

SECOND GENERATION ETHANOL THROUGH ALKALINE FRACTIONATION OF PINE AND ASPEN WOOD

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Pre-treatment studies on pine and aspen wood with alkaline fractionation were performed, the experimental results obtained being used as input for assessing the conversion of an existing pulp mill to ethanol and lignin production. By the LignoBoost process, the extracted lignin could be used in the lime kiln to replace fuel oil, while the lignin not needed in the lime kiln could be sold as a by-product. In addition to fuel applications, lignin could be used in a wide range of bio-based product applications, which would increase the value of the extracted lignin and increase the total revenues.

A WinGEMS model was used to calculate mass and energy balances, and the results were used for an economic evaluation of the concept. The assessment indicated that the proposed alkaline concept would have reasonable production costs from both pine and aspen wood, comparable with the bioethanol produced from grain in Northern Europe today, *i.e.* about 0.45 €/L ethanol (~5 SEK/L). The production rate of a typical mill producing 1000 tonnes of pulp per day before conversion would be in the order of 140 000 m³ of ethanol per year, as depending on the raw wood material. The corresponding lignin production would range from 25 000 to 63 000 tonnes per year.

The use of alkaline delignification to produce a substrate with low lignin content for the enzymatic hydrolysis builds entirely on known and well-proven technology, yet it needs to be further developed. The process chain from enzymatic hydrolysis to ethanol is very similar to that used today for grain ethanol. Altogether, the technical risk should therefore be low.

Keywords: bioethanol, alkaline pretreatment, converted pulp mill, pine, aspen, mass balance, energy balance, economic assessment, lignin production

INTRODUCTION

The demand for liquid biofuels is increasing in Europe, driven by EU directives on promotion of biofuels, and also by increasing oil prices and growing public awareness of the consequences of the greenhouse effect. In the meantime, changes are taking place in the pulp and paper industry, driven by a long-term decrease in the real price of pulp. This leads to the need, especially for small pulp mills, of exploring new product niches. The production of liquid biofuels could be one such niche.

Several studies have concluded that the thermochemical conversion of lignocellulosic biomass materials to liquid fuels has the potential to be more energy-efficient than biochemical conversion.¹ The barriers have been high, however, since the thermochemical processes require large-scale implementation and still carry a considerable technical risk. Biochemical processing, on the other hand, is a well-established route to produce alcohols from sugars and starch,

these processes being commercial, too, for the production of ethanol as a motor fuel. Much effort has therefore been directed at developing processes for the production of sugars from lignocellulosic materials that may be fermented in the same way as the sugars produced from starchy materials, such as corn and wheat.

The process here taken into study is an alkaline one, starting with pure cellulose in the hydrolysis stage, which makes it unique, compared to other processes aiming at producing ethanol from lignocellulose. It should be possible to use a raw material of lower quality and lower price than wood in the pulp industry. The advantages of this process *versus* acidic pre-treatment and wood hydrolysis are that the recovery of lignin and chemicals is simplified and that hydrolysis can take place at lower temperatures. A lignin with low ash content and high dryness can be recovered as a potentially valuable by-product, using the

LignoBoost process for lignin extraction developed by Innventia and partners.² Alkaline pre-treatment as part of an ethanol production scheme has been proposed and tested by several researchers,³ although it has not advanced beyond a laboratory scale.

Ethanol production from lignocellulose needs considerable equipment investments for delignification, hydrolysis, evaporation and steam production. Many of these process units already exist in a pulp mill. Converting an existing pulp mill to an ethanol production plant may therefore have the potential for large-scale production with relatively low investments.

The development of such a concept has been undertaken at Innventia,⁴ this issue being also approached in the current Nordic Energy Research project entitled “New, innovative pre-treatment of Nordic wood for cost-effective fuel-ethanol production”, a collaboration between Sweden, Norway, Finland, Denmark and Iceland, aiming at developing new pre-treatment techniques that will reduce the overall production costs for fuel-ethanol obtained from Nordic woody biomass.

Pre-treatment studies on pine and aspen wood with alkaline fractionation were performed and the experimental results were used as an input for assessing the conversion of an existing pulp mill to ethanol and lignin production. By employing the LignoBoost process, the extracted lignin could be used in the lime kiln to replace fuel oil, while the lignin not needed in the lime kiln could be sold as a by-product. In addition to fuel applications, lignin could be used in a large field of bio-based product applications, which would increase the value of the extracted lignin and increase the total revenues.

