SIXTH FRAMEWORK PROGRAMME

PRIORITY [6.1]

[SUSTAINABLE ENERGY SYSTEMS]

INTEGRATED PROJECT

Publishable report (NILE project)

Evaluation by computer simulation of the influence of lignin separation on mass flow and cost for lignocellulosic bioethanol plants

Project acronym: NILE

Project full title: New Improvements for Lignocellulosic Ethanol

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1 Context and methods

1.1 Introduction

Lignin is the second most abundant renewable matter in nature. Most of the plant material on earth contains this substance. Lignin free or low lignin plant products can only be found in fruits, fruit bodies and roots. All other parts of the plant, like stems and leaves, contain substantial amounts of lignin. If it comes to the use these later parts for biofuel production, the question of what to do with this lignin becomes crucial. In any system in which biofuel is produced from another type of biomass than fruit bodies (e.g. corn or oils pressed from fruit bodies), the lignin issue is of great importance. Furthermore, the part of biomass which is containing lignin, called lignocellulose, is by far the biggest part of the natural material available on terrestrial earth for sustainable production of energy and chemicals.

Lignin is of a completely different chemical nature than the other main components of biomass, like cellulose and hemicellulose and cannot be converted into ethanol.

Typically, the lignin content of lignocellulosic material is between 15 and 30%. This means that if the other components of biomass are transformed into ethanol at theoretical yield, which is -depending on the mechanisms involved- slightly higher than 50%, in any lignocellulose based bioethanol factory, the amount of lignin produced will be at least half of the produced ethanol. Typically it's rather the same amount as ethanol. With the yields of the present state of art, there is in the majority of the cases even more non hydrolysed residues, of which most is lignin, than ethanol

Furthermore, lignin is potentially an import market product as raw material for chemical and life science industries. Its aromatic compounds have multiple speciality chemical properties and show important bioactive effects.

Some studies for energy need in bioethanol plants show that the energy content of lignin is higher than the need for ethanol production. Therefore, even if a part of the lignin is used for process energy there will always be an energy excess which can be used for other purposes like external energetic uses or as chemical raw material.

The evaluation of the potential impact of lignin separation and of different options for lignin separation and its use for non energy purpose appears for these reasons to be a highly important task.

1.2 The problem to be solved

1.2.1 General objectives of the simulation

The work here reported addresses the following objectives:

- Development of a simple simulation tool that allows to check at any stage of research- before, during and after the research work- the influence of a big amount of parameters on a *complete* industrial system for economical and ecological efficiency of the process, including the different options for lignin separation.
- Development of a tool that for energy data and investment can be calibrated with any type of other external data: literature data, input from other software like ASPEN or IKARUS,

calculations done ad hoc[1] or offers from equipment producers. In the work here done the two first possibilities will be used in order to be able to compare our work with other simulations. This shall also allow to compare the price level of the investment figures used among several partners in the project.

- Development of a tool that, after calibration, can for the selected specific types of systems, calculate all the relevant economic and mass stream data using standard engineering approaches (like exponential law for investment and linear relations for energy consumption[2]), but being able, once the calibration is done, to very quickly evaluate a big amount of variants by calculating in one step the implications of any set of the numerous parameters involved, without being obliged, during the evaluation phase, to pass from different specialised software to another.
- Development of a tool with limited complexity for the user but that still contains information about significant parameters like investment costs, energy consumption or waste treatment cost and which automatically adapts the values for such complex parameters to changing process parameters.
- Development of a tool based on Excel spreadsheet software which calculates the global mass, energy and economic balances of an entire bioethanol production factory.
- Simulation of different initial scenarios in order to evaluate which are the most important parameters on which the lignin related research in the Nile project has to concentrate
- Contribute to the understanding of the sensitivity of the models towards uncertainties and variations of the process parameters
- Simulate the different options for lignin non energetic uses and compare the cost benefit resulting for given market values of this lignin
- Finally as far as the results of the NILE project will be sufficiently final and representative for such purpose, the various options of lignin separation will be simulated in a final case study involving straw and softwood as raw material

1.2.2 Problems to be solved in the first step

In a first step, the work concentrated on the development of the computer simulation tool itself and on a first application with values as good as available at that time. For this achievement the goals can be organised in four tasks: collection of data, construction of a mass and energy flow sheet, economic evaluation, evaluation of first complete scenarios.

1.3 Description of work on collection of data

For solving the problem of data availability several approaches were developed:

- Assessment of literature data. Fortunately, there is quite a lot of data published about bioethanol production. Even for aspects like investment cost and energy efficiency, there exists a lot of elements in literature. These literature data represent a good benchmarking reference that allows to adjust the work here done to what has been presented by other groups in the past.

[1] Detailed calculations could be introduced into the model, but this has not been done for the moment
[2] Except for distillation where an exponential law was used as well

- For some elements, no literature data was available. This was namely the case for most elements regarding lignin separation at the front end. For this case, engineering data available company internally have been used.

1.4 Description of work on mass and energy flow sheet

In this subtask, the main problems addressed were of two types:

- definition of the structure of the calculation (final selection of the parameters, organisation of the individual sheets, formulas to be used etc.). The options selected for these questions are described in the following paragraphs
- optimisation and debugging of the first version. This work needed special attention. Some initial choices of the excel options, turned out to be problematic. Easy creation of new sheets and easy copy-paste of information is not possible with some Excel options. Some work had to be redone with new formulas in order to obtain a more user friendly organisation.

1.4.1 Principle of organisation of the model

The principle of the calculation is to have one Excel sheet for every major process step, which is called MODULE. All of these modules have an identical structure. What changes is the transfer formula between the input stream and the output stream. All inputs are either coming from another process step or corresponding to a physical input of chemicals, energy, raw materials etc. All outputs are either going to another process step or to a physical output of the system to the environment (effluents, output to air, solid residues, market products etc.).

Products added in every process step are listed is a separate column labelled "Added Products".

The transfer formula defines the way the input streams of each module are converted into output streams

1.4.2 Modules and sheets

On the left side of every module an identical list of the components of the module input can be seen. This list is freely defined on the first module. Changes on this first list are automatically transmitted to all modules. For improved readability and easier work, an identical list of products is also automatically shown on the right. All values are in percent of the total flow in this step as well as in absolute values which are all in tons/hour.

All % values in weight % on undried raw material	Input from	Masses on total humid raw material		Added Products		Output Masses		Out of System	All mass values in tons/hour
Total Flow		168.00%	19.76	260.50%	30.6	428.50%	50.41		Total Flow
Dry Matter		85.00%	10.00	0.00%	0.0	88.50%	10.41		Dry Matter
Organic		77.63%	9.13	0.00%	0.0	77.63%	9.13		Organic
Lignin	Screening_Impregn	16.12%	1.90	0.00%	0.0	16.12%	1.90	0	Lignin
Hexosan	Screening_Impregn	32.88%	3.87	0.00%	0.0	31.89%	3.75	0	Hexosan
Pentosan	Screening_Impregn	16.97%	2.00	0.00%	0.0	1.70%	0.20	0	Pentosan
C6 Sugars	Screening_Impregn	0.00%	0.00	0.00%	0.0	0.00%	0.00	0	C6 Sugars
C5 Sugars	Screening_Impregn	0.00%	0.00	0.00%	0.0	15.28%	1.80	0	C5 Sugars
Other	Screening_Impregn	11.66%	1.37	0.00%	0.0	12.65%	1.49	0	Other
Ash		7.37%	0.87	0.00%	0.0	10.87%	1.28		Ash
Na2SO4		0.00%	0.00	0.00%	0.0	0.00%	0.00	0	Na2SO4
H2SO4		0.00%	0.00	0.00%	0.0	3.50%	0.41	0	H2SO4
Other	Screening_Impregn	7.37%	0.87	0.00%	0.0	7.37%	0.87	0	Other
Liquids		83.00%	9.76	253.53%	29.8	340.00%	40.00		Liquids
H2O	Screening_Impregn	83.00%	9.76	253.53%	29.8	340.00%	40.00	0	H2O
Ethanol		0.00%	0.00	0.00%	0.0	0.00%	0.00	0	Ethanol

Table 1.4-1 Example for the organisation of a standard module

Transfer formula can be written freely by using any Excell calculation formula. For allowing to identify them easily they are highlighted in dark orange. Not highlighted output fields are just doing a standard addition of input and added products.

Input fields are highlighted in brighter orange in the column "Added Products". By default, all input values are zero and highlighted. Input can either be done in percentage values or in absolute t/h values. In the later case, highlighting has to be changed manually.

Process chemicals are listed as separated lines at the end of the components list (table 1.4-2). Their values are entered in the "Added Products" column with identical highlighting conventions as in the previous section.

The same applies for utilities.

Process Chemicals (added in Module)			0.00%	0.0
H2SO4			0.00%	0.0
NaOH			0.00%	0.0
Yeast			0.00%	0.0
Enzymes			0.00%	0.0
Utilities			0.00%	0.0
Steam (t/h)			0.00%	0.0
Compressed Air (m3/h)				39.2
Cooling water (m3/h)				0.0
Electricity (kW)				59.8

Table 1.4-2 Example of area for process chemicals and utilities

A special case of transfer formula is the splitting and merging of material streams. Typical examples are a filtration, an evaporation, a joining of several process stream originating from different modules. For various reasons it turned out to be most efficient to have a separate area in the Excel sheet reserved for such splitting and joining operations, called split or merge tables. This allows namely to easily calculate what happens without too heavy and incomprehensible formulas. In case of problems with the calculated values, all partial and total mass streams for every component of the mass streams can be examined in detail as they are listed in an easily controllable way.

All mass values in tons/hour	Total	Main Stream to Hydrolysis 2	Filtrate	Control Sum
Total Flow	51.5880706	30.87680006	20.7112705	51.5880706
Dry Matter	10.4116	7.486160059	2.92543994	10.4116
Organic	9.133	6.759840588	2.37315941	9.133
Lignin	1.9	1.9	0.0	1.896
Hexosan	3.8	3.8	0	3.75196
Pentosan	0.2	0.113441262	0.08625874	0.1997
C6 Sugars	0.0	0	0	0
C5 Sugars	1.5	0.0	1.5	1.527705
Other	1.8	0.998439326	0.75919567	1.757635
Ash	1.2786	0.72631947	0.55228053	1.2786
Na2SO4	0.0	0	0	0
H2SO4	0.4	0.233812837	0.17778716	0.4116
Other	0.9	0.492506633	0.37449337	0.867
Liquids	41.1764706	23.39064	17.7858306	41.1764706
H2O	41.2	23.39064	17.7858306	41.1764706
Ethanol	0.0	0	0	0
Gaseous products	0	0	0	0
SO2	0.0	0	0	0
CO2	0.0	0	0	0
O2	0.0	0	0	0

Table 1.4-3 Example of a split table

1.4.3 Main parameters

Every module is headed by a process parameter section which has the function of a main panel showing all variable parameters used in this module.

