24, 28.5, 50 and 72 hours of incubation and analysed to determine the concentrations of glucose, xylose, lactic acid, acetic acid, ethanol (by HPLC) and pH. For sampling the bottle was put under pressure by adding N2 gas in the bottle and removal of the needles. The bottle was then turned up-side-down and prick a needle was pricked through the septum to let liquid escape.

#### **Results and discussion**

The chemical composition of the various fermentation broths at various fermentation times are depicted in Figure 39. Table 17 summarizes the glucose and ethanol data and gives the calculated ethanol/glucose yields. Figure 40 and Figure 41 shows graphs of the course of glucose and ethanol concentrations. The pH in the hydrolysate fermentations was always between 4.4 and 4.6, while the pH in the fermentation with the glucose medium gradually decreased from 4.5 to 3.1 (data not shown).



*Figure 39* Chemical composition of the fermentation broth as function of hydrolysate or medium type and fermentation time

# Table 18Glucose and ethanol concentrations at start and end of fermentation of<br/>various hydrolysates and medium and ethanol/glucose yield factors

Biomass type	Glucose concentration at start of fermentation (g/L)	Glucose concentration at 72 h fermentation (g/L)	Ethanol concentration at 72 h fermentation (g/L)	Yield factor ethanol/converted glucose (g/g)
EFB CAPCOM G dilute	11.6	0	5.7	0.49
EFB CAPCOM I dilute	13.4	0	6.1	0.46
Bagasse CAPCOM A	3.8	0	1.9	0.50
dilute				
Glucose medium	77.0	0	34.0	0.44
EFB CAPCOM G	18.4	3.0	8.3	0.54
concentrated				
EFB CAPCOM I	33.5	4.4	14.1	0.48
concentrated				
Bagasse CAPCOM A concentrated	14.2	0.2	7.4	0.53









All dilute hydrolysate fermentations were just perfect. Glucose is fully consumed within a day, xylose is not and ethanol is produced.

Concentrated fermentations G and I showed some inhibition and had a longer lag phase, but in the end most glucose was consumed and converted into ethanol. Concentrated fermentation A showed a smaller lag phase and almost all glucose was converted. Inhibition resulting in a longer lag phase is mostly easily to overcome by further process development (yeast gets adapted).

Acetic acid was present from the start, most probably caused by the degradation of hemicellulose in earlier stages. Concentration did not increase much during the fermentation (not a severe bacterial contamination). The concentration of lactic acid showed a small increase (probably by bacterial contamination) but amounts were an order of magnitude lower than the ethanol production. The ethanol/glucose yield factors can be considered as normal to high as an indication of a fermentation without much undesired side-reactions. The theoretical maximum yield is 51%, but in practice in full scale plants normally 45% is reached. The slightly higher yields in our laboratory bottles may be due to conversion of other C6 sugars additional to glucose, and conversion of furfural into glycerol instead of conversion of glucose into glycerol. Glycerol is normally produced to restore the reduction balance under anaerobic conditions and the yeast uses glucose to do so, but whenever furfural is present (normal for thermally treated biomass) the yeast uses furfural instead glucose, thus saving glucose for the conversion into ethanol.

The diluted fermentation of CAPCOM I (steam exploded EFB) yielded the most ethanol per kg of biomass dry matter. Since the hydrolysis was carried out using 50 g biomass dry matter per litre and the fermentation contained 98% of this hydrolysate and 6.1 g ethanol was produced per litre, the yield was 0.12 g ethanol/g EFB dry matter. This amount can be increased by further optimisation of the steam explosion operation and the enzymatic hydrolysis and by using micro-organisms that can convert both C6 and C5 sugars. The estimated maximum is 0.28 g ethanol/g EFB dry matter, so there is room for improvement. Next, the concentration should be increased by carrying out hydrolysis and fermentation at biomass concentrations of 230 g dry matter/L. This way, if a large part of the C6 and C5 sugars are converted into ethanol, an ethanol concentration of 64 g/L (8.2 % v/v) should be possible.

#### 4.3.4 Conclusions

Enzymatic hydrolysis of steam exploded EFB in a high dilution works well with an estimated 75% of the cellulose converted into glucose and 80% of the hemicellulose converted into monosaccharides, and it is proven that this is due to the steam treatment. Without steam treatment EFB is hardly accessible to enzymes.

Washed and steam-treated EFB yields slightly lower amounts of monosaccharides.

At high biomass concentrations enzymatic hydrolysis shows much lower monosaccharide yield factors, which may be due to poor mixing and/or the presence of compounds in inhibitory concentrations. The monosaccharide yields of steam-treated bagasse and sugar cane trash are low, both in dilute and concentrated hydrolysis.

Biomass samples steamed at higher temperature tends to show lower monosaccharide yields from hemicellulose, which may be due to loss of these sugars by conversion into furfural.

Samples Capcom A, G and I can be fermented to produce ethanol in anaerobic fermentations with Saccharomyces cerevisiae. In the dilute fermentations glucose is fully consumed within a day, xylose is not and ethanol is produced.

Concentrated fermentations G and I shows some inhibition and has a longer lag phase, but in the end (72 hours) most glucose is consumed and converted into ethanol. Concentrated fermentation A shows a smaller lag phase and almost all glucose is converted. Inhibition resulting in a longer lag phase is mostly easily to overcome by further process development (yeast gets adapted).

The ethanol/glucose yield factors found in the Capcom fermentations are between 46% and 54% and can be considered as normal to high as an indication of a fermentation without much undesired side-reactions and additional C6 sugars from hemicellulose.

The fermentations should be regarded as a first encounter with the Capcom samples and as a proof of principle. No serious problems have been observed. However, there is room for future improvement e.g. by using a micro-organism that can convert both C5 and C6 sugars into ethanol.

# 5 Conclusions Proof of Concept

Counter current extraction in SMB process

- 90% Reduction of K and Cl is well possible
- Perform extraction first, then pretreatment (otherwise considerable loss of organic material with extract)
- Characteristic time for mass transfer is around 0.5-1 hour (very dependent on biomass structure)

• Miscanthus has high water holding capacity (leads to high water consumption in extraction) Pretreatment

- Pretreatment was performed at different severity factors
- Pellets were produced from raw and pretreated biomass
- Pretreatment enables proper pelleting of SCT and EFB
- Logistic characteristics
  - Durability
    - reasonable (>95% for raw biomass pellets and some pretreated pellets)
    - $\circ$  to good (>97% for some pretreated pellets at higher severity factors)
    - Moisture uptake
      - retarded for pretreated pellets
      - too high (also apparent from visible mold growth)
  - Biological degradation
    - o delayed for pretreated samples
    - increased growth thereafter

Fuel application of pellets

- Grindability
  - $\circ$   $\quad$  some pretreated material was comparable to wood
  - $_{\odot}$   $\,$  other pretreated material were comparable to pellets prepared from raw biomass
- NO<sub>x</sub> emissions lower than coal
- Fines strongly reduced after extraction
- Less fouling with extracted biomass (especially for EFB)

Fermentation applications

- Only EFB pretreated at low severity was easily hydrolysed to sugars
- Fermentation of hydrolysates showed a larger lag phase (especially with concentrated solutions)
  - this indicates toxicity effects
  - $\circ$  full conversion after lag phase, indicating that toxicity can be overcome by adaptation
- Ethanol yield was good (0.5 kg ethanol/kg glucose)

# 6 Literature

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