

## CO-PRODUCTION OF BIO-ETHANOL, ELECTRICITY AND HEAT FROM BIOMASS RESIDUES

J.H. Reith  
 H. den Uil  
 H. van Veen  
 W.T.A.M. de Laat<sup>1)</sup>  
 J.J. Niessen<sup>1)</sup>  
 E. de Jong<sup>2)</sup>  
 H.W. Elbersen<sup>2)</sup>  
 R. Weusthuis<sup>2)</sup>  
 J.P. van Dijken<sup>3)</sup>  
 L. Raamsdonk<sup>3)</sup>

<sup>1)</sup> Royal Nedalco BV

<sup>2)</sup> Agrotechnological Research Institute ATO BV

<sup>3)</sup> Technical University Delft

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J.H. Reith, H. den Uil & H. van Veen, Energy research Centre of the Netherlands- Unit Biomass; P.O. Box 1, 1755 ZG Petten, The Netherlands. tel. +31 224 564371, fax +31 224 568487; e-mail: reith@ecn.nl;  
W.T.A.M. de Laat & J.J. Niessen, Royal Nedalco BV; e-mail: w.delaat@nedalco.nl;  
E. de Jong, H.W. Elbersen & R. Weusthuis, Agrotechnological Research Institute ATO BV, e-mail: e.dejong@ato.wag-ur.nl;  
J.P. van Dijken & L. Raamsdonk, Technical University Delft, e-mail: j.p.vandijken@tnw.tudelft.nl

**ABSTRACT:** The use of lignocellulosic biomass residues as a feedstock offers good perspectives for large scale production of fuel ethanol at competitive costs. An evaluation was performed to assess the international status of *lignocellulose-to-bioethanol* technology and the economical and ecological system performance, to identify R&D approaches for further development. Deriving fermentable sugars from the hemicellulose and cellulose fractions of lignocellulosic materials via suitable pretreatment and enzymatic cellulose hydrolysis is a critical R&D issue. Further development of pretreatment via mild, low temperature alkaline extraction or weak acid hydrolysis using CO<sub>2</sub> dissolved in pressurized hot water ('carbonic acid process') shows good perspectives. Enzymatic cellulose hydrolysis with the currently available industrial cellulases accounts for 36-45% of ethanol production costs. At least a 10-fold increase of cellulase cost-effectiveness is required. Despite substantial R&D efforts, no suitable fermentation system is currently available for the fermentation of pentoses (mainly xylose) from the hemicellulose fraction. Several strains of anaerobic, thermophilic bacteria are able to convert all (hemi)cellulose components into ethanol. Follow-up R&D will focus on isolation of suitable strain(s) from this group. The system evaluation shows a 40-55% energetic efficiency (LHV basis) for conversion of lignocellulosic feedstocks to ethanol. Thermal conversion of non-fermentable residues (mainly lignin) in a Biomass-Integrated-Gasifier/Combined Cycle (BIG/CC) system can provide the total steam and electricity requirement for the production process and an electricity surplus for export to the grid, giving a total system efficiency of 56-68%. Water consumption in the process (28-54 liter water/liter ethanol) is much higher than in current ethanol production (10-15 l/l ethanol). The large amount of process water (used in the pretreatment and cellulose hydrolysis sections), necessitates concentration of the sugar solutions by evaporation to obtain an industrially acceptable final ethanol concentration in the fermentation broth (>8.5 vol%). Follow-up R&D will focus on reduction of water use, internal water recycling and energy integration of the evaporation step with the ethanol purification section. The estimated production costs of bio-ethanol from 3 types of (ligno)cellulosic residues are 0.75-0.99 €/l (34-45 €/GJ), which is considerably higher than the current costs of fuel ethanol from corn starch (0.34 €/l; 16.2 €/GJ) and gasoline (7.3 €/GJ). A sensitivity analysis shows that cellulase costs will have to be reduced with at least a factor 10 and capital costs need to be reduced by 30% to reach ethanol production costs competitive with ethanol from starch crops.

**Keywords:** bio-ethanol, combined application biomass, liquid biofuels, feasibility studies

### 1 INTRODUCTION

Large scale application of bio-ethanol in fuel blends will contribute to reduction of CO<sub>2</sub> and other emissions from the transport sector. Approx. 17 Million tons/year of fuel ethanol are currently produced from sugar cane and starch crops in Brazil, the U.S.A. and some EU countries at a cost of about 0.34 €/liter (16.2 €/GJ) which is 2-fold the price of gasoline (7.3 €/GJ). The EU market for fuel ethanol will grow considerably in the coming years, as a result of the EU policy to substitute 8 % of fossil transport fuels by renewable biofuels by the year 2020. The use of (ligno)cellulosic biomass residues as a feedstock will allow a substantial increase of fuel ethanol production capacity and a reduction of the ethanol production costs to a competitive level. *Lignocellulose-to-ethanol* production technology has been investigated intensively in the U.S.A., Canada, Sweden and Finland [1-5]. In the Netherlands there is a rapidly growing industrial interest in alternative feedstocks for bio-ethanol production. A consortium from industry and the R&D sector has been formed for further development and commercial implementation of the technology. The first step is to evaluate the –international- state-of-the art, the economic feasibility and the ecological performance. The results of this evaluation and the resulting R&D approaches are

presented in this paper. The identified R&D issues will be addressed in a 4-year follow-up R&D programme.

### 2 FEEDSTOCKS IN THE NETHERLANDS

A wide variety of (ligno)cellulosic biomass types are potentially available for ethanol production in The Netherlands. The total amount of technically suitable feedstocks is approx. 12 Million tons (dry weight) per year. Potential fuel ethanol production from the hemicellulose + cellulose fractions of these streams is approx. 2.5 Million tons bio-ethanol. The potential feedstocks are highly variable and include a range of agro-industrial residues, agricultural wastes, forestry residues and other wastes. Since most streams are dispersed over the country and many (will) also have other applications, a large scale *lignocellulose-to-ethanol* plant (> 150 ktons bio-ethanol/year; requiring 700 ktons of dry feedstock) will have to use a variety of feedstocks in order to secure feedstock availability ('multi-feedstock plant'). Furthermore, the option to import biomass over longer distances should be available.