Process Parameters			
Key parameters	Cellul. loss to byproducts	3.00%	Lynd 1996, p. 748
	Sugar yield on hemic.	90.00%	Lynd 1996, p. 748
Miscellaneous	Concentration acid	98.00%	
	Concentration caustic	0.00%	
	Biomass/Water	25.00%	Lynd 1996, p. 748

Table 1.4-4 Example of a process parameter section

Sources of data can be indicated by using the Excel labelling function.

The main parameters used in this work are the following:

- raw material: composition in terms of components
- pre-treatment: water/biomass ratio, loss of cellulose in degradation products, sugar yield from hemicellulose, C5 recovery yield, water content of filtration cake
- lignin separation: water/biomass ratio, loss of cellulose in degradation products, recovery yield of lignin, water content of filtration cake, energy efficiency of drying, dryness of powder
- hydrolysis: water/biomass ratio, sugar yield from cellulose, water content of filtration cake
- ethanol production: ethanol yield on C6, ethanol yield on C5, concentration of ethanol, energy efficiency of distillation
- waste treatment: energy efficiency of drying, dryness of solid residue, COD (=chemical oxygen demand) reduction of biological treatment

For the C5 sugars it has been supposed for a first simplified modelling that all of them are separated in the pre-treatment step.

The remaining values are defined by the addition of process chemicals and utilities that can be found in their corresponding section.

1.4.4 Global flow sheet

The automatic display of the calculated values at every process step was a major challenge of this work. The objective for this was to obtain one Excel sheet which summarises all mass flow values and shows them for each process step in an easily identifiable way on a one page flow sheet.

The difficulty was to find a way of presentation that allowed to include all data in a readable form. The big amount of information makes it difficult to fit everything in a readable format. Finally a quite dense presentation has been retained that allows to be taken over into Word files in one single horizontal page (see Figure 1.4-1).

Process steps (modules) appear there as orange boxes that are labelled with the process name, which corresponds precisely to the name used for every step in the Excel sheet.

The main process streams are indicated by yellow arrows. Every stream is named with a corresponding label (white colour).

The mass flows at every module (inputs, outputs and flow in between modules) are indicated by black arrows and the corresponding values in brackets.

Utilities and added process chemicals are showed by cream coloured arrows.

System outputs (market products, output to environment) have red arrows.

The initial goal to have an automatic generation of the process flow sheet was difficult to achieve. No functions allowing that in a simple way could be identified in Excel.

In the first model, unfortunately, the creation of a consistent flow sheet had to be carried out manually and represents an important part of work for every scenario. Many elements must be re-adjusted manually. But once a scenario is done the existing sheet can be used very efficiently for displaying the value in order to do consistency check and trouble-shooting.

A global verification sheet allowing to sum up all inputs and and compare them to the outputs has further been developed. This allows to make sure that no error in stream assessment and calculation has been made. Indeed: in case of such errors they are very likely to show up in this calculation as a non zero balance between inputs and outputs.

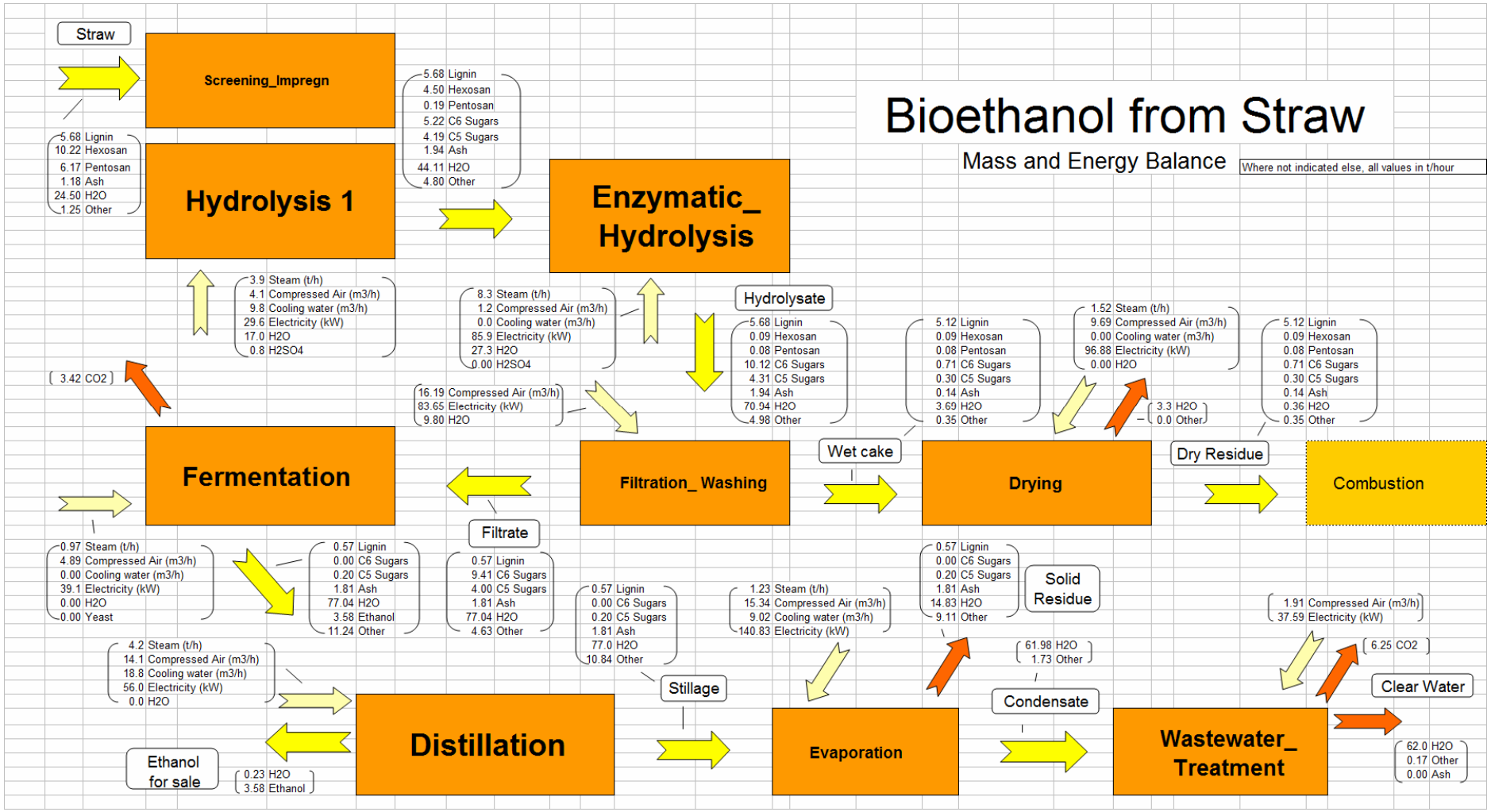

Figure 1.4-1 Example of a global flowsheet (without lignin separation). Fictional system parameters only for illustration purpose

1.5 Description of work on economic evaluation

Here again the problem can be decomposed into the gathering of data and the realisation of the calculations.

For data gathering, a geographical frame (country of the project) had to be fixed. The assessment of all economic parameters (chemical cost, utilities, salaries etc.) represented a further group of problems to be solved.

Furthermore, the realisation of the calculations requested a choice of the economic model to be used: calculation of a payback system for the investment, calculation of financial cost (interests and capital costs), calculation of return on investment.

1.5.1 Investment costs

Investment costs have been evaluated for every process step. A basic evaluation was done for a standard size of the equipment. The actual value was then calculated by using standard extrapolation formula as currently used in engineering (scaling factors of 0.6 exponential). The parameters determining the extrapolation were selected for every process step in a way to make them adapted for the nature of the equipment used.

The following parameters were used for the different process steps:

- pre-treatment: total mass flow
- lignin extraction: total mass flow
- lignin precipitation (LPS): total mass flow
- lignin drying: evaporated water flow
- hydrolysis: total mass flow
- fermentation: total mass flow
- distillation: evaporated water flow
- drying of fermentation residue: evaporated water flow
- evaporation of distillation residue: evaporated water flow
- biological treatment (waste water treatment): flow of organic material

The calculation base is for equipment produced and delivered in the European Union. Considering other regions of the globe as possible suppliers might considerably improve the cost structure of the equipment.

1.5.2 Operational costs

The evaluation of this part (including financial cost) might represent the biggest uncertainty in this project. This is due to strong local dependency of operational cost (e.g. electricity prices which can be very variable from one country to the other), but also to unknown information difficult to evaluate (for example: the real need for man power and maintenance for this type of production plant). The following is explaining the options selected for our calculations.

Utilities and process chemicals were evaluated according to a French industrial level cost base at the end of the year 2004 (4^{th} quarter 2004).

Manpower was estimated as based on an average salary for three shifts (resulting in 5 teams per 3 shifts in order to take into account free days, holidays and other leaves). For a plant size of 10 ton/hour of dry raw material, 12 workers per team were assumed.

The price of enzyme was not available, but was for the first step adjusted in a way to have global prices for hydrolysis that are in the same range as the sulphuric acid costs, that would be necessary for realising the same hydrolysis task.

Yeast was for the first step supposed to be recyclable and if any additional had to be produced on site and all cost for its production was supposed to be included in investment for fermentation and other operational cost.

For pelletisation of the residue before combustion, only operation cost was considered. Possible investment costs are absorbed in the production cost for pellets that was here used (10 Euro/ton for 100 Euro/ton of energy value for sales).

Regarding the calculation of financial cost, different options were evaluated. In order to make the present evaluation fit with other work of the authors, finally a simplified model was used (a global 20% as margin). The main goal of the work here is to see the dependency of production cost from the different options for lignin separation and uses.

1.6 Scenarios to be evaluated

Multiple scenarios are possible for bioethanol production plants as considered in the Nile project. The following list gives the main aspects as well as the technical options for each of them:

- Hydrolysis process: Acid hydrolysis, enzymatic hydrolysis, separate hydrolyis and fermentation (SHF) or simultaneous saccharification and fermentation (SSF)
- Type of lignin separation (front end: extraction after pre-hydrolyis, end of pipe: extraction on the solid residue after final hydrolysis, extraction process: alkaline or with organic solvents)
- Type of pre-treatment (HCl, H2SO4, steam explosion, SO2)
- With or without C5 separation after pre-treatment by filtration
- Options for treatment of residues and liquids
- Type of raw material: Spruce or Wheat straw

An adapted choice had to be done for reducing the number of variables for this first stage. This had to be done in a way that the data generated were still representative for the general question this is the role of lignin in a future bioethanol plant.

2 First simulations

2.1 Preliminary remark

This report shows various calculation results -a type of computer based experimentation- on the interest of lignin separation for other use than energy production in the process. The different results have been obtained over a period of 4 years and at each step of the work different model conditions have been applied, with generally speaking an increase in the introduced details from the early first simulations (just below) throughout the project, until the most detailed calculations of the final "cutting edge" models.