Process description

Figure 1 shows a simplified flow sheet of the ethanol converted pulp mill model constructed in the process simulator WinGEMS. The incoming wood chips are first delignified, when most of the lignin is dissolved in the black liquor, after which the black liquor is evaporated and burned in the recovery boiler. Part of the black liquor is also sent to a LignoBoost process, in which CO₂ is injected to precipitate lignin. The acid is used for washing lignin and for pH control in the ethanol plant. If sulphuric acid is used, there will be a build-up of sulphur in the

liquor cycle that needs to be controlled by purging ash from the recovery boiler. This, in turn, will lead to a loss of sodium, which requires some make-up in the form of sodium hydroxide. The smelt from the recovery boiler enters a causticizing area, for regenerating the hydroxide ions used for alkaline fractionation. The cellulose fraction resulted from alkaline fractionation is used for the production of ethanol, the operations involved in conversion being illustrated in Figure 1. The amount of CO₂ produced in the SSF operation is enough to replace the demand in the LignoBoost process. The usage of water residues remained after the distillation procedure is important for getting an economically feasible process. The solid residue is dewatered, part of it is used as a substrate for enzyme production, while the rest is recirculated to the recovery area and burned in the recovery boiler. The thin stillage resulted from the dewatering step consists of dissolved solids evaporated and burned in a power boiler.

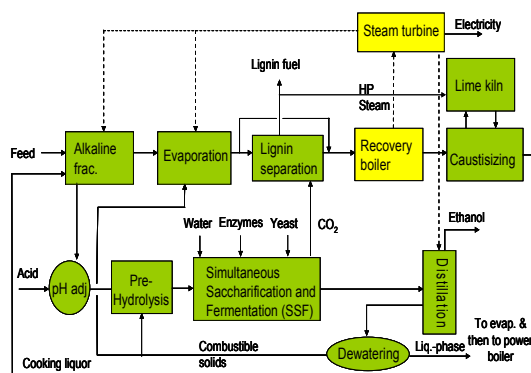


Figure 1: Simplified flow sheet of the ethanol converted pulp mill concept

EXPERIMENTAL

The experiments were meant to define the conditions applied in the alkaline fractionation stage for the separation of wood into a carbohydrate fraction – for ethanol production – and to a lignin fraction – for the extraction of lignin from the black liquor. Pine (*Pinus sylvestris*) and aspen (*Populus tremula*) were used as raw materials. For reference, alkaline fractionation was used – according to the well-known soda pulping technique – to delignify the wood chips to a lignin content of 5 and 2.5% in the pulp for pine and aspen, respectively. Other pre-treatment conditions with addition of AQ, acid pretreatment, addition of ethanol, etc. were also tested, yet the traditional reference case appeared as the most suitable and was therefore recommended and used in the techno-economic

assessment. Table 1 summarizes the key data obtained in the experimental investigation, used

as input for the techno-economic assessment.

Table 1
Alkali charge in alkaline fractionation and results used in techno-economic assessment

| Experimental study | Pine | Aspen |
|---|------|-------|
| Alkali charge, % on wood | 20.5 | 18.7 |
| Total yield, % on wood | 45.7 | 52.8 |
| Fermentable sugars in raw material, % on wood | 62.4 | 51.9 |
| Fermentable sugars in pulp, % on wood | 40.0 | 40.1 |
| Lignin in pulp, % on pulp | 5.0 | 2.5 |

RESULTS AND DISCUSSION

The simulation program WinGEMS has been used to solve the mass and energy balance for a converted pulp mill, to amplify the process with combined production of ethanol and lignin. The output of the model has been transferred to Microsoft Excel and used for economic assessment.

Mass and energy balance

Table 2 lists the available amounts of wood in a typical Nordic mill, for a possible production of ethanol. About 140 000 m³ ethanol for both pine and aspen could be produced from 1800 t raw material per day.

An ethanol yield – in the SSF operation – of 82% of the theoretical yield has been assumed for both pine and aspen, while the alkaline fractionation yields were obtained from the experimental study shown in Table 1.

The extraction of lignin is estimated with the adiabatic combustion temperature as a guideline controlling the amount of lignin that could be extracted for each case. The produced black liquor from pine wood contains more lignin than the corresponding black liquor from aspen wood; it is thus possible to extract more lignin from pine than from aspen.

Table 2
Annual ethanol production rate scaled with wood input at a typical pulp mill

| Mass balance ethanol production | Pine | Aspen |
|--|--------|--------|
| Raw material, t/d | 1800 | 1800 |
| - <i>ditto</i> , t/year | 637500 | 637500 |
| Ethanol production, m ³ /year | 143000 | 144500 |
| Ethanol yield of inc. wood, L/t raw material | 224 | 227 |

Table 3
Possible lignin extraction with adiabatic combustion temperature as guideline, followed by estimation of the amount of lignin necessary to replace fuel oil*

| Mass balance lignin production | Pine | Aspen |
|---|--------|--------|
| Lignin in wood, % | 28.5 | 22.5 |
| - <i>ditto</i> , t/year | 181688 | 143438 |
| Lignin in black liquor, t/year | 167442 | 132241 |
| Extracted lignin, t/year | 63263 | 25122 |
| Extracted of total lignin in black liquor, % | 38 | 19 |
| Energy needed in lime kiln, GJ/m ³ ethanol | 4.6 | 4.3 |
| Energy needed in lime kiln, t lignin/year | 25187 | 23636 |
| Sold lignin, t lignin/year | 38076 | 1486 |

