# Swedish Pulp Mill Biorefineries

A vision of future possibilities

ER 2008:26

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## Förord

Tillgången på skogsråvara har under mer än ett sekel utgjort grunden för betydande industriella aktiviteter i Sverige. Sågade trävaror samt produktion av massa och papper har länge varit dominerande användningsområden för råvaran men utnyttjandet för energiändamål har vuxit sig allt starkare under de senaste decennierna. Utbyggnaden av biomassabaserad kraftvärmeproduktion är det främsta exemplet. Klimatfrågan har under det senaste decenniet aktualiserat intresset för att framställa biodrivmedel från skogsråvara, ett forskningsområde som fått ökad betydelse för Energimyndighetens forskningssatsningar.

Utvecklingen har lett fram till frågor kring råvarukonkurrens, produktionseffektivitet och näringslivsutveckling och därmed till hur råvara kan utnyttjas på bästa sätt för olika tillämpningar. I detta sammanhang har intresset ökat för hur olika produkter kan framställas inom ramen för olika typer av kombinat. Terminologin varierar i litteraturen. Det talas om energikombinat, biokombinat, bioraffinaderier, vilket speglar det ökande intresset för detta område men också att det ännu saknas klara definitioner av dessa begrepp.

Under 2005-2006 genomfördes projektet P22400-1, ”Swedish Pulp Mill Bio Refineries”, vid Chalmers tekniska högskola. Projektets slutrapport sågs som så intressant att dess resultat borde komma till kännedom för en vidare krets, varför Energimyndigheten nu ger ut den i sin rapportserie.

Projektet omfattade en litteraturgenomgång av projekt med denna inriktning, som genomförts under perioden 1996-2005. Avgränsningen i denna rapport är således att massabruk är utgångspunkten för bioraffinaderiet.

Rapporten är skriven på engelska och riktar sig till beslutsfattare, forskare, konsulter och övriga aktörer med intresse för detta område.

Huvudansvarig för rapporten är professor Thore Berntsson, Chalmers tekniska högskola. I arbetet medverkade också Peter Axegård, Birgit Backlund, Åsa Samuelsson, Niklas Berglin och Karin Lindgren från STFI-Packforsk.

Birgitta Palmberger
Avdelningschef

# Preface

Wooden biomass resources have provided the basis for significant industrial activities in Sweden for more than a century. Sawn timber products and pulp and paper have dominated the use of wooden raw material for a long time, but its use for energy purposes has grown stronger during the last decades. The expansion of biomass-based combined heat and power generation is the principal example. During the last decade the climate issue has evoked the interest of producing renewable motor fuels from wood biomass, a research area, which has received increased attention for the research agenda of the Swedish Energy Agency.

The development has raised questions regarding competition for raw material, production efficiency and industrial development and consequently how the raw material can be utilised in the best way for various applications. In this context, the interest has grown how various products can be manufactured within different kinds of industrial combines. Terminology differs in the literature. Terms like energy combines, bio combines, biorefineries are mentioned and this reflects the growing interest for this area but also the lack of definitions for these concepts.

In the years 2005-2006 the project P22400-1,"Swedish Pulp Mill Bio Refineries" was carried out at Chalmers Institute of Technology. The final report of the project was considered to be of interest for a wider group of people and the Swedish Energy Agency has therefore decided to publish it in its report series.

The project contains a literature review of projects relating to biorefineries, which have been conducted during the decade 1996-2005. The report is delimited to pulp plants as the basis for the biorefinery.

The report is written in English and is intended for decision makers, governmental agencies, researchers, consultants and other stakeholders, with an interest in this field.

The principal author of the report is professor Thore Berntsson, Chalmers Institute of Technology. In addition, Peter Axegård, Birgit Backlund, Åsa Samuelsson, Niklas Berglin and Karin Lindgren at STFI-Packforsk have also contributed to the report.