For medium term development (<10 years) a focus on feedstocks such as verge grass and/or natural grass and agro-industrial residues -e.g. wheat milling residue- seems

a good strategy, with respect to availability and cost. For the longer term (> 10 years), as the production scale increases, the feedstock range should be broadened with additional residues and (imported) woody energy crops (e.g. willow).

### 3 OVERALL PROCESS DESCRIPTION

The envisaged *lignocellulose-to-ethanol* technology will comprise the following unit operations.

1. First biomass treatment/handling (milling/chipping) for size reduction and opening up of the fibrous material for further treatment and production of a pumpable slurry.
2. Pretreatment for mobilization of the lignin and (hemi)cellulose biopolymers and further breakage of structural components to optimize access for enzymes in further processing.
3. Liquefaction; hydrolysis of the highly viscous polysaccharide matrix to a liquid stream of sugar oligomers. This step can be performed in an acid/base and/or heat catalysed reaction with the possible aid of enzymes.
4. Saccharification; enzymatic hydrolysis of sugar oligomers to fermentable monomeric sugars, mainly glucose (C6) and xylose (C5).

The processes in steps 2 through 4 represent major R&D issues, as discussed in sections 4 and 5.

5. Liquid/Solid separation of the lignin fraction for use as a fuel for electricity and steam production (CHP).
6. Evaporation; dependent on the sugar concentration after saccharification, the solution needs to be concentrated by evaporation to a sugar level sufficient for a final ethanol concentration of at least 8.5 vol% in the fermentation broth. The evaporation step needs to be energetically integrated with steps 9-12.
7. Fermentation of C6 (glucose) and C5 (xylose) sugars to ethanol.

Efficient fermentation of both C5 and C6 sugars (from the hemicellulose and cellulose fractions respectively) is a critical R&D issue, as outlined in section 6.

8. Separation of yeasts by mechanical L/S separation, usually centrifugation ('decanting').
9. Distillation for separation and upgrading of ethanol from the fermentation broth to 'raw' ethanol (ca. 45 vol%).
10. Rectification; concentration of 'raw' ethanol to approx. 96 vol%.
11. Dehydration of ethanol to fuel specifications (> 99.9 vol%) by 'molecular sieves'.

Distillation, rectification and dehydration are proven and competitive technologies, requiring no further RD&D.

12. Dewatering and drying of 'stillage', the 'bottoms fraction' from the distillation process.
13. Thermal conversion of 'non-fermentable organics', comprising: lignin (from 5), dewatered 'stillage' (from 12) and waste water treatment sludge, to steam and electricity in a CHP installation. Conventional combustion/steam boiler systems will require modification of fuel conditioning and feeding

technology. Application of a more advanced Biomass-Integrated-Gasification/ Combined-Cycle system (BIG/CC) will require substantial development. The CHP system can provide all steam and electricity required for fuel ethanol production, whereas a surplus of electricity is supplied to the public grid.

The critical R&D issues in the outlined technology are discussed in more detail in the following sections.

### 4 BIOMASS PRE-TREATMENT

Deriving fermentable sugars from lignocellulosic biomass is one of the major R&D issues. Lignocellulosic biomass is composed of cellulose, hemicellulose and lignin. Both the cellulose and hemi-cellulose fractions are a potential source of fermentable sugars. Hemicellulose hydrolysis can be readily achieved under mild acid or alkaline conditions. The cellulose fraction is more resistant and requires more rigorous treatment. Following the initial biomass handling by milling, the production of fermentable sugars is approached in two steps:

1. a pretreatment process in which hydrolysis of hemicellulose sugars occurs and the cellulose polymers are made accessible for further treatment; dependent on the type of process, the lignin fraction may be separated and recovered in this step;
2. enzymatic cellulose hydrolysis, using cellulase enzyme cocktails, produced on location or acquired from enzyme manufacturers.

The ideal pre-treatment technology should lead to:

- a high (final) yield of fermentable sugars,
- low or zero formation of side products inhibiting subsequent cellulose hydrolysis and ethanol fermentation. These 'inhibitors' are mainly organic acids and aromatic compounds (e.g. furfurals) formed from the hemicellulose and lignin fractions; The extent of inhibitor formation depends on the process conditions in the pretreatment step.
- absence of requirement for chemicals recycling,
- low or zero waste production, and
- low capital investments.

A range of pretreatment technologies currently under development [2,3,7-12] were evaluated (Table 1).

The evaluation shows that the pretreatment technologies which have been studied in great detail over the last decades, e.g. strong and weak acid hydrolysis and steam pretreatment, still suffer from major drawbacks. The most important are: the formation of inhibitors, the need to regenerate acids, formation of inorganic waste streams, the high operational temperatures and pressures, and the corrosiveness of the pretreatment. It is unlikely that those hurdles can be taken in the near future.

**Table 1:** Qualitative evaluation of pretreatment processes.

The '+' and '-' signs indicate a positive or negative characteristic respectively. For the different categories a '+' score implies: 'high yield of fermentable sugars', 'no or low inhibitor production', 'no requirement for chemicals recycling', 'no/low waste production' and 'low investment costs' respectively.