It appeared interesting to the authors to show this evolution over a several year project work and to present the calculation results and details for every stage of the work. The authors believe that going

through these different results, allows to get a better impression on the importance of the here examined question, than this would be possible by just giving the final most detailed models, which are not completely confirmed by experimental data because of limited time and money in this project. Only the final commercial implementation of a process can definitively decide these questions. Also the general impression the authors got from this work, was that the more details were introduced in the calculations the more it became difficult to understand in which conditions lignin separation would be the most promising, and the more it became also difficult to support all parameters with experimental data.

However the authors trust that when going through all the details of the work the reader will get his own opinion on the question, which hopefully will be close to the -cautious- conclusions formulated at the end of the report.

2.2 Selected scenarios for early simulations

2.2.1 Preliminary results for Wheat straw

It is generally assumed that lignin extraction is easier for straw or other annual plants (higher yields of extractable lignin). For this reason, the first evaluation concentrated on straw as raw material. A basic case without lignin separation was used as a reference.

Pre-treatment on straw is in the project done with steam explosion using H2SO4.

The first simulation was carried out by using alkaline extraction (NaOH) on the solid part after pre-treatment and filtration (front-end lignin separation with C5 separation).

The initial case studied was 10t/hour of dry biomass, to assess the impact of the lignin use on the economics of the overall biorefinery process at a relatively small scale. This gives also a reasonable size for lignin market development. Such a plant could therefore constitute a realistic first step in the commercial upscale for lignin non energetic uses in bioethanol production plants.

The assumed overall ethanol yields from raw biomass were 40% for C6 and 35% for C5.

The selected process is using investment ratios and energy consumptions suggested by the NREL publications, namely Lynd et al. (1996)[3]

The figures here used are based on the "advanced technology" scenario, adjusted for some points with less optimistic data where ever this seemed necessary to the authors of this report.

The general process concept was adapted to the schemes used else where in the project at this stage of advancement (no power cycle but drying and pelletisation of the residue). However separate hydrolysis and fermentation (SHF) was assumed.

[3] Lynd et al., App. Biochem. Biotechn., p. 741-761, (57/58), 1996

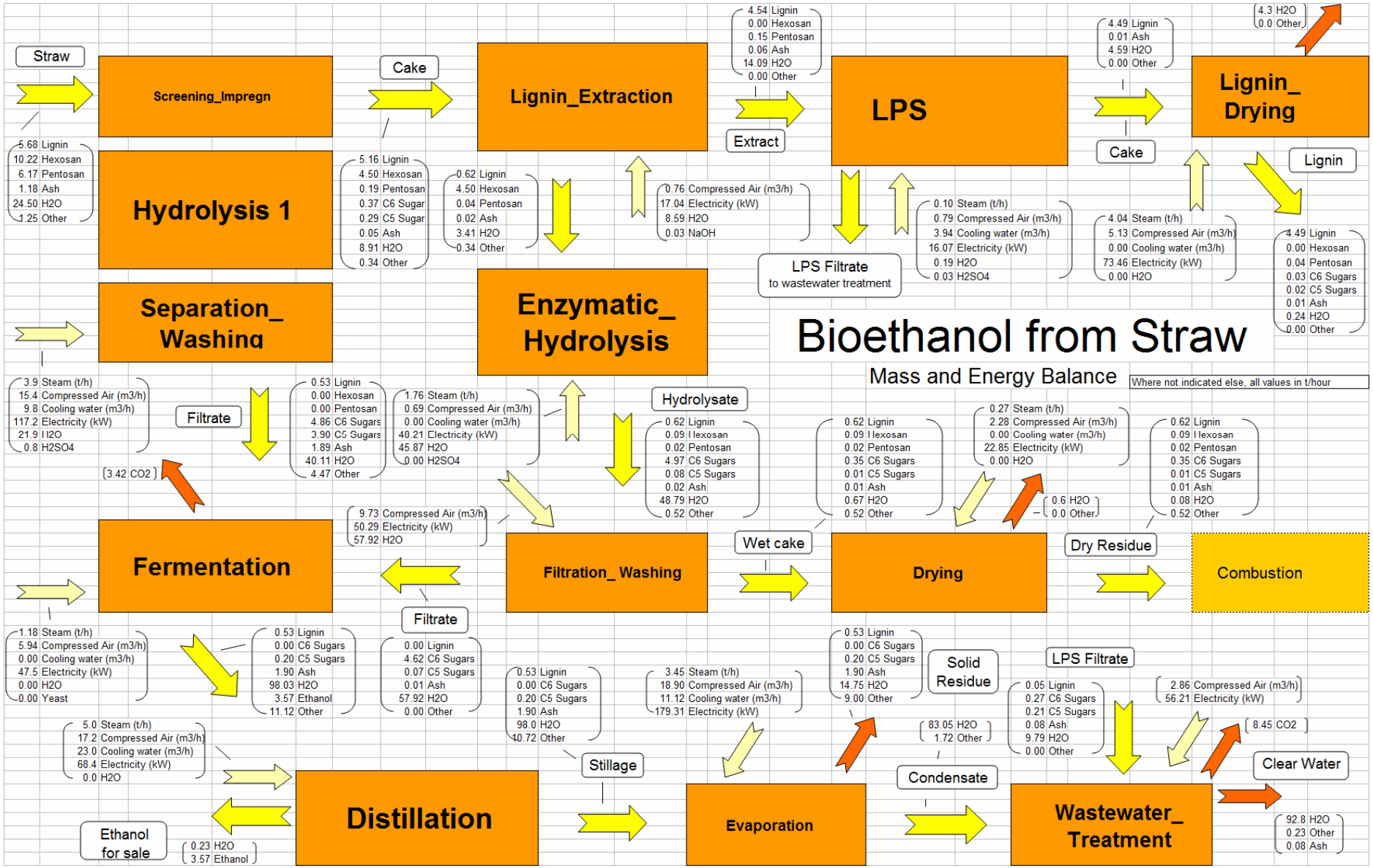

Figure 2.2-1 Example of a global flowsheet (with lignin separation). Fictional system parameters only for illustration purpose

The lignin extraction yield was supposed to be 85%.

The flow sheet for the reference case without front-end lignin separation, is identical with the exception that the cake from the pre-treatment is going directly into the enzymatic hydrolysis. The process steps "Lignin-Extraction", "LPS" and "Lignin Drying" are dropped.

2.2.2 Economic results for wheat straw

The investment was estimated to be 34 million Euro for the base case and 37 million Euro with lignin separation. The later figure takes into account the cost for alkaline extraction and lignin precipitation and drying. Benefits for reduced mass streams thanks to the separation of lignin have been calculated. But also increase of investment for the lignin separation variant for the steps of evaporation and waste treatment was included in the calculations (because of the additional stream coming from alkaline extraction).

The solid residue after hydrolysis was supposed to be transformed into pellets, usable for decentralised energy production. The fuel value for pellets was estimated to be 100 Euro/ton (dry basis). The lignin revenue for a marketable lignin was supposed 250 Euro/ton ex works.

Using these assumptions, a complete simulation of mass balance, energy need and investment cost for every process step has been carried out. These detailed calculations showed that under the selected hypothesis the potential reduction of production cost for 1kg ethanol is from 89 Eurocents/kg to 66 Eurocents/kg, or 51 Eurocents/l.

It can be concluded, at this stage, that the separation of lignin at the front end does virtually allow to obtain substantially reduced cost for straw ethanol production. This preliminary conclusion has, in the following chapters, to be confirmed by further improvements in the model and –as far as available- experimental data about lignin extraction yield, ethanol yields on C6 and C5 sugars as well as by more detailed calculations of investment costs and energy balances.

2.2.3 Results Spruce

A similar preliminary simulation was carried out for softwood Spruce. Although in this case the lignin separation yields seem to be clearly lower, the calculations were applied also to a raw material with a typical Spruce composition. For the remaining, identical options were used for this scenario than for the case of straw. A lignin extraction yield of 40% was assumed.

The reduction obtained is less than in the previous case and going from 85 Eurocents/kg to 75 Eurocents/kg. The main reason for this is the reduced yield of lignin which gives lower revenues but with additional investment and chemicals cost similar to the case with higher lignin separation. However, even in that case, it can be preliminarily concluded that lignin separation pays for more than the cost generated by the separation.

2.2.4 Updating of simulations with lower yield data

Before doing further work on the sensitivity of the models, material balance data, mainly for the different yields and process step concentrations, has been collected and defined in cooperation with other project partners. The resulting yields were in general much less optimistic than for the earlier case from literature that has been examined in the preliminary work.

The finally retained figures were: 80% C5 yield in prehydrolysis, 90% of C6 yield in enzymatic hydrolysis, 79% of ethanol (on theoretical 51%) in fermentation and 40% recovery yield of lignin. The model also used conservative assumptions about concentrations of the process streams (20% in prehydrolysis and 10% in enzymatic hydrolysis). In the text that follows, several options with higher concentrations are also analysed.

With these parameters the global production price was slightly higher because of the reduced yields, but the difference between the two models was less pronounced (same size of plant as initial models: 10 tons of straw (on dry)/h, delivering here 15200 tons of ethanol per year):

- Without lignin front-end separation: 82 cts/kg or 65 cts/L,
- With lignin front-end separation: 77 cts./kg or 61 cts/L.

2.2.5 Ethanol concentration

An important factor for production cost is the concentration of the ethanol before distillation. With the new figures this was of course lower than for the earlier simulations. Several dozens of process variants have been examined for understanding the influence of different scenarios on that question. The table below gives a summary of the results.

Case number	C5 separation after pre-treatment	Lignin separation	Dry matter in prehydrolysis	Water insoluble solids (WIS) in enzymatic hydrolysis	Ethanol in distillation feed
1	Yes	40%	20%	12.00%	2.41%
2	Yes	40%	20%	20.00%	2.96%
3	Yes	40%	29%	20.00%	3.52%
4	Yes	None	17%	20.00%	2.31%
5	No	None	17%	10.00%	2.96%
6	No	None	20%	13.5%*	3.81%
7	Ethanol extraction	90%	Not applicable	20.00%	6.70%

* highest possible value in the model

Table 2.3-1 Influence of the different process parameters on ethanol concentration in distillation

The sensitivity to raw material composition has also been evaluated. In the NILE project, the different partners used different straw compositions at this stage of the project. The one used in this model was available internally and is in between the extremes. However an optimistic composition (higher hexose and pentose) was used to verify the sensitivity to the selected composition. With the most optimistic compositions available within NILE the increase in case 5 was from 2.96 to 3.14 % and in case 6 from 3.81 to 4.05%.