Birgitta Palmberger
Head of department
Swedish Energy Agency

## Contents

# 1 Executive summary

## 1.1 Introduction

Pulp production is an important industry in Sweden and is based on a renewable and carbon dioxide neutral raw material: wood from forests. Most of this pulp is used for paper production. However, increasing competition from countries with fast-growing forests makes it necessary to increase the competitiveness and to find new and highly refined products to complement the existing pulp-based products.

Today, modern science could make it possible to develop techniques for refining almost the whole wood-matter, pulp mill side streams and bark compounds into platform chemicals, electricity, high quality fuels and structured feed-stock for chemicals and materials. The major challenge is to convert the state of basic scientific knowledge into industrial practise.

### *Definition*

There is no strict "scientific" definition of a biorefinery. There is not even a commonly agreed practical definition. The general objective of a biorefinery is of course to upgrade biomass to different kinds of more valuable products. A biorefinery can be a "standalone" unit for upgrading biomass or integrated in a pulp or pulp and paper mill. This report deals with biorefineries integrated with a pulp mill.

Our definition of an integrated biorefinery is:

> *Full utilization of the incoming biomass and other raw materials for simultaneous and economically optimized production of fibres, chemicals and energy.*

Examples of products from a pulp mill biorefinery are:

- Chemicals and Materials (Phenols, adhesives, carbon fibres, activated carbon, binders, barriers, adhesives, antioxidants, surfactants, chelants, solvents, adhesives surfactants, descaling agents, specialty polymers, pharmaceuticals, nutraceuticals, cosmetics etc.
- Biofuels (pellets, lignin fuel, methanol, DME, ethanol etc)
- Electricity (BLGCC, condensing power etc.)

The new or increased amounts of traditional products can be made from internal and/or external biomass. Three different levels can be identified:

- A high degree of energy saving in future mills, especially chemical pulp mills, will lead to large amounts of excess internal biomass which can be transferred to products mentioned above.

- Components in e.g. the black liquor, forest residues and bark can be upgraded to more valuable ones and the energy balance of the mill is kept through fuel import, wholly or partly depending on the level of mill energy efficiency. This imported fuel can be biomass or other types.
- External (imported) biomass (in some cases together with excess internal biomass) can be upgraded using synergy effects of docking this upgrading to a pulp mill.

Electricity has been included as one of the possible biorefinery products. The electricity production in a mill can be increased in several ways which cannot be directly considered as biorefineries, e.g. recovery boiler high efficiency, and intermediate superheating. In this report only measures for increased electricity production which are direct alternatives to other biomass upgrading measures have been included.

*Background for the interest of biorefineries*

The interest for biorefineries has increased significantly during recent years. The main reasons are:

- A trend of decreasing prices on pulp and paper and increased wood costs.
- Increased competition from low cost producers of pulp and paper in South America and Asia
- The energy efficiency and hence the excess of biomass, is increasing/can be considerable increased in pulp mills
- Increased energy prices and new policy instruments (non petroleum based chemicals and materials, renewable materials etc.)

## 1.2 Opportunities for excess internal biomass

As discussed above, a pulp mill integrated biorefinery can use both internal and external (imported) biomass. Below one important aspect is discussed, i.e. possible availability for internal biomass in the future.

The three major parts of wood are cellulose (40-50 %), hemicelluloses (30-35 %) and lignin (20-30 %). In a typical chemical mill pulp wood is used to produce fibres (cellulose and some hemicellulose) and electricity/steam (hemicellulose and lignin), as shown in. In a biorefinery some of the lignin and/or hemicellulose (sometimes also cellulose could be used for other products than pulp) must be available for other products. The energy balance of such a mill must therefore enable an excess of internal biofuel. Modern chemical pulp mills have a slight excess of biofuel and no fossil fuel except for the lime kiln. Of the Swedish lime kilns on the average about 60 % of the fuel is derived from mineral oil and the remaining 40 % from biomass such as gasified bark, pulverized chips and tall oil residues.