Pretreatment process	Yield of fermentable sugars	Inhibitor production	Recycling of chemicals	Waste production	Investment costs
Weak acid	++	--	--	-	+/-
Strong acid	++	--	--	-	-
Steam explosion	+	--	++	+	-
Organosolv	++	++	--	+	--
Wet oxydation	+/-	+	++	+	+
Mechanical methods	-	++	++	++	+
Alkaline extraction	++/+	++	--	-	++
Carbonic acid	++	++	++	++	+

Pretreatment processes were identified which don't possess many of the above mentioned drawbacks i.e.:

- mild alkaline [Ca(OH)<sub>2</sub>, NaOH] extraction at low temperature [8-10]; this technology leads to high yields of fermentable sugars and low formation of 'inhibitors'; effective regeneration of alkali is required to prevent wastes;
- weak acid hydrolysis using CO<sub>2</sub> dissolved in pressurized hot water ('carbonic acid process')[12,15], possibly combined with (mild) steam pretreatment. This method is attractive because it has a high sugar yield, low formation of inhibitors, and produces zero wastes. The required concentrated CO<sub>2</sub> is available in large quantities from the fermentation process on location.

The identified pretreatment options are recommended for further development. However, because these are relatively recent developments, many technical and economical parameters have not yet been evaluated. The most important parameters for investigation in the follow up R&D project are: the range of biomass types which can be used, the maximum sugar concentration which can be achieved in the fermentation broth, scaling up problems and economic viability.

## 5 ENZYMATIC CELLULOSE HYDROLYSIS

The cost-effective production of glucose from cellulose by enzymatic hydrolysis is clearly one of the key issues in R&D for the coming years. Our evaluation shows that enzymatic cellulose hydrolysis is the major cost driver in bio-ethanol production, i.e. 40-55% of the net production costs per ton ethanol (see section 6, Table 3) at the effectivity of currently available industrial cellulases. An increase of the cost-effectiveness by at least a factor 10 is required to reach competitive ethanol costs. The major bottleneck is end-product inhibition of the enzyme by glucose.

In the USA the key industrial enzyme producers Novozymes and Genencor have recently received a grant from NREL/DoE of approx. 36 Million Euro to increase the cost effectiveness of cellulase (for use

with mild acid pretreated corn stover) by a factor 3 at least but preferably a factor 10. Recently developed technologies in enzyme engineering incl. gene shuffling techniques and *in silico* screening, may contribute to these targets. A consequence of the currently limited cellulase effectivity is the choice for *Simultaneous Saccharification and Fermentation (SSF)* [2] in order to keep glucose concentration at a low level, thereby reducing end-product inhibition. The concept of *Separate Saccharification and Fermentation S&F*; [1,3] is expected to have better optimization potential and potentially lower capital cost, but this issue has to be studied further in the R&D trajectory. A crucial item for the development of an S&F process is the requirement for a beta-glucosidase that is not inhibited by glucose, which has to be included in the current cellulase mixtures as obtained from *Trichoderma reesii*. The desired enzyme properties do exist in nature according to literature [13]. Nearby or *on-site* production of cellulases could be necessary on the long term to reduce ethanol production costs to the required competitive level.

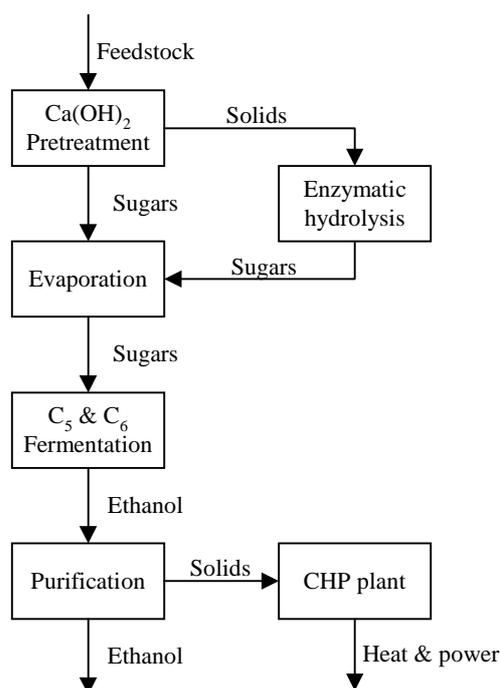
## 6 PENTOSE FERMENTATION

Pentoses obtained from the hemicellulose fraction have to be fermented in order to make the production of alcohol from biomass an economically feasible process. Preferably by co-fermentation of C6 sugars (glucose) and C5 sugars (mainly xylose). The pentoses (xylose) in the feedstock, cannot be fermented by the currently used industrial strains of the bakers' yeast *Saccharomyces cerevisiae*. Despite the substantial research efforts in the past decades, targeted a.o. at *Zymomonas mobilis*, and *E.coli* no suitable microorganism is as yet available for C6 & C5 co-fermentation, with sufficient robustness [14]. Broadening the substrate range of *S. cerevisiae* by genetic modification is an attractive approach, but so far major problems are encountered with respect to xylose uptake rates and overproduction of xylitol due to redox problems.

There are several bacterial strains (including *Clostridia*, *Thermoanaerobacter ethanolicus*) known to be able to convert all components of lignocellulosic materials into ethanol [11]. Some strains even with a high yield, which is an exceptional quality. Less favourable characteristics are the possible lower tolerances for high product (ethanol) and substrate concentrations and the formation of fermentation co-products, such as acetate and H<sub>2</sub>. Furthermore, there is a lack of expertise with these micro-organisms, especially under industrial conditions. Follow-up R&D will focus on new isolation and selection methods to acquire the most suitable strain(s) for conversion of (hemi)cellulose into ethanol and to optimize their tolerance for substrates, products and inhibitors, followed by process development.

## 7 SYSTEM EVALUATION

In the system evaluation the prospects of producing ethanol from lignocellulosic biomass(residues) at competitive costs with current ethanol production from sugar cane or starch crops has been assessed. The system evaluation has been performed for a system with Ca(OH)<sub>2</sub> pretreatment. A simplified flowsheet for the production process is given in Figure 1.



**Figure 1.** Simplified flowsheet for ethanol production from lignocellulosic biomass. The scheme focusses on the routing of organic materials in the process. Regeneration of Ca(OH)<sub>2</sub> for the pretreatment step was included in the evaluation, but not indicated in the figure.