Ethanol extraction of lignin is a very good option from this point of view. But even there the WIS in enzymatic hydrolysis would have to be at least 12% in order to reach 4% ethanol concentration. With 20% WIS it would be 6.7% (case 7)

3 Work on further improvement of models

3.1 Overview on the work in this step

In a further step, the simulation work has concentrated on verification of the multiple system variants in order to get a better understanding of the key factors of a bioethanol production system and more particularly of the possible influence of lignin separation on technical parameters and on

ethanol production costs. For this purpose it was important to verify numerous aspects of the basic simulation model:

- energy costs have been made compatible with other NILE project data (different project internal and published models use quite different energy needs)
- the distillation energy as a function of ethanol concentration has been modelised
- ethanol concentration has been further studied and the different factors influencing it have been better understood
- the influence of the raw material composition was analysed in detail

For this purpose, four types of simulations have been recovered from earlier work and all have been updated and debugged:

- basic simulation without C5 separation after pre-treatment, without lignin separation
- as above but with C5 separation after pre-treatment (goal: improve yield of biotechnology through reduction of organic acids, phenolic and other inhibitors)
- with lignin front-end alkaline separation, with C5 separation after pre-treatment
- As preceding, but without C5 separation after pre-treatment

For each of these systems, multiple simulations have been carried out. Among the varying factors were:

- concentrations of process streams during pre-treatment and during enzymatic hydrolysis (in most cases this is adjustable by changing the amount of fresh water added in stream)
- three different raw material compositions
- percentage of recovered lignin (40 to 99%)
- dry matter obtained in the filter cake after prehydrolysis and after enzymatic hydrolysis
- yields on ethanol for C6 and C5 components (different hydrolytic steps and fermentation)
- sales price of lignin

3.2 Updated energy costs

During the verification work of the model parameters, all the energy data available were analysed. The sources used different ways of presentation and a considerable work was necessary to organise the data in a consistent manner that allowed comparison. From this it resulted that quite different energy data are used by different authors (external sources and project partners). Namely for steam consumption an important difference was detected.

Table 3.2-1 shows the steam data obtained with the more optimistic assumptions (pre-treatment at 215° C, 45% dry, SSF at 10% solids, 37° C, 72 hours).

	MJ/Liter	kg steam/ L EtOH	t steam/h*
Pretreatment	1.5	0.6	1.4
Drying	1.9	0.7	1.8
Distillation	9.8	3.8	9.2
Evaporation	4.0	1.6	3.8

* for a 10 tons straw/hour plant

Table 3.2-1 New steam consumption data used in the simulations

Fore the sake of consistency, these lower steam data have been implemented in our models for all the following simulations. All energy data other than the specifically mentioned in table 3.2-1 are as before (based on NREL data).

3.3 Modelisation of distillation energy

Distillation energy is the most important contribution to the energy needs of bioethanol. It depends mainly on the ethanol concentration. This dependency can generate energy consumptions for distillation varying by more than 50%. To improve our model, the available data on that topic were collected and analysed. Fig. 3.3-1 shows the data after conversion into a graphic that is treatable by Excel. A regression equation was determined and the corresponding equation introduced into the calculations of the spreadsheets.

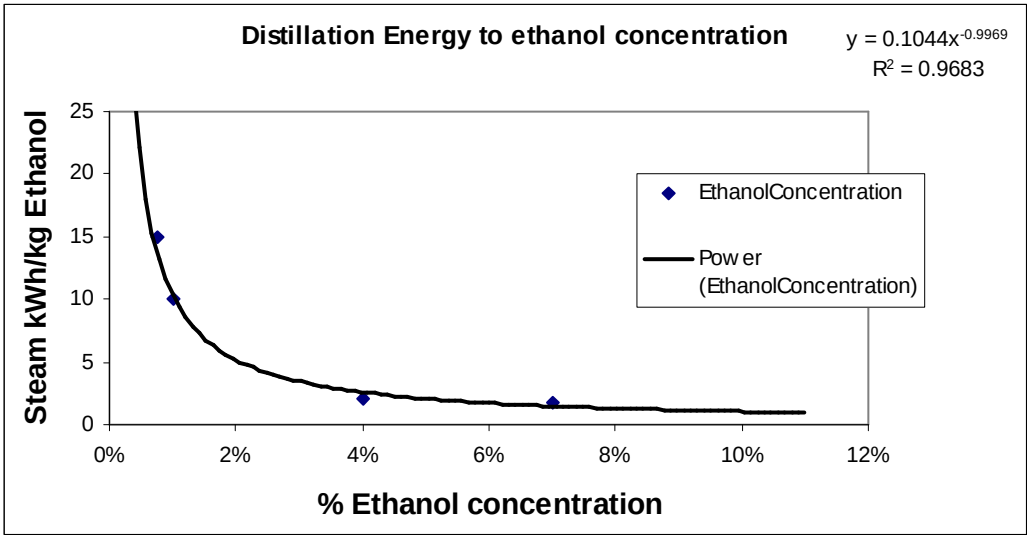

Figure 3.3-1 Plot and regression equation for distillation energy

3.4 Further work on ethanol concentration before distillation

The identification of factors that can increase the ethanol concentration before distillation has been a constant worry within the work for this project. The target ethanol concentration in the project was 4%. First calculations (see tab 2.2-1) show that in most of the case studies done so far we had problems to meet this target. Therefore additional work has been done to understand the reason for this.

The results obtained on the different topics are summarised in the following:

- Concentrations of process streams. In the reviewed models the highest possible concentrations for process streams were re-applied. Two cases were compared (see table 3.4-1): 20% dry matter in prehydrolysis and 12% WIS in enzymatic hydrolysis (hereafter called "low concentration") and 29% dry matter in prehydrolysis and 20% WIS in enzymatic hydrolysis (hereafter called "high concentration"). The high concentration case corresponds to the highest concentrations experimentally under verification in NILE or other projects (as far as known to the authors). As it can be seen also in table 3.4-1, passing from the low concentration to high concentration increases considerably the ethanol concentration (from 3.99 to 5.76% and from 4.35 to 7.25% for respectively without and with lignin recovery).
- Separation after prehydrolysis. Table 3.4-1, also shows that with such separation the ethanol concentration collapses to almost half. According to these new models, the increased yield achieved of this separation of inhibitors must therefore be very important to counterbalance this. However this allows a quite good recovery of the the C5 sugars which

might be used in another process (see chapter below on C5 separation). In all other cases this separation cannot be recommended.

- Lignin yield. Lignin separation clearly favours the ethanol concentration. The potential is anywhere between 5.76 and 8.86% depending on the lignin recovery yield (from 0 to 99% recovery).

#		Dry Matter in Prehydrolysis	Water Insoluble Solids (WIS) in enzymatic hydrolysis	Lignin Recovery	EU/kg 94%	EU/L 94%	Investment Mio. Euro	% EtOH in distillation
12	With separation after prehydrolysis	20%	12%	none	0.826	0.652	22.5	2.14%
9		29%	20%	none	0.787	0.621	21.6	2.75%
10	Without separation after prehydrolysis	20%	12%	none	0.671	0.530	18.3	3.99%
8		29%	20%	none	0.634	0.500	16.8	5.76%
20a	With separation after prehydrolysis	20%	12%	40%	0.598	0.472	22.3	4.35%
21		29%	20%	40%	0.568	0.449	20.2	7.26%
23		29%	20%	99%	0.405	0.320	20.7	8.86%

is the number of the simulation in the simulation log file

Table 3.4-1 The main variants of importance for the obtainable ethanol concentrations before distillation

- Adjustment of filter cake after prehydrolysis. In the case of lignin separation it was also found that the filter cake after prehydrolysis had in some cases to be more humid to allow the 20% WIS goal in the enzymatic hydrolysis.
- Raw material composition. More favourable raw material compositions clearly increase the ethanol concentration (see related chapter hereafter)

These new calculations show that the target concentration can be easily met with the reviewed models (except in the case of separation of streams after pre-treatment).

3.5 Influence of raw material composition

The straw composition here used (average composition internally available, see first part of the following table) seems to be on the lower side of desirable and possible quality of industrial material. Other organics seems rather high as well as ash. Therefore a more optimistic composition has been evaluated (simulations # 35 and 36) and this allowed to reduce the cost by about 15%!

Furthermore a "dream composition" was evaluated (simulations # 41 and 44), with very high lignin content (40%), almost only hexosans (50% compared to only 5% pentosans) and low organics as well as ash. A complete lignin separation would in this case allow production costs of as low as 8.6 Eurocents/liter!

#	Lignin	Hexosans	Pentosans	Other organics	Ash	Lignin Recovery	EU/kg 94%	EU/L 94%	Investment Mio. Euro	% EtOH in distillation
8	19%	39%	20%	14%	9%	none	0.634	0.500	16.8	5.76%
21						40%	0.568	0.449	20.2	7.26%
22						80%	0.458	0.362	20.7	8.25%
23						99%	0.405	0.320	20.7	8.86%
35	21%	43%	23%	8%	5%	40%	0.491	0.388	20.3	7.91%
36						99%	0.338	0.266	20.8	9.67%
41	40%	50%	5%	2%	3%	40%	0.442	0.349	21.8	5.71%
44						99%	0.109	0.086	22.3	7.92%

is the number of the simulation in the simulation log file

Table 3.5-1 Results obtained with different raw material compositions (all based on high concentration models)

3.6 Potential for increased yields

After optimisation of the models, it seems interesting to redo a comparison for higher yields as had earlier in this project. Namely the 79% on theory for fermentation seems rather low and can be expected to be improved. For this reason, it seems relevant to study the relative importance of lignin separation also for higher yields. The table below shows that with such improvement (the advanced technology scenario of Lynd 1996) the production costs can be considerably reduced.
Strikingly, the cost reduction potential for lignin (about 80% recovery) stays almost exactly the same for reduced yields or the more optimistic case (around 25%)!

	Prehydrolysis		Enzym. Hydrolysis		Fermentation						
#	C5 yield	C6 yield	C5 yield	C6 yield	Yield on theory C6	Yield on theory C5	Lignin Recovery	EU/kg 94%	EU/L 94%	Investment Mio. Euro	% EtOH in distillation
7b	66%	95%	90%	90%	79%	79%	none	0.602	0.475	16.8	6.15%
21	66%	95%	90%	91%	81%	81%	40%	0.568	0.449	20.2	7.26%
22	66%	95%	90%	91%	81%	81%	80%	0.458	0.362	20.7	8.25%
18a	77%	97%	90%	94%	95%	95%	none	0.486	0.383	16.1	7.64%
15a	77%	97%	90%	94%	95%	95%	82%	0.371	0.292	20.1	10.12%

is the number of the simulation in the simulation log file

Table 3.6-1 Potential of increased yields for reduction of production cost (all based on high concentration models)

4 Final simulations (cutting edge models)

4.1 Summary about the development of the cutting edge models

The first set of simulations presented above, were done with a simplified model approach. It was not possible to take into account all details and the first objective was to obtain in a reasonable time a few models that allow first simulations and give a first idea about how lignin separation influences the economic feasibility of bioethanol from lignocellulose.