*The lignin not used in the lime kiln has been assumed to be sold as a renewable fuel

The results of lignin extraction from pine and aspen black liquors are listed in Table 3, along with an estimate of the amount of lignin needed to replace fuel oil in the lime kiln. The surplus of lignin not needed in the lime kiln is assumed to be sold as a renewable fuel. Other more value-added

applications are studied at Innventia in other projects.

The main effects on the energy balance, as a consequence of the simultaneous production of ethanol and lignin, are illustrated in Table 4. The evaporation plant consumes LP-steam and is the main energy

demanding equipment in the ethanol converted pulp mill. The production of steam in the recovery boiler is lower for pine, due to the higher amounts of extracted lignin. The bark and evaporated thin stillage are burned in the power boiler to balance the steam demand within the process. The energy content from the bark and the evaporated thin stillage is sufficient to balance the steam demand for aspen, but not for pine. In the case of aspen, a part of the bark could be sold, a reverse situation being observed for pine, *i.e.* the auxiliary fuel needs to be purchased to assure the steam demand.

Economic assessment

Table 5 shows the costs of raw materials, chemicals and power used in the study to estimate the capital and the operating costs of the concept. It is difficult to establish a cost for the enzymes, once their commercial use is limited today. According to the estimations of enzyme manufacturers, the

cost is of about 0.1 €/L ethanol or less. In such a case, the enzymes need to be produced on-site and from cheap substrates. A cost of 0.1 €/L ethanol has been used in the study for the base case scenario, although it varied in a sensitivity analysis. The price of wood varies continuously and, therefore, a sensitivity analysis has been performed. The cost for lignin and bark also varied in the sensitivity analysis.

Table 6 shows the total capital cost for the simultaneous production of ethanol and lignin. The investment costs for the existing equipment largely influence the final cost for ethanol production. An investment of 167 M€ for the existing equipment has been assumed for the base case scenario (the exchange rate has been recalculated from 1€ = 9.2 SEK, in von Schenck *et al.*, 2007, to 1 € = 11 SEK). This figure is based on the investment cost for the “type mill” within the FRAM program.⁴

Table 4

Main effects on the energy balance as a consequence of the simultaneous production of ethanol and lignin

| Effects on the energy balance | Pine | Aspen |
|-------------------------------|------|-------|
| Consumption, GJ/t ethanol | | |
| Steam in evaporation plant | 16 | 15 |
| Other equipment | 34 | 34 |
| Total consumption | 50 | 49 |
| Production, GJ/t ethanol | | |
| Recovery boiler | 26 | 33 |
| Power boiler | 23 | 16 |
| Secondary heat | 0.7 | 0.7 |
| Total production | 50 | 49 |

Table 5

Costs for raw material, chemicals and power incl. green certificates used in economic assessment (1 € = 11 SEK)

| Costs | Base case |
|--|-----------|
| Wood, €/t wood | 75* |
| Acid, €/t acid | 40 |
| Enzymes, €/t ethanol | 115* |
| NaOH, €/t NaOH | 270 |
| Power, incl. electricity certificates, €/MWh | 59 |
| Lignin, €/GJ | 5* |
| Bark, €/GJ | 2.5* |
| Labour, €/man year | 41800 |
| Maintenance, % of investment | 2 |

* Has been varied

The investment cost for the existing equipment has also been varied in a

sensitivity analysis, to see how it will affect the total production cost. The cost for the

ethanol line with pre-hydrolysis, SSF and a distillation procedure, etc. was calculated for a 4 h residence time in pre-hydrolysis and 48 h in SSF, respectively.

Table 7 shows the total operating cost as well as the total ethanol production for the two base case scenarios. The cost of the raw materials, followed by the cost of the enzymes is the most significant one in the

operating cost. Lignin extraction exceeds the amount needed in the lime kiln for both pine and aspen, which results in a surplus that can be sold. Part of the bark could be sold for aspen, yet it needs to be purchased for pine. Power production is higher than power consumption in both cases, which results in a surplus of power that could be sold to the grid.