The feedstock is pretreated with a Ca(OH)<sub>2</sub> solution at 80 °C. Sugars formed during Ca(OH)<sub>2</sub> pretreatment

are routed to the evaporation step. The solid residue of the Ca(OH)<sub>2</sub> pretreatment (mainly cellulose and lignin) is fed to the enzymatic hydrolysis for further conversion into fermentable sugars. In order to obtain an industrially acceptable final ethanol concentration<sup>1</sup>, of at least 8.5 vol.% in the fermentation broth, the sugar solutions from the Ca(OH)<sub>2</sub> pretreatment and enzymatic hydrolysis are concentrated by evaporation. The concentrated sugar solution is converted into ethanol by simultaneous C<sub>5</sub> and C<sub>6</sub> fermentation. The fermentation product is purified to fuel ethanol specifications (>99.9 vol%) by successive distillation, rectification and dehydration. The unconverted feedstock [i.e. lignin and part of the (hemi)cellulose] is split off in the distillation step<sup>2</sup>. After dewatering and drying, the unconverted organic material is gasified. The fuel gas produced is used for heat and power production in a combined cycle system. Heat and electricity required for the process are withdrawn from the CHP-plant. Surplus electricity is supplied to the grid.

Based on the system description given above, a model for the process was constructed in Microsoft Excel. The performance of individual process steps is based on data available in literature, and on industrial practice. The process has been evaluated for 3 feedstocks:

1. Verge grass; a low-cost lignocellulosic residue
2. Willow prunings/'tops'; representative for e.g. forestry residues and (future) lignocellulosic energy crops;
3. Wheat milling residue; a (hemi)cellulose and starch containing agro-industrial residue

For each feedstock, the ethanol output of the process was fixed at 156 kton/year. This amount represents about 1% of the current consumption of transport fuels in the Netherlands (=451 PJ/year). Major results for the mass- and energy balances for the different feedstocks are summarized in Table 2, and for the economic evaluation in Table 3.

<sup>1</sup> The final ethanol concentration in industrial fermentations is approx. 10 vol.%. A high final ethanol concentration (> 8.5 vol%) in the fermentation broth is required to reduce the energy consumption in the consecutive distillation to an acceptable level.

<sup>2</sup> An alternative is to separate the lignin fraction directly following pretreatment.

**Table 2:** Summary of mass- and energy balance for a 156 kton/year bio-ethanol plant.

		Verge- grass	Willow tops	Wheat milling residue
Feedstock composition:				
- (Hemi)cellulose	(wt.%)	61	75	82 <sup>1)</sup>
- Lignin	(wt.%)	21,5	23	0
- Other organics	(wt.%)	10,5	0,5	18 <sup>2)</sup>
- Ash	(wt.%)	7	1,5	0
Feedstock	(kton/year)	1295	1110	939
Gross water consumption	(l/l ethanol)	54	46	28
Energy efficiency <sup>3)</sup>				
- Ethanol	(% LHV)	40	47	55
- Electricity <sup>4)</sup>	(% LHV)	15	15	12
- Total	(% LHV)	56	62	68

1) Including 20% starch.

2) Protein

3) Net energy output. Internal steam and electricity consumption in the process are fully covered by the CHP.

4) Surplus electricity supplied to the grid.

The results in Table 2 show that feedstock consumption for the 156 kton/year plant is primarily determined by feedstock composition. A high content of fermentable components in the feedstock, as for wheat milling residue, results in relatively low feedstock consumption. The gross water consumption of the process is quite high with 28-54 liter per liter ethanol. In current industrial ethanol production water consumption is approx. 10 to 15 liter per liter ethanol. The high water consumption results from the process water used in the Ca(OH)<sub>2</sub> pretreatment and enzymatic hydrolysis sections, and from the water washing of solids prior to enzymatic hydrolysis. Although the major part of this water can be internally recycled (after purification), the systems' water management and associated costs have to be studied in more detail. Furthermore, due to the large amounts of process water used, concentration of the sugar solution (by evaporation) is required. Without such a concentration step, the sugar concentration would only allow a final ethanol concentration in the fermentation broth of 3-5 vol.%. This would cause an unacceptably high energy consumption in the distillation section.

Just like for the feedstock consumption, the energetic efficiency of ethanol production is primarily determined by feedstock composition. A high content of fermentables in the feedstock results in a high energetic efficiency for ethanol production. Net electricity production is influenced by the amount of feedstock not converted into ethanol as well as by electricity consumption in the process. Total system efficiency increases when the feedstock is more suited for ethanol production, i.e. has a high content of fermentables.

Based on the mass and energy balances generated by the process model, estimates for capital costs and operating and maintenance costs have been made.

The results of the economic evaluation (Table 3) show that total capital investment ranges from 235-313 million € (or 1500-2000 €/ton ethanol per year), dependent on the feedstock considered.

**Table 3:** Summary of economic evaluation for a 156 kton/year ethanol plant

		Verge- grass	Willow tops	Wheat residue
Feedstock	(€/ton d.w.)	20	70	80
Total investment	(M€)	313	285	235
O&M costs				
- Feedstock	(M€/year)	13	39	38
- Cellulase	(M€/year)	102	97	59
- Others <sup>1)</sup>	(M€/year)	19	14	11
- Total	(M€/year)	134	149	108
Production costs ethanol				
- Feedstock	(€/l)	0.06	0.19	0.19
- Cellulase	(€/l)	0.51	0.48	0.30
- Other O&M	(€/l)	0.09	0.07	0.06
- Capital	(€/l)	0.37	0.34	0.28
- Gross ethanol price	(€/l)	1.04	1.08	0.82
- Electricity <sup>2)</sup>	(€/l)	-0.11	-0.10	-0.07
- Net ethanol cost	(€/l)	0.92	0.99	0.75

1) Others=Ca(OH)<sub>2</sub>, ash disposal, maintenance and labor.

2) Revenues surplus electricity are assumed to be €0.051/kWh.