4.1.1 Improvements in the model

In the further work, several improvements were done which are outlined below. Detail explanations follow in the next chapter. Further on, also the behaviour of the new cutting edge models is studied in direct comparison to the earlier models

- Investment level was checked with regard to what is done by the other project partners involved in simulations
- In earlier models the separation efficiencies in the filtrations (after each of the two hydrolytic steps) were calculated using the remaining humidity in the filter cakes, assuming that the concentration in the liquid in the filter cake is the same. During the progress of the project work more and more the idea was introduced to use counter current washing – with claims of up to 99% washing efficiency- by the other simulation partners. For this reason also the work done on lignin was adapted to this and the models were modified in this direction.
- In the "other organics" and in the "other ash" some parts can be insoluble. Earlier models supposed them all soluble, which is probably quite right for wood raw materials, but likely to be slightly wrong for straw and other annual plants containing nitrogen and silicates. Therefore several new variables were introduced for taking into account these insolubilities in the "other organics" and in the "other ash" (in each washing step: after pre-hydrolysis, after main hydrolysis, after lignin extraction).
- Also the solubilisation of a small part of the lignin was introduced as a parameter (set to 10% in all the following standard simulations)
- The calculation of the WIS (water insoluble solids) was adapted to the last changes mentioned just above. For adjustment of the water in the enzymatic hydrolysis a definition of WIS was used that takes into account all the insolubles.
- Earlier models supposed no C6 hydrolysis in the pre-treatment and no additional C5 monomer yields in the enzymatic hydrolysis. Recent information mentions however the possibility to have some not neglectible yields in both reactions. The C6 sugar yield was put to 27% and the C5 sugar yield in the following hydrolysis step was given the same value as the corresponding C6 yield.
- The yeast continued to be supposed recyclable and growing on the substrate (and by this contributing to some of the % lost on the theoretical yields of ethanol on sugar).
- However the enzymes were in all simulation of chapters 4.2 and 4.3 supposed to be produced on site. Using some preliminary data on such investment cost that were presented in the project, an additional amount of investment corresponding to 12% of the investment without enzymes production was added to the capital costs.
- For the lignin separation, new options were introduced:
    - Lignin separation without C5 separation after pre-treatment. This allows to have higher concentrations also in the case of lignin separation.
    - The flow resulting from the lignin precipitation (LPS) can now be alternatively introduced in the enzymatic hydrolysis or at the end to the waste water treatment.
    - A end of pipe lignin purification was introduced into the model, by allowing to make a lignin extraction on the solid residue after enzymatic hydrolysis.

- The raw material composition used in all further work (if not specified else) is for straw the more favourable composition of the early simulations and for Spruce the identical as in the earlier simulations.
- For economic and ecological reasons recovery of the chemicals used in the lignin front end separation would be of interest. An evaluation on this point has been carried out, but where not stated differently no sodium recovery was considered in the simulations of chapter 4.
- The conversion of the C5 fraction as well (and not only the C6 parts including cellulose and other hexoses) is one of the main challenges for future bioethanol plants. The results about this were not available at the writing of this report, but an estimation of the possible influence of this aspect has still been carried out.

4.1.2 Illustration of some variations encountered

After the first series of upgrading of the models, including comparative work on different scenarios to check the consistency of the models, a few simulations were launched in order to check how the interest of lignin separation would come out at that point. The used parameters were as they were at this stage of the work, originating of some case studies done just before this and not including the additional parameters of chapter 4.2

Although these are not the final conditions retained, we are nevertheless dealing here with possible conditions that could be realised in some cases of industrial system's development (except maybe the lower investment that seems now too low if seen from the point of view of the end of the project). The system was based on 10 tons dry of straw/hour and 40% dry matter in pre-treatment and without sodium recovery in the lignin separation. Price and cost information was like earlier (namely a lignin sales price of 250 Euro/ton). The other parameters were as mentioned in the table 4.1-1.

It's important to insist on the fact that these are models identical to what was used in the later work in this chapter, but without the further changes described under 4.2.

	Prehydrolysis		Enzym. Hydrolysis			Fermentation							
#	C5 yield	C6 yield	C5 yield	C6 yield	WIS	Yield on theory C6	Yield on theory C5	C5 Separation	Lignin Recovery	EU/kg 94%	EU/L 94%	Investment Mio. Euro	% EtOH in distillation
84	56%	22%	91%	90%	5%	79%	79%	off	none	0.714	0.563	38.3	1.3%
85	56%	22%	91%	90%	5%	79%	79%	on	none	0.679	0.535	39.5	1.3%
86	56%	22%	91%	90%	5%	79%	79%	on	99%	0.626	0.494	45.7	1.5%
87	56%	22%	91%	90%	20%	79%	79%	off	none	0.447	0.352	24.5	6.4%
88	56%	22%	91%	90%	20%	79%	79%	on	none	0.447	0.353	26.1	4.7%
89	56%	22%	91%	90%	20%	79%	79%	on	99%	0.433	0.342	34.6	5.0%

is the number of the simulation in the simulation log file

Table 4.1-1 Some early simulations during the final step of the work (not including the additional parameters)

As it can be seen in the table, in these cases C5 separation is not detrimental in the base model without lignin separation whatever the concentration is in the enzymatic hydrolysis. With low concentration models, C5 separation is even profitable! Furthermore, the lignin separation with 99% recovery rate is just slightly beneficial for low concentrations (12% reduction of ethanol cost) and almost neutral for the higher concentration models (only 3% reduction)!

4.2 More details about some improvements/changes in the models

In the following, more details are given on some of the modification of the new models, on their importance for the simulation and on the values retained for the final simulations.

4.2.1 Verification of investment costs

In the early simulations, the investment costs for the ethanol plant (lignin recovery part excluded) were based on the already mentioned NREL publication (Lynd 1996). As in the progress of the project work, investment data became available from other partners, several efforts were undertaken to evaluate how the different investment levels were related to each other.

The strategy chosen for this evaluation was to simulate an exact mass flow mirror of a system in our simulation model and to compare the investment cost that results with our formulas to the investments found by other partners with the same mass flow data.

The first comparison was about a Spruce system at 5% WIS in hydrolysis and without C5 fermentation according to a publication by Wingren (2003)[4]. For this case, it was possible to create a precise copy of the mass flows. The information of Lynd was corrected by the cumulated inflation from 1st quartal 1994 to last quartal 2009. For determination of this average, inflation in the U.S. was calculated with an inflation calculator available on Internet which gave an average increase in cost of life by 2.5 % per year. The resulting investment was converted in Euro and compared to the investment announced by Lund University (converted from Swedish Crowns to Euro, and increased by 15% for compensating from the publication date up to 2009). The result was that the so calculated updated cost of our model was 20% lower than the investment obtained with the Wingren data. This can be considered as a rather good agreement, given the very different sources of the information (one in the US, one in Europe).

The situation was quite different for a straw case. Although the method used was the same in order to express each investment in terms of a Euro 2009 base, the resulting investments we obtained were about two times smaller than the reference model. However there was some uncertainty about the factor between total direct cost and fixed capital investment (a standard factor calculated by most software).

Taking into account all available information, we decided that it was consistent to introduce a factor of 1.5 for increase of investment. All the investments for all the calculations that follow are based on this higher investment.

4.2.2 Counter current washing

The introduction of the counter current washing is of a major importance for the system parameters of a bioethanol/lignin plant, as it can be seen in Tab 4.2-1. Namely the production cost is rather sensitive for this feature.

For better understanding it has to be noted that the lower recovery rate in the table corresponds approximately to a normal pressing/washing without counter current. From the table it results that with a good counter current washing the ethanol concentration is significantly higher (17% increase) and the production cost significantly lower (9% reduction). This is of course due to the higher amount of ethanol produced with better separation of the streams.

Regarding the interest of lignin front-end separation, with a good counter current washing the lignin benefits are less striking, although still substantial, the improvement on ethanol production cost going down from 28.5% to 25%.

[4] Wingren, A., Galbe, M., Zacchi, G.: Techno-Economic Evaluation of Producing Ethanol from Softwood: Comparison of SSF and SHF and Identification of Bottlenecks , Biotechnology Progress, 19(4), 1109-1117, 2003

#	Prehydrolysis: Recovery rate of dissolved products	Enzym. Hydrolysis: Recovery rate of dissolved products	Lignin Recovery	EU/kg 94%	EU/L 94%	Investment Mio. Euro	% EtOH in distillation
360	80%	80%	none	0.540	0.426	36.9	8.9%
361	80%	80%	99%	0.387	0.305	39.7	13.1%
362	99%	99%	none	0.490	0.387	37.9	10.5%
363	99%	99%	99%	0.368	0.290	40.8	15.0%

is the number of the simulation in the simulation log file

Table 4.2-1 Influence of the recovery rate in the two countercurrent washings (high concentration models)

4.2.3 Work on insoluble "other organics" and "other ash"

Table 4.2-2 shows how different options for insoluble parts of the various "other" fractions influence ethanol production cost and ethanol concentration in the distillation. The influence is significant. With 100% insolubles we get a very different result than if we suppose that everything is soluble. Rather surprisingly the production cost goes down with high insolubles.

#	Prehydrolysis: Insolubles in other organics	Insolubles in other ash	Lignin Recovery	EU/kg 94%	EU/L 94%	Investment Mio. Euro	% EtOH in distillation
364	100%	100%	none	0.449	0.354	38.2	7.9%
365	100%	100%	99%	0.326	0.257	41.5	10.0%
366	0%	0%	none	0.490	0.387	37.9	10.5%
367	0%	0%	99%	0.368	0.290	40.8	15.0%

is the number of the simulation in the simulation log file

Table 4.2-2 Influence of the different insoluble parts (high concentration models)

Remarkable is also the fact that the positive effect of lignin separation goes down in case of no insolubles (from 27.5% improvement to 25%), although the starting point for ethanol cost is higher in the later case.

4.2.4 Lignin separation without C5 separation after pre-treatment

In earlier models it was supposed that the C5 sugars and other solubles are separated by filtration/washing before going to the lignin extraction step with the insolubles. However there might be a clear economic interest to renounce to this step also in the case of lignin front end separation. We have here selected the low concentration case for our simulations in the table, as this shows some interesting behaviour that disappears for higher concentrations.