Table 6
Capital cost for the ethanol converted type mill model

| Capital cost, base case | Pine | Aspen |
|---|------|-------|
| Existing equipment, M€ | 167* | 167* |
| Hydrolysis, fermentation and distillation, M€ | 30 | 30 |
| Lignin separation, M€ | 7 | 4 |
| Total investment, M€ | 204 | 201 |
| Annuity factor | 0.1 | 0.1 |
| Allocated capital costs, €/m ³ ethanol | 142 | 139 |
| - ditto, M€/year | 20 | 20 |

* Has been varied

Table 7
Total ethanol production cost for pine and aspen*

| Operating costs and benefits | Pine | Aspen |
|---|------|-------|
| Wood, €/m ³ ethanol | 335 | 332 |
| Acid prior to SSF, €/m ³ ethanol | 0.7 | 0.7 |
| Acid in LignoBoost, €/m ³ ethanol | 2.6 | 1 |
| Enzymes, €/m ³ ethanol | 91 | 91 |
| NaOH make-up, €/m ³ ethanol | 13 | 7 |
| Power, €/m ³ ethanol | -36 | -35 |
| Lignin, €/m ³ ethanol | -35 | -1.3 |
| Bark, €/m ³ ethanol | 16 | -16 |
| Labour, €/m ³ ethanol | 18 | 17 |
| Maintenance, €/m ³ ethanol | 28 | 28 |
| Net operating cost and benefits, €/m ³ ethanol | 433 | 424 |
| - ditto, M€/year | 62 | 61 |
| Total production cost | | |
| Investment, €/m ³ ethanol | 142 | 139 |
| Operating, €/m ³ ethanol | 433 | 424 |
| SUM, €/m ³ ethanol | 576 | 563 |

* 1€ = 11 SEK. The total production cost is for the base case scenario, *i.e.* the equipment, enzymes, wood, lignin and bark costs were not varied

Figure 1 shows the effects on the total ethanol production cost from pine, when costs for the existing equipment, raw material, enzymes, lignin and bark have been varied. The costs of the different studied parameters have been varied $\pm 100\%$ from the

base case scenario showed in Table 5. Results indicate that the raw material cost, followed by the cost for the existing equipment and enzymes are the parameters that most affect the total production cost.

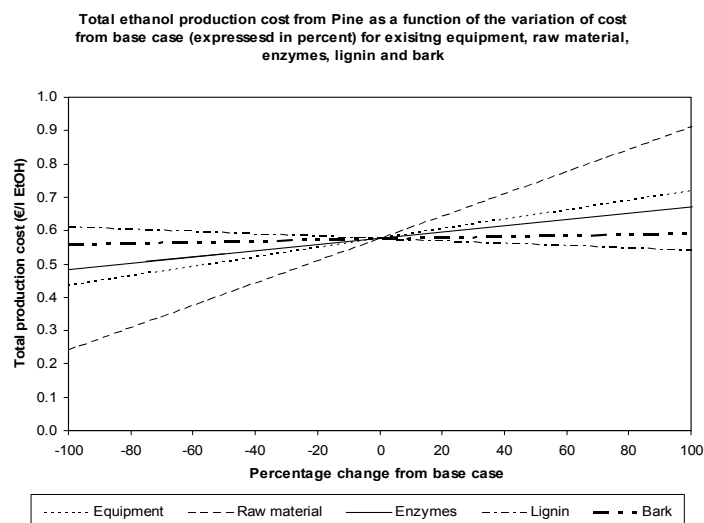


Figure 1: Total ethanol production cost for the base case scenario of pine (0%) and with varied cost ($\pm 100\%$) of the existing equipment, raw material, enzymes, lignin and bark

CONCLUSIONS

The material and energy balances were completed in a WinGEMS model and the economics of some alternatives was assessed by some price scenarios. The results indicate that the proposed concept would have made potentially viable the production costs, if at least the cost of the existing equipment could be lowered from the base case scenario. If the cost of the existing equipment is set to zero, an ethanol production cost would be in line with the bioethanol produced from grain in Northern Europe today, *i.e.* about 0.45 €/L ethanol (~ 5 SEK/L).

Lignin can be produced in a very pure form, as the process is self-sufficient in power and almost self-sufficient in steam. The pine case needs to purchase some bark or auxiliary fuels and burn in the power boiler, to balance the steam requirements. The extracted lignin is used in the lime kiln to replace fuel oil, while the surplus of lignin not needed in the lime kiln is sold as a fuel for both pine and aspen. More lignin could be sold in the case of pine. An observation to be made is that lignin could be used in a large field of applications, which would increase the value of the extracted lignin and thus decrease drastically the total ethanol production cost.

The production rate of a typical mill producing 1000 tonnes of pulp per day before conversion would be of about 140 000 m³ of ethanol per year, as depending on the wood raw material. The corresponding lignin production would range from 25 000 to 63 000 tonnes per year.

Using alkaline delignification to produce a substrate with low lignin content for the enzymatic hydrolysis is entirely based on known and well-proven technology. The process chain from enzymatic hydrolysis to ethanol is very similar to that used today for grain ethanol. The difference is that the raw material used for hydrolysis is relatively pure cellulose instead of starch. Altogether, the technical risk should be therefore low.

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