The process sections pretreatment + hydrolysis, evaporation, fermentation + purification and CHP production each account for about 25% of the capital investment. The costs of cellulase, assumed to be 6000 €/ton of enzyme, are the major contribution to O&M costs.

The ethanol production costs were calculated assuming an internal rate of return (IRR) of 15% over a period of 15 years. The costs of cellulase consumption account for 36-45% of the gross ethanol production costs (40-55% of the net ethanol costs). The high costs of the cellulase consumption and the required capital investment result in net ethanol production costs which are far above the current costs of corn ethanol of 0.34 €/liter. A sensitivity analysis shows that cellulase costs will have to be reduced with at least a factor 10 and capital costs need to be reduced by 30% to reach ethanol production costs competitive with ethanol from starch crops.

## 8 CONCLUSIONS AND FURTHER R&D

- **Feedstocks.** In the Netherlands 12 Million tons (dry weight) of highly variable lignocellulose residues are available as feedstock for production of 2.5 Million tons of fuel ethanol per year. Large scale bio-ethanol plants will require multiple feedstock types to assure sufficient and year-round feedstock supply. For medium term development (<10 years) a focus on feedstocks such as verge grass and agro-industrial residues -e.g. wheat milling residue- is a

good strategy, with respect to availability and cost. For the longer term (> 10 years) the feedstock range should be broadened with additional residues and (imported) woody energy crops (e.g. willow).

- Pretreatment. The production of fermentable sugars from (hemi)cellulose is approached in two steps i.e. 1) a pretreatment process to hydrolyze the hemicellulose fraction and mobilize the cellulose polymers 2) enzymatic cellulose hydrolysis. Two pretreatment processes were identified with good perspectives for development i.e.:

- mild alkaline [Ca(OH)<sub>2</sub>] extraction at low temperature; this technology leads to high yields of fermentable sugars and low formation of 'inhibitors'; regeneration of alkali is required to prevent wastes;
- weak acid hydrolysis using CO<sub>2</sub> dissolved in pressurized, hot water ('carbonic acid process'), possibly combined with (mild) steam pretreatment. This method leads to high sugar yields, low formation of inhibitors, and produces zero wastes. The required concentrated CO<sub>2</sub> is available in large quantities from the fermentation on location.

The most important parameters for investigation in follow up R&D are: the range of biomass types which can be used, the maximum sugar concentration which can be achieved in the fermentation broth, scaling up problems and economic viability.

- Cost-effective enzymatic cellulose hydrolysis is clearly a key issue in R&D for the coming years. Cellulase costs have to be reduced by a factor 10 to reach ethanol production costs comparable to ethanol from starch crops. Follow up R&D will be aimed primarily at the optimization of the effectivity of currently available and novel industrial cellulases.

- Pentose fermentation. Pentoses (C5 sugars, mainly xylose) obtained from the hemicellulose fraction have to be fermented in order to make the production of ethanol from lignocellulose economically feasible, preferably by co-fermentation of C6 sugars (glucose) and C5 sugars (xylose). Broadening the substrate range of *Saccharomyces cerevisiae* by genetic engineering is an attractive approach, but so far major problems are encountered with respect to xylose uptake rates and overproduction of xylitol due to redox problems. Several bacterial strains (including *Clostridia*, *Thermoanaerobacter ethanolicus*) are able to convert all components of lignocellulosic materials into ethanol, in some cases with a high yield. Follow-up R&D will focus on new isolation and selection methods to acquire the most suitable strain(s) for conversion of (hemi)cellulose into ethanol and to optimize their tolerance for substrates, products and inhibitors, followed by process development.

- The system evaluation shows a 40-55% energy efficiency (LHV basis) for conversion of lignocellulosic feedstocks to ethanol. Conversion of non-fermentable biomass streams in a gasifier/CC system provides the total electricity and steam requirement for the production process. In addition, 12-15% of the feedstock is converted into surplus electricity for export to the grid, giving a total system efficiency of 56-68%. Follow-up R&D will address optimal design and energy integration of the CHP

system, as well as environmental aspects (emissions, application of ashes).

- Water consumption in the process is quite high with 28-54 liter water/liter ethanol produced, which is much higher than in current ethanol production (10-15 l/l ethanol). Due to the large amount of process water used in the pretreatment and enzymatic hydrolysis, concentration of the sugar solutions is required to obtain industrially acceptable final ethanol concentrations in the fermentation broth (>8.5 vol%). The evaporation step accounts for ~25% of total capital investment. Follow-up R&D will focus on reduction of water use, internal water recycling and energy integration of the evaporation step with the ethanol purification section.

- Based on the estimates of the capital cost and operating and maintenance costs, the production cost of ethanol from (ligno)cellulose is 0.75-0.99 €/l (34-45 €/GJ). This is considerably higher than the cost of corn ethanol (0.34 €/l; 16.2 €/GJ) and the market price of gasoline (7.3 €/GJ). For all feedstocks considered, the costs of the cellulase for enzymatic cellulose hydrolysis and the capital costs are the major cost drivers. According to a sensitivity analysis, cellulase costs need to be reduced with a factor 10 and capital costs by 30% to attain bio-ethanol production costs comparable to ethanol from sugar cane and starch crops.