#	Separation after prehydrolysis	Recycling of LPS filtrate	Lignin Recovery	EU/kg 94%	EU/L 94%	Investment Mio. Euro	% EtOH in distillation
368	off	off	none	0.664	0.524	54.7	2.49%
369	off	off	99%	0.547	0.431	67.1	3.93%
370	off	on	99%	0.490	0.387	53.1	3.93%
371	on	off	none	0.700	0.553	59.1	1.75%
372	on	off	99%	0.532	0.420	57.3	2.35%
373	on	on	99%	0.530	0.418	56.8	2.35%

is the number of the simulation in the simulation log file

Table 4.2-3 Influence of C5 separation after pre-treatment and of LPS filtrate recycling for front end lignin separation (low concentration models WIS 5%)

The reference situation is here to separate lignin without recycling of LPS filtrate. As one can calculate in table 4.2-3, for low concentration models the separation after pre-treatment is against expectation more advantageous (20% reduction in ethanol cost) than if this separation is not done (17.5%).

4.2.5 Options on recycling of filtrate of LPS

Referring again to table 4.2-3, it can be seen that the recycling of the LPS filtrate does introduce substantial benefit when done without separation after prehydrolysis. This advantage disappears when the later separation is switched on. However is must be clarified that these are purely mass stream calculations that include only changes in investment due to different size of the equipments. Possible increases due to more expensive materials that resist to acidic conditions or to addition of alkali for neutralisation are at this stage not accounted for. Such further calculation was not done because it is not clear what will be the pH after mixing. There is substantial alkali coming from the lignin extraction step (there is no counter current washing in this step), which might be enough to get acceptable conditions for hydrolysis. But this has not been experimentally verified so far and would have to be introduced into the models as soon as laboratory data are available.

4.2.6 Purification of end of pipe lignins

During this project an experimental evaluation of purification of end of pipe lignins from the solid material resulting from filtration after enzymatic hydrolysis has been done. Therefore a simulation model corresponding to such purification has also been constructed. For showing the sensitive point in these modelling we have selected a revenue of 350 Euro/ton for the purified lignin.

From table 4.2-4 we see that with 40% lignin separation the additional revenue is balanced by the additional production cost. This means that we are about at the break even point for lignin separation for this scenario. With higher yields the ethanol production cost starts again going down. Therefore the production cost of lignin must in this case be clearly lower. This has to be compared with front end models where we have production cost of about half of 350 Euro, because of the synergistic effects with other process steps in the ethanol plant. In the case of end of pipe purification there are no such effects. Neither is there any dependency of other parameters than the pure lignin related investment, the additional chemicals and the yield of lignin extraction. Also the ethanol concentration is logically not influenced by the lignin extraction.

#		Dry Matter in Prehydrolysis	Water Insoluble Solids (WIS) in enzymatic hydrolysis	Lignin Recovery	EU/kg 94%	EU/L 94%	Investment Mio. Euro	% EtOH in distillation
374	Without separation after prehydrolysis	20%	5%	none	0.664	0.524	54.7	2.49%
375		35%	20%	none	0.490	0.387	37.9	10.50%
376	Without separation after prehydrolysis	20%	5%	40%	0.658	0.519	83.2	2.49%
377		35%	20%	40%	0.489	0.385	66.8	10.50%
378		35%	20%	99%	0.372	0.293	68.4	10.50%
379	With separation after prehydrolysis	20%	5%	40%	0.665	0.524	62.5	1.75%
380		35%	20%	40%	0.486	0.384	44.9	5.52%
381		35%	20%	99%	0.373	0.295	46.1	5.52%

is the number of the simulation in the simulation log file

Table 4.2-4 Results obtained with end of pipe separation of lignins

4.3 Sensitivity to process parameters

In the following the same process variants are checked as in chapter 3, in order to see if after the additional modifications the behaviour of the models is similar.

4.3.1 Ethanol concentration depending on the parameters

It is interesting to compare the different ethanol concentrations before distillation obtained for the early models to those of the final cutting edge models. Table 4.3-1 gives these values that can be compared to those of table 3.4-1. The resulting ethanol concentrations are here significantly higher than those obtained in the earlier work. This can easily be explained by the changes in the process parameters: the raw material composition, the newly added C6 sugar generation in the pre-treatment and C5 sugar generation in the enzymatic hydrolysis, the counter current washing, the new parametrisation of the insolubles. All these parameters tend to increase the ethanol concentration and the sum of their effects turns out to be rather efficient.

In order to verify the consistency of our models, the above parameters were set to the earlier values in our cutting edge models and the resulting ethanol concentrations were compared to those in table 4.3-1. This was done for the following simulations in the log file:

- run 319 with old conditions gave 2.03% to be compared to run 12 with 2.14%
- run 322 with old conditions gave 3.31% to be compared to run 10 with 3.99%
- run 328 with old conditions gave 3.75% to be compared to run 20a with 4.35%

This shows a very good consistency. Given that we used a WIS of 10% in the new runs instead of 12%, it seems normal that the values are lower. However, verification shows that this is not enough for explaining the reduction. In any case, the conclusion is that our new models do not favour higher ethanol concentrations as it might be concluded at a first glance. On the contrary, they even slightly disfavour it and give for the remaining surprisingly reproducible concentration results when compared to the earlier models.

#		Dry Matter in Prehydrolysis	Water Insoluble Solids (WIS) in enzymatic hydrolysis	Lignin Recovery	EU/kg 94%	EU/L 94%	Investment Mio. Euro	% EtOH in distillation	With earlier conditions applied to cutting edge models
319	With separation after prehydrolysis	20%	10%	none	0.606	0.478	49.6	2.72%	2.03%
321		35%	20%	none	0.527	0.416	41.1	5.35%	
322	Without separation after prehydrolysis	20%	10%	none	0.577	0.455	44.4	4.77%	3.31%
324		35%	20%	none	0.506	0.399	37.5	9.94%	
328	Without separation after prehydrolysis	20%	10%	40%	0.505	0.398	47.1	6.21%	3.75%
329		35%	20%	40%	0.449	0.354	40.9	12.60%	
331		35%	20%	99%	0.351	0.277	40.5	15.80%	

is the number of the simulation in the simulation log file

Table 4.3-1 The main configurations and their ethanol concentrations before distillation.

The production costs are of course very different and no more comparable with the older simulations. Although the investment has increased substantially, the increased concentrations, better separation of streams (therefore we produce much more ethanol) and other changes in the model reduce for most cases the production cost of ethanol. Among the other changes in the model is the fact that the better control of the insolubles allows to recover more as usable energy (pellets in our case). Indeed the revenue from pellet production has significantly increased.

However the relations in percentage of the production cost for the different process configurations are almost constant, although the spread between the variants is slightly reduced. For example the difference between the highest and the lowest cost per liter is 51% in the early work, but only 42%

now. This confirms a general tendency observed also elsewhere: the cutting edge models are really cutting edge in the sense that they have a more sensitive parametrisation system that needs more careful simulation work to show the advantages for lignin separation. They show still a very good reduction of ethanol production cost, but the reductions are slightly lower for cutting edge models if the technical performance increases (like here higher concentration, but also higher yields or better separation of streams).

4.3.2 Influence of improved yields

For higher yield models table 4.3-2 shows a similar behaviour than what can be seen in table D3.6-1. However the gain on percent of ethanol production cost is less stable and in general lower than in the early model. For example the best case has only 18% improvement (compared to 24% earlier). This might be explained by looking at the variations for the investment. They are clearly lower, except run 335 (about stable). However at lower recovery and lower yield increase (run 333) we have a 10% reduction (compared to 6% earlier) and run 334 is about the same as what we had earlier. But we are clearly at higher concentrations (% EtOH). These seems to confirm the observation already made that high concentration cutting edge models show a slight reduction of interest for lignin recovery, although it's still clearly and strikingly favourable.

	Prehydrolysis		Enzym. Hydrolysis		Fermentation						
#	C5 yield	C6 yield	C5 yield	C6 yield	Yield on theory C6	Yield on theory C5	Lignin Recovery	EU/kg 94%	EU/L 94%	Investment Mio. Euro	% EtOH in distillation
332	66%	95%	90%	90%	79%	79%	none	0.506	0.399	37.5	9.9%
333	66%	95%	90%	91%	81%	81%	40%	0.457	0.360	41.0	12.4%
334	66%	95%	90%	91%	81%	81%	80%	0.390	0.308	40.9	14.3%
335	77%	97%	90%	94%	95%	95%	none	0.384	0.303	36.2	13.6%
336	77%	97%	90%	94%	95%	95%	80%	0.314	0.247	39.4	18.1%

is the number of the simulation in the simulation log file

Table 4.3-2 Potential of increased yields for reduction of production cost (all based on high concentration models)

4.3.3 Influence of raw material composition

The results for different raw material compositions in table 4.3-3 are quite similar to what has been discussed for table 3.5-1. On the contrary to all results above, the percentages of reduction are almost constant except for run 344 which shows an increase of the reduction (it's in fact a very similar system to 333 above that gave the same result) and except for the highest lignin case (run 356) where the reduction is less pronounced like in other cutting edge models.

#	Lignin	Hexosans	Pentosans	Other organics	Ash	Lignin Recovery	EU/kg 94%	EU/L 94%	Investment Mio. Euro	% EtOH in distillation
339	19%	39%	20%	14%	9%	none	0.572	0.451	37.0	9.66%
344						40%	0.494	0.390	40.3	12.19%
345						80%	0.411	0.324	40.2	14.10%
346						99%	0.370	0.292	39.9	15.25%
350	21%	43%	23%	8%	5%	40%	0.432	0.341	40.9	12.60%
351						99%	0.309	0.244	40.5	15.80%
355	40%	50%	5%	2%	3%	40%	0.405	0.319	43.4	8.35%
356						99%	0.132	0.104	42.2	11.81%

is the number of the simulation in the simulation log file

Table 4.3-3 Results obtained with different raw material compositions (all based on high concentration models)

4.3.4 Influence of a chemicals recovery system

For the sake of giving an estimation, the influence of a possible sodium recovery system on a Spruce based process was evaluated for potential savings with such an option. On this purpose, a recovery process based on membrane electrolysis was included in the calculations. Additional investment and electricity were calculated. The recovery rate of the chemicals was supposed being 90%.

The model here used was at an intermediate concentration (WIS of 10%), with a SSF process and at a size of 24 tons dry raw material per hour.

The value in table 4.3-4 show that additional reduction of ethanol production cost can be expected from this. In the case here examined, the possible extra savings are around 7% independently of the lignin yield.

	Prehydrolysis		Enzym. Hydrolysis						
#	C5 yield	C6 yield	C5 yield	C6 yield	Lignin Recovery	EU/kg 94%	EU/L 94%	Investment Mio. Euro	% EtOH in distillation
411	68%	26%	0%	68%	none	0.406	0.320	86.9	4.1%
412	68%	26%	0%	68%	40%	0.379	0.299	91.5	4.7%
413	68%	26%	0%	68%	80%	0.299	0.236	89.7	5.4%
414	68%	26%	0%	68%	40%	0.350	0.276	94.4	4.7%
415	68%	26%	0%	68%	80%	0.273	0.215	93.5	5.4%

is the number of the simulation in the simulation log file

414 and 415 are with sodium recovery

Table 4.3-4 Results obtained with a Spruce model and sodium recovery

4.3.5 Influence of additional conversion of the C5 fraction

In the case of a straw based process, also the influence of the potential conversion of all C5 components were evaluated. The model here used was at an intermediate concentration (WIS of 10%) and at a size of 24 tons dry raw material per hour.

The results show that the benefits of lignin separation are quite exactly the same for this case as in a model with no C5 conversion (about 4% for 40% lignin recovery, about 18% for 80% lignin recovery). Although the ethanol concentration is much higher and the investment lower, the much lower ethanol production cost of the reference case without lignin separation, makes that finally no difference can be detected with regard to this question.

	Prehydrolysis		Enzym. Hydrolysis		Fermentation						
#	C5 yield	C6 yield	C5 yield	C6 yield	Yield on theory C6	Yield on theory C5	Lignin Recovery	EU/kg 94%	EU/L 94%	Investment Mio. Euro	% EtOH in distillation
400	87%	3%	0%	90%	90%	0%	none	0.643	0.507	91.5	2.9%
401	87%	3%	0%	90%	90%	0%	40%	0.617	0.487	96.3	3.2%
402	87%	3%	0%	90%	90%	0%	80%	0.526	0.415	94.9	3.7%
403	87%	3%	90%	90%	90%	85%	none	0.392	0.309	86.9	4.8%
404	87%	3%	90%	90%	90%	85%	40%	0.378	0.298	91.8	5.3%
405	87%	3%	90%	90%	90%	85%	80%	0.323	0.255	90.5	6.1%

is the number of the simulation in the simulation log file

Table 4.3-5 Results obtained with additional conversion of the C5 fraction

4.4 Comments on the results obtained during the different steps of this report

The different steps of simulation presented in the preceding text give an interesting and varied picture of the behaviour of lignocellulosic bioethanol plants with lignin separation. Advantages that seem to be clear under certain conditions might be much less pronounced or even disappear under other conditions. The presented data show that there are no clear obvious conclusions on the precise quantitative economical importance of any of the parameters examined for lignin separation systems. Configurations that are very promising in a given context may become less or much less promising in other conditions. Although qualitatively clear advantages could be observed for lignin front end separation, a multitude of small details having apparently little importance were nevertheless observed that all together brought about significant changes in the quantitative behaviour of the models.

This observation leads us to introduce the notion of working point of a model which means the state of all other parameters of a system around which the variation of one single parameter is calculated. One of the main findings of the work done in this project is that this notion of working point is fundamental to any simulation study of lignin separation. Depending on which working point has been selected, variations in ethanol production cost can be more or less pronounced.

The main problem with this is that the experimental data available at the moment of writing of the report, do not allow to sufficiently identify the region in which this working point is located. Too many uncertainties remain about the best concentrations that are technically possible, as well as about the precise system configurations. Also an important limitation is that the complete system including lignin recovery could not be tested in the project due to limitations of time and budgets. Namely for example it is not known which would be the real influence of lignin separation on the yields of the hydrolysis and fermentation. Although optimistically one would expect improvements of the yields[5], we don't really know if the yield would even be at least the same as without lignin separation.

For fixing the working point sufficiently only very specific studies including work on extended optimisation by pilot plants could give the necessary detail information. For that, an extensive testing programme would be necessary allowing to optimise the different parameters. But even in that case this would only be valid for a very specific small region around a selected working point and does not allow to exclude other better conditions around other working points in other not connected regions of the highly multidimensional space of all possible working points!

This is one of the important points that have been observed during the simulation work done in this project: changes in the system configuration, including even apparently not important small shifts in the working point of the system, can bring about surprising changes in the behaviour of the models.

For example, for the more detailed parametrisation introduced in cutting edge models, several unexpected results did appear.

In the beginning of our work with cutting edge models, the benefits for lignin separation were much more limited than what appeared earlier and the necessary lignin sales price appeared to be higher than 250 Euro/ton (see chapter 4.1.3). However during the detail work on these new models (chapter 4.2 and 4.3), the introduction of new parameters resulted again in models with significant interest for 250 Euro/ton.

Another example: At a first glance, the cutting edge models seemed to have a much higher ethanol concentration than the earlier models. However when this was analysed more in detail it turned out

[5] Several unpublished examples are known to the authors, where clear advantages for yields have been stated

that it was not the model itself that gives higher concentration, but the accumulated small changes in several new parameters. When these changes were reset to the old state, concentrations with the cutting edge model were even lower than with the earlier simulations!

As a third example, the separation of the solubles after pre-treatment -although in general resulting being too costly- came in some cases out profitable even with pure mass stream considerations, that is without supposing increased yields thanks to lower presence of inhibitors.

One of the difficulties resulting from this study is that small changes in the raw material (for example having 1% more lignin or 0.5% more insolubles) can easily induce much bigger relevant changes in the outcome (order of 10% or more on ethanol cost). This is already the case if one takes just into account the purely mass stream calculation issues. If changes in the operating conditions are considered this can increase still the induced variation and change completely the outcome of a study, or even result in an inversion of tendencies if a switch to another working point region is occurring.

However some general tendencies can still be quite reliably detected. Lignin front end separation is clearly inducing multiple positive synergistic effects with the other process steps. They are more or less pronounced depending on the working point, but in any case they are significant for economic evaluation, in the sense that in all cases of front end separation the resulting lignin production cost is lower, by 50% or more, than if this lignin would be produced without counting the savings in the rest of the ethanol plant.

Another important observation is that the improvement of the performance of the ethanol production system does not necessarily increase the benefit of lignin separation. On the contrary, we have found parameters (like efficiency of the counter current washing, increase in WIS for enzymatic hydrolysis) that weaken the positive effect of lignin separation when they get to a higher level. However we do not know with certitude that this is the case for all possible other working points of the system. Furthermore even if the benefits in percent of ethanol price diminish in some case with better technical performance, they stay in our studies still in an order of magnitude that is highly interesting for future lignocellulosic ethanol production factories.

4.5 Final simulations

At the end of the work, for each of the raw materials, straw and Spruce, a final series of simulations was run. For the definition of the working point of these simulations, the data most likely to be technically feasible was used, as it was available within the project at the moment of the writing of this report, namely including highest confirmed concentrations and yields.

For the size of the plant, 24t/hour of dry raw material was used. According to the latest information available, the investment was increased by an additional 33% with regard to the data used in the preceding chapter (4.2 and 4.3). For personal cost, 25 persons (including operators and supervisors) at an average salary cost of 50000 Euro/year were retained, as outlined in Wingren 2003.

Cost for chemicals and utilities were the same as used throughout this work, as well as the sales price for pellets and the cost for the raw material. For evident reasons (rise of the general price level for energy and chemicals) this should be further updated. But no consistent set of data including all these elements was available at the moment. Furthermore the markets are fluctuating and it is not really clear at what levels the energy prices will stabilise in the coming years. Therefore, in order to maintain the global consistency of the results, the same data set was used as in the earlier chapters, at lower energy price level as valid throughout the first five years of the last decade (about 2001-2005).

Enzymes cost and yeast were considered as in the beginning, that is enzymes cost at similar level of cost as for sulphuric acid giving the same result in an acidic hydrolysis process and yeast considered as recyclable with additional yeast for compensation of losses grown on process substrate (Wingren 2003).

The concentrations and yields are as given in each chapter. The calculation of the water addition in the enzymatic hydrolysis was done based on water insoluble solids (WIS). In both cases a WIS of 10% was selected. Compared to the earlier options we use here thus rather intermediate concentrations, but which are considered as reliable. Higher concentrations can be expected and are aimed at by different research teams, but they were not confirmed at the moment of the writing of this report. As done by other partners in the project, no C5 enzymatic hydrolysis and fermentation was considered (C5 yields are zero) as other data was not confirmed up to the date of reporting.

Lignin separation was supposed to be after pre-treatment, with alkaline extraction, without filtration of the pre-treated cake (what we call earlier "without C5 separation") and with recycling of the LPS filtrate. Unless otherwise stated, the lignin sales price considered was 250 Euro/ton. Sodium recovery is not included, unless other mention. No profit for better yields or reduced enzymes consumption was considered. If such advantages could be proven technically, the results for lignin separation would be still clearly better.

4.5.1 Straw based process

For the process using straw, all data were according to the input of the other partners in the project working on straw based models. The here used raw material composition had an even higher lignin content than the earlier more favourable composition of straw (identical to the final composition used by other partners). The components were: Lignin 23.2%, hexosans 41.7%, pentosans 25.2%, other organics 5.1%, ash 4.8%.

All other organics were supposed soluble and all ash in the raw material was supposed insoluble. 5% of the lignin was considered as dissolved in the pre-treatment. A loss of cellulose of 3.9% in the same step was included in the calculations. The dry matter in the pre-treatment was 35% and the dry matter of the filter cake after enzymatic hydrolysis was 36%. A counter current recovery of 99% was assumed, using 20m3/h of additional wash water.

With the yields given in the table below, this resulted in lignin related savings of 17.5% (with lignin price of 250 Euro/ton) or 32.5% (with lignin price of 350 Euro/ton). If the C5 fraction is also converted into ethanol, this does not substantially change the results (data not shown). It has to be pointed out that no benefits for yields or enzyme consumptions were calculated so far (as no optimised and confirmed experimental data was available). Also the consideration of sodium recovery would still increase the savings (see data for Spruce below).