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## Bio-ethanol, electricity and heat from biomass residues

### R&D issues and approach



**J.H. Reith, H. den Uil & H. van Veen**  
ECN Unit Biomass



**W. de Laat & J.J. Niessen**  
Royal Nedalco BV



**E. de Jong, H.W. Elbersen & R. Weusthuis**  
Agrotechnological Research Institute ATO BV



**J.P. van Dijken & L. Raamsdonk**  
Technical University Delft

## Bio-ethanol in transport fuels

- **oxygenate >> improved engine performance**
- **reduction of CO<sub>2</sub>, SO<sub>x</sub>, particles emissions**
- **application**
  - gasoline & diesel blends
  - hydrous ethanol (95,5 vol%; Brazil)
- **current production from sugar cane/ starch crops: 17 Mton/yr**

## Global fuel ethanol production

Country	feedstock	fuel ethanol Mton/yr
Brazil	sugar cane	11.0
USA	corn	6.0
Canada	corn	0.2
France	sugarbeet/wheat	0.1
Spain	wheat	0.1
Sweden	barley	0.04

## Potential EU market

Year	target % substitution	50% bioethanol Mton/yr	25% bioethanol Mton/yr
2005	2	2.5	1.25
2010	5.75	7.5	3.75
2020	8	10.5	5.25

## Bio-ethanol from lignocellulosic residues

- large availability of low cost feedstocks
- competitive ethanol costs
- high CO<sub>2</sub> mitigation potential in transport fuels
- ‘spin-off’ applications
  - lactic acid → polylactic acid (PLA) >> packaging
  - ethanol → ethene

## Feedstocks in the Netherlands (1)

- variety of suitable biomass/residues available
- 12 Mton dry weight >>2.5 Mton fuel ethanol
- plant 150 kton EtOH/yr>>700 kton dw
- no uniform 'local' streams of sufficient size
  - multifeedstock plant/year round availability
  - long distance supply/import

## Feedstocks in the Netherlands (2)

- medium term development (< 10 yrs); focus on

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Wheat milling residue	500 kton 80 Euro/ton dw	77% fermentable sugars 42 % cellulose, 10% pentosan, 20% starch, 17% protein, 5% betaglucosan
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Verge grass	225 kton 20 Euro/ton dw	75% fermentable sugars 45% cellulose, 30% hemicellulose, 15 % lignin, 12% protein
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- long term development (> 10 yrs); focus on

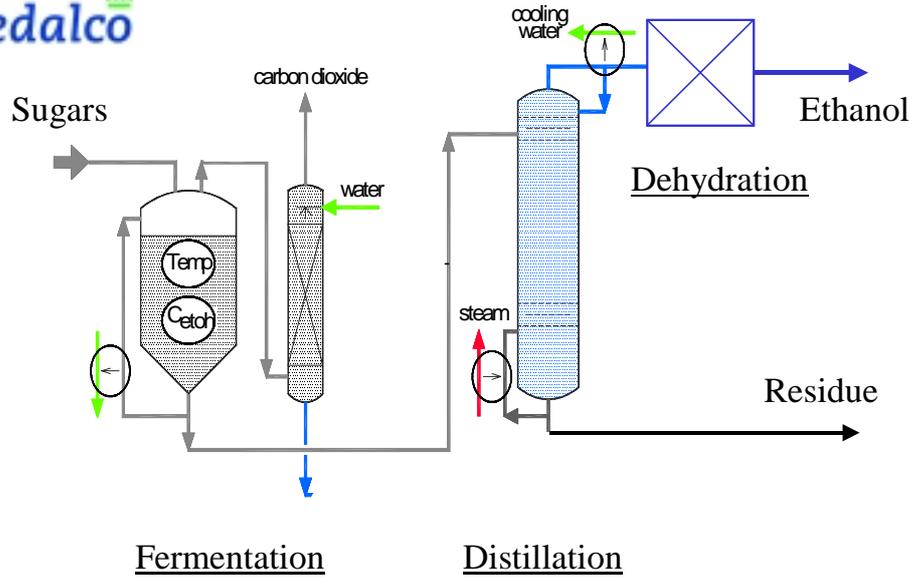
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Willow (imported)	?? kton ± 70 Euro/ton dw	77% fermentable sugars 50 % cellulose, 27% pentosan, 23% lignin, 2% protein
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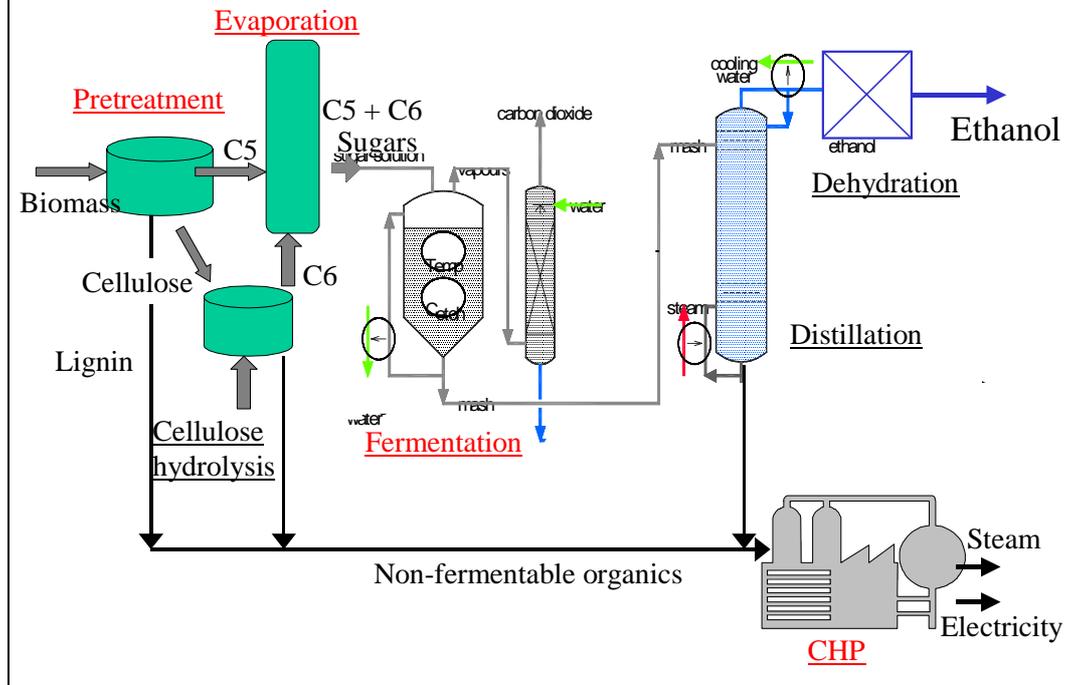
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## Current process

Royal  
**Nedcalco**



## Lignocellulose-to-ethanol process



## **R&D challenges**

### **1. Pretreatment**

- Difficult conversion of sugar polymers (cellulose, hemicellulose) to monomers (glucose, xylose)
- Formation of fermentation 'inhibitors'
  - >> organic acids/aromatics
  - >> prevention, removal, tolerant micro-organisms

### **2. Enzymatic cellulose hydrolysis**

- Limited effectivity industrial cellulases

### **3. Co-fermentation of C5 & C6 sugars**

## **Dilute acid/steam pretreatment**

**10 minutes 190 °C, 0,5% H<sub>2</sub>SO<sub>4</sub>**

**After hydrolysis 'overliming' with Ca(OH)<sub>2</sub>**

**Result: 130 kg gypsum / ton ethanol**

## Pretreatment

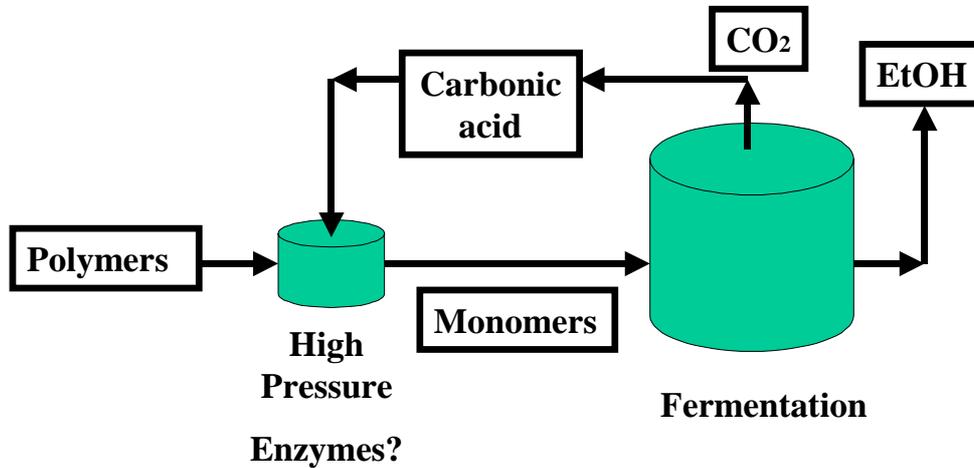
PROCESS	Yield fermentable sugars	Inhibitors	Chemicals recycling	Wastes	Investments
Weak acid	++	--	--	-	+/-
Strong acid	++	--	--	-	-
Steam explosion	+	--	++	+	-
Organosolv	++	++	--	+	--
Wet oxidation	+/-	+	++	+	+
Mechanical	-	++	++	++	+
Alkaline extraction	++/+	++	--	-	++
Carbonic acid	++	++	++	++	+

## Pretreatment

PROCESS	Yield fermentable sugars	Inhibitors	Chemicals recycling	Wastes	Investments
Weak acid	++	--	--	-	+/-
Strong acid	++	--	--	-	-
Steam explosion	+	--	++	+	-
Organosolv	++	++	--	+	--
Wet oxidation	+/-	+	++	+	+
Mechanical	-	++	++	++	+
<b>Alkaline extraction</b>	<b>++/+</b>	<b>++</b>	<b>--</b>	<b>-</b>	<b>++</b>
<b>Carbonic acid</b>	<b>++</b>	<b>++</b>	<b>++</b>	<b>++</b>	<b>+</b>

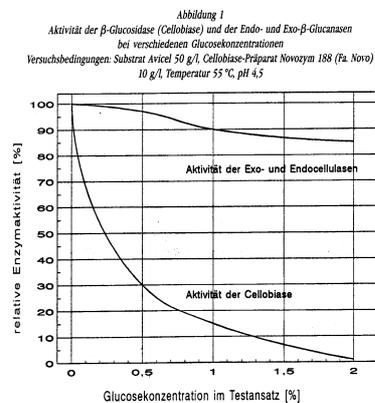
## 'Carbonic acid' process

Zengh et al. 1998 Biotechnology Progress **14**, pp.890-896



## Enzymatic cellulose hydrolysis

**Main obstacle:**  
**end-product (glucose) inhibition**

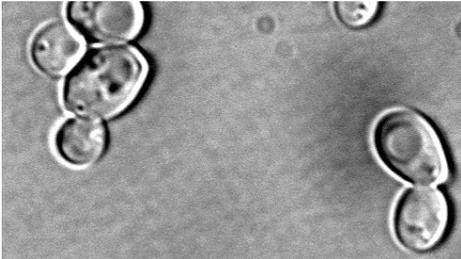


- **Improved cellulases required:**
  - at least 10 fold higher specific activity
  - include  $\beta$ -glucosidase ('cellobiase') without glucose inhibition
- **R&D: optimization of available & novel cellulases**

## C5 & C6 co-fermentation: broadening substrate range of *Saccharomyces cerevisiae*

### Obstacles:

- xylose (C5) uptake
- overproduction of xylitol due to redox problems



*S. cerevisiae* wildtype cells (W303 derivative)  
light micrograph;  
Peter Hollenhorst & Catherine Anne Fox

 **Saccharomyces Genome Database**

[http://genome-www.stanford.edu/Saccharomyces/yeast\\_images.html](http://genome-www.stanford.edu/Saccharomyces/yeast_images.html)

## C5 & C6 co-fermentation by anaerobic, thermophilic bacteria

### Potential

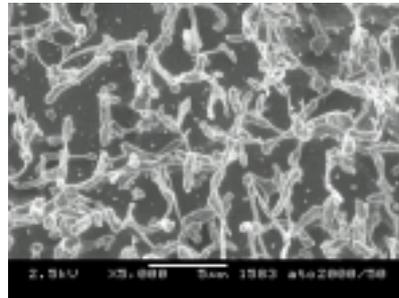
- broad substrate spectrum
- high ethanol yield on C6 and C5 sugars