	Prehydrolysis		Enzym. Hydrolysis		Fermentation							
#	C5 yield	C6 yield	C5 yield	C6 yield	Yield on theory C6	Yield on theory C5	Lignin Recovery	EU/kg 94%	EU/L 94%	Investment Mio. Euro	% EtOH in distillation	Cost reduction
431	87%	3%	0%	90%	90%	0%	none	0.701	0.553	127.4	2.7%	0.0%
432	87%	3%	0%	90%	90%	0%	40%	0.673	0.531	131.3	3.0%	4.0%
433	87%	3%	0%	90%	90%	0%	80%	0.578	0.456	128.5	3.5%	17.5%
434	87%	3%	0%	90%	90%	0%	40%	0.620	0.489	131.3	3.0%	11.5%
435	87%	3%	0%	90%	90%	0%	80%	0.473	0.373	128.5	3.5%	32.5%

is the number of the simulation in the simulation log file

434 and 435 are with a lignin sales price of 350 Euro/ton

Table 4.5-1 Results obtained in the final simulations for straw

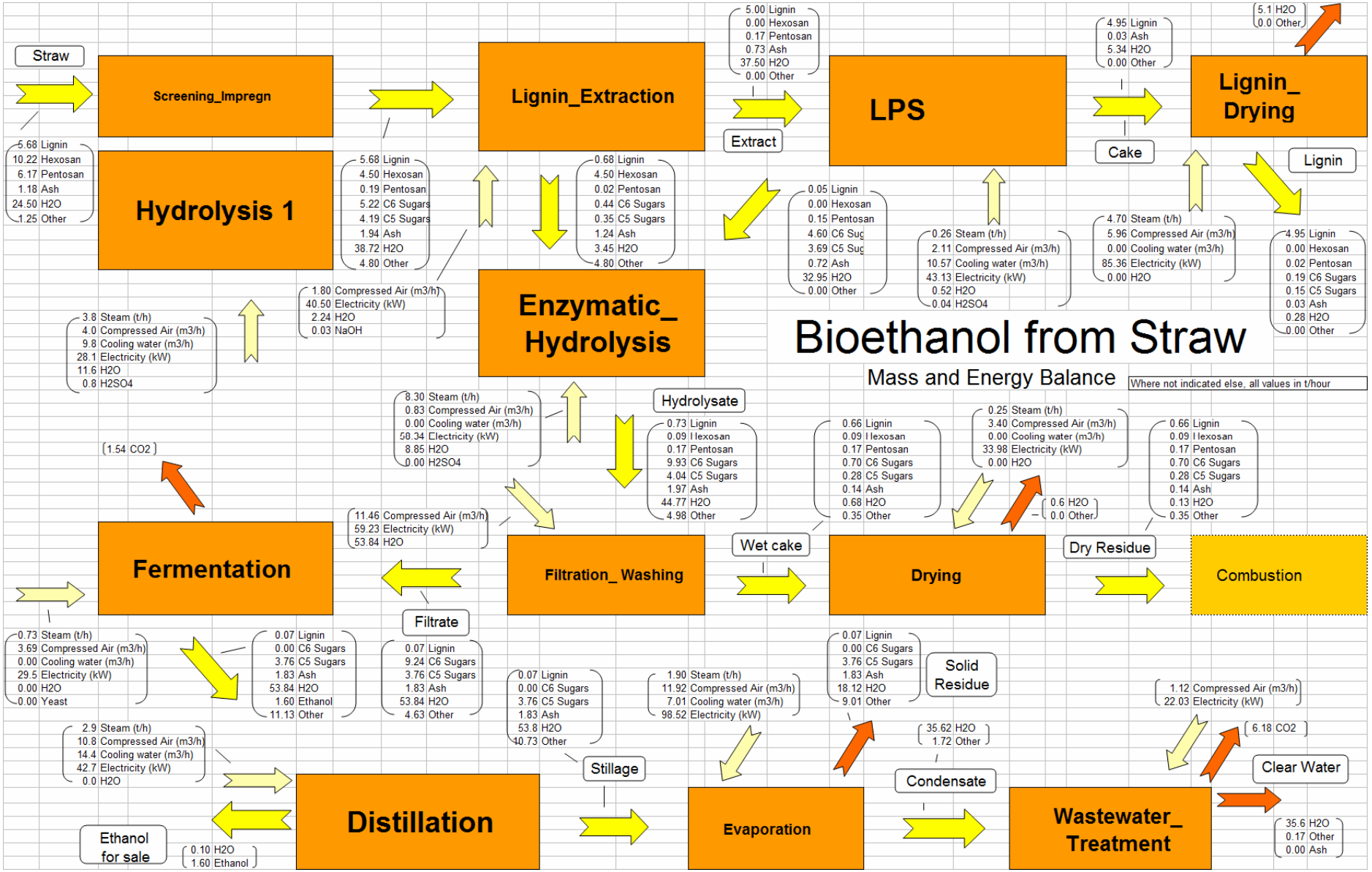

Figure 4.5-1 Example of a global flowsheet (with lignin separation) as used for the final simulations. Fictional system parameters only for illustration purpose

4.5.2 Spruce based process

Also for the process using Spruce all data were according to the input of the other partners in the project working on Spruce based models. The here used raw material composition was identical to the one used in the previous chapter: Lignin 27.5%, hexosans 62.4%, pentosans 7.0%, other organics 1.5%, ash 1.5%

All other organics were supposed soluble, as well as all ash. 10% of the lignin was considered as dissolved in the pre-treatment. A loss of cellulose of 3% in the same step was included in the calculations. The dry matter in the pre-treatment was 40% and the dry matter of the filter cake after enzymatic hydrolysis was 54%. A counter current recovery of 99% was assumed using 10m3/h of additional wash water.

For the ethanol production a simultaneous saccharification and fermentation (SSF) was considered.

With the yields given in the table below this resulted in maximal lignin related savings of 25.3% (with lignin price of 250 Euro/ton) or 45.6% (with lignin price of 350 Euro/ton). Also here no benefits resulting from lignin separation for yields or enzymes consumptions were calculated. The data here calculated show that a sodium recovery would still increase the savings substantially, but that an increase of 100 Euro/ton of the lignin sales price would have a more important impact on the ethanol production cost.

	Prehydrolysis		SSF							
#	C5 yield	C6 yield	C5 yield	C6 yield	Lignin Recovery	EU/kg 94%	EU/L 94%	Investment Mio. Euro	% EtOH in distillation	Cost reduction
416	68%	26%	0%	68%	none	0.437	0.345	120.0	4.1%	0.0%
417	68%	26%	0%	68%	40%	0.408	0.322	123.3	4.7%	6.6%
418	68%	26%	0%	68%	80%	0.326	0.258	119.9	5.4%	25.3%
422	68%	26%	0%	68%	40%	0.380	0.300	126.4	4.7%	13.1%
423	68%	26%	0%	68%	80%	0.300	0.237	124.0	5.4%	31.4%
424	68%	26%	0%	68%	40%	0.364	0.287	123.3	4.7%	16.7%
425	68%	26%	0%	68%	80%	0.238	0.188	119.9	5.4%	45.6%

422 and 423 are with sodium recovery

424 and 425 are with a lignin sales price of 350 Euro/ton

Table 4.5-2 Results obtained in the final simulations for Spruce

5 Conclusions

For bioethanol production from lignocellulosic raw materials like straw and Spruce, an evaluation of the interest of lignin separation for other than energy purposes was successfully carried out. This was based on Excel spreadsheets for computer simulation of the mass balance and of ethanol production cost.

Multiple configurations of the different process variants including a huge number of technical and economic parameters were evaluated. Throughout the duration of the NILE project, the different alternatives were successively simulated and in continuous interaction with the other partners all the available data about experimental results were integrated into the models. The critical factors under examination in the project were, continuously as they appeared, included as variables in the calculations.

The resulting picture was much more complex than what one would have expected. As in the beginning the challenge seemed to be the identification of the main critical factors, during most of the project the work concentrated on this issue. In several simulations, sensitivities to variations of the main process variables were calculated. However, as more detailed information was coming up during the realisation of the project, it resulted that more and more of these variables had to be introduced. While more and more of these parameters were adapted to what was used by the other project partners (i.e. with regard to yields, energy consumption, investment etc.), it turned out that the lignin related models were very sensitive to the changes introduced in every new revision.

At the end, a confirmed model was available that behaved very similar to the models of the other project partners based on ASPEN PLUS process simulation software and IKARUS for investment cost estimation (but without lignin separation).

However, only towards the end of the project it became also clear that the selection of the working point was crucial for the cost variations due to lignin separation. Whereas in the beginning it appeared that variations on ethanol production cost depended mainly on the percentage of lignin separated and on the sales value for this separated product, it turned out at the end that these variations could be between almost zero and 20-50% or more depending on the process conditions for the reference case.

This difficulty is due to the fact that these calculations depend on 30 variables or more (much more if one includes every economic price of the inputs to the model) of which in every configuration many have a slight influence on the outcome. Due to the big amount of variables and due to some non linear behaviour of the models, it is possible that the cumulated changes become much more important than the small changes in each variable.

Nevertheless, the following final conclusions from the work here done can still be drawn at the end of the project:

- Successful modelling of complete bioethanol systems involving lignin separation for non energy purposes was done. After implementation of energy and investment data from other project partners, this simulation could be achieved in one single Excel file not needing any data transfer to other software
- Consistency of the models was verified by comparison of several hundreds of different simulations and by eliminating errors and improving the calculation methods at each step of the work.
- Several simulation models done by other partners using ASPEN/IKARUS software, have been successfully miroired by our models and gave, after calibration with energy and

investment information from these models, identical mass flow and comparable economic results.

- The resulting model achieved the goal of simplifying the calculations for purposes of efficient continuous evaluation of the implications of a big amount of parameters. However these are simplified models that have for the moment no thermodynamic calculation included[6] only external data from literature and other project partners are used.
- In all examined cases, positive effects could be stated in the case of lignin separation. Mainly for front-end separation the effects were positive, although in some simulations with lower lignin yields lignin, market values of more than 250 Euro/ton had to be supposed to make the effects economically striking.
- Realistic conditions have been found where lignin separation is potentially a significant factor for the profitability of bioethanol production from lignocellulosic raw materials, that is for achieving from 10% to more than 50% of cost reduction.
- Synergistic effects like reduction of investment in the not lignin related part of the system are substantial in the case of front end separation where they reach in many cases 50% or more of the lignin production cost. Whereas no such effects are possible in case of end of pipe purification of lignin.
- Only 40% separation yield of lignin has a tendency to not be enough for clear economic advantages, namely with 250 Euro/ton lignin market value. Optimisation of pre-treatment conditions should therefore in any case be realised to get higher lignin yields.
- No complete set of experimental data of what would happen after lignin separation in the subsequent steps of the system was available. Therefore the final simulations did not account for any benefits on yields or enzyme/yeast cost. After sufficient work on optimisation of the process in its totality it could be expected that benefits might influence our results positively. Vice versa, if despite of extensive work on such optimisation only less performing data would be found, the here presented data might also have to be corrected negatively.

For giving an outlook on further work to be accomplished in upcoming new projects, two main points should be considered:

- A more detailed sensitivity analysis on the totality of the system parameters could possibly be realised in order to understand better which working points of the models are positive for lignin separation and where are the main sensitivities for further research work. For this purpose, new tools have to be developed for visualisation and optimisation in multidimensional vector spaces (3 dimensions or more).
- Extensive experimental optimisation work would be necessary, including the pre-treatment conditions to increase the lignin yields, hydrolysis and fermentation conditions and yields after lignin separation, as well as enzyme consumption. Also further work on chemicals recovery is highly recommended, as well as work on lignin separation with organic solvent (ethanol or other).

However, motivation to work on lignin separation cannot be driven by cost simulations only, but must also be driven by market needs and by ecological interest to use lignin product as replacement of other raw materials, namely based on fossil resources or because of their more problematic

[6] Which could be done, in principle, at a later stage

toxicological profile. However the work here done also gives an illustration that many favourable conditions exist in which lignin non energetic use can contribute substantially to economic feasibility and profitability of bioethanol production. These routes must therefore by all means be investigated in any future work about biorefinery multiproduct systems based on lignocellulosics.