### Obstacles

- formation of co-products
- substrate & ethanol tolerance

### R&D approach

- screening for EtOH production
- optimize ethanol + inhibitor tolerance



*C. saccharolyticus* (70 °C)

Photo: ATO BV

## Systems analysis

- **156 kton/yr ethanol plant**
- **feedstocks**
  - verge grass
  - wheat milling residue
  - willow prunings/'tops'
- **mild alkaline pretreatment; Ca(OH)<sub>2</sub>, 85% Ca recycle**
- **enzymatic cellulose hydrolysis; industrial cellulases**
- **thermal conversion non-fermentables in BIG/CC**

## Mass & energy balance

		Verge- grass	Willow tops	Wheat milling residue
<b>Mass balance</b>				
Feedstock	(kton dw/yr)	650	550	470
Water	(l/l ethanol)	54	46	28
<b>Energetic efficiency</b>				
- Ethanol	(% LHV)	40	47	55
- Electricity to grid	(% LHV)	15	15	12
- Total	(% LHV)	56	62	68

- **process energy demand (steam + e) fully covered**  
(steam: 80% to pretreatment + ethanol purification)
- **surplus electricity: -10% gross EtOH cost**
- **high water use (process + washing): 28-54 l/l ethanol**  
(vs. 10-15 l/l ethanol in current production)

## Investment costs

Section	Verge-grass		Willow tops		Wheat milling residue	
	MEuro	%	MEuro	%	MEuro	%
- Pretreatment	30	18	27	18	21	17
- Cellulose hydrolysis	12	7	10	7	9	7
- Evaporation	45	27	38	25	24	19
- Fermentation	16	9	16	10	16	12
- Ethanol purification	18	11	18	12	18	15
- BIG/CC	46	27	42	28	37	30
<b>Installed Equipment</b>	<b>166</b>	<b>100</b>	<b>151</b>	<b>100</b>	<b>125</b>	<b>100</b>
Other costs	147		134		111	
<b>Total investment</b>	<b>313</b>		<b>285</b>		<b>236</b>	
Inv. Euro/ton ethanol.yr	2000		1825		1500	

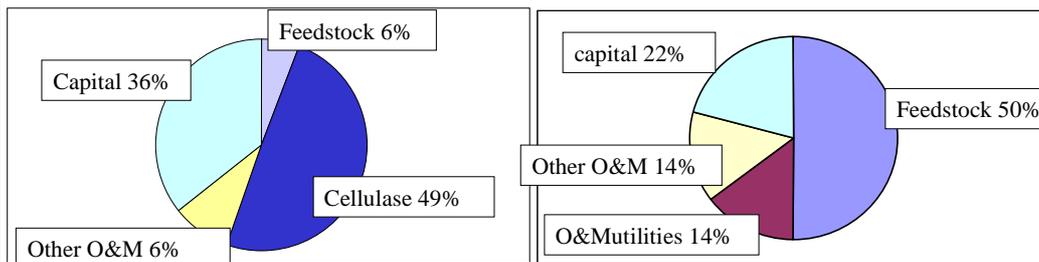


### • process integration:

- energy integration evaporation & distillation/rectification
- water management (reduction, recycle)

## Ethanol production costs

**Verge grass: 0.92 Euro/l** (44 E/GJ)    **Corn: 0.34 Euro/l** (16.2 E/GJ)



**cellulase + capital costs are major cost drivers**

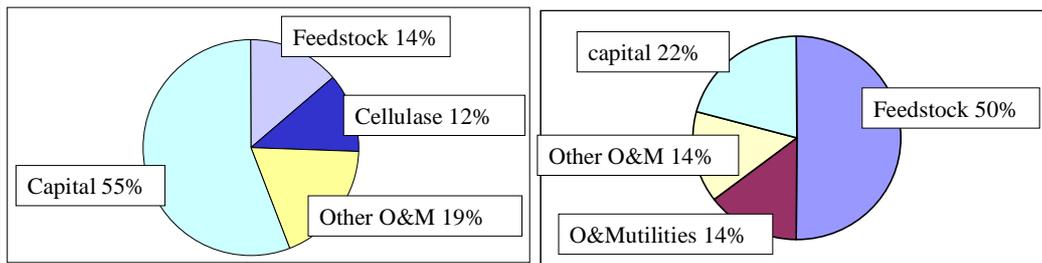
## Ethanol production costs

### Sensitivity analysis:

- 10 fold reduction of cellulase costs
- 30% reduction capital investments

**Verge grass: 0.33 Euro/l**

**Corn: 0.34 Euro/l**



## Ecology

		Verge grass	Willow tops	Wheat milling residue
Feedstock	(kton d.w.)	650	550	470
<b>CO<sub>2</sub> reduction</b>				
- Bio-ethanol	(kton/yr)	339	339	339
- Surplus electricity	(kton/yr)	251	213	145
<b>Total</b>		<b>589</b>	<b>551</b>	<b>484</b>
CO <sub>2</sub> reduction	(kton/kton EtOH)	3.8	3.5	3.1
<b>Ashes</b>	(kton/yr)	<b>60</b>	<b>20</b>	<b>10</b>

- **CO<sub>2</sub> reduction: 3.1 - 3.8 kton /kton ethanol**
- **ashes: 10-60 kton (2-9%)**  
 >> **recycle in fertilizer or building material ?**

## R&D: 2003-2006

- **feedstock<>pretreatment<>hydrolysis<>fermentation**
  - mild alkaline extraction & CO<sub>2</sub>/thermal treatment
  - optimize effectiveness available & novel industrial cellulases
  - ethanol & lactic acid fermentation
- **screening for novel C5 & C6 fermenters**
- **BIG/CC, process integration**
- **fuel specifications & distribution**



## economieecologietechnologie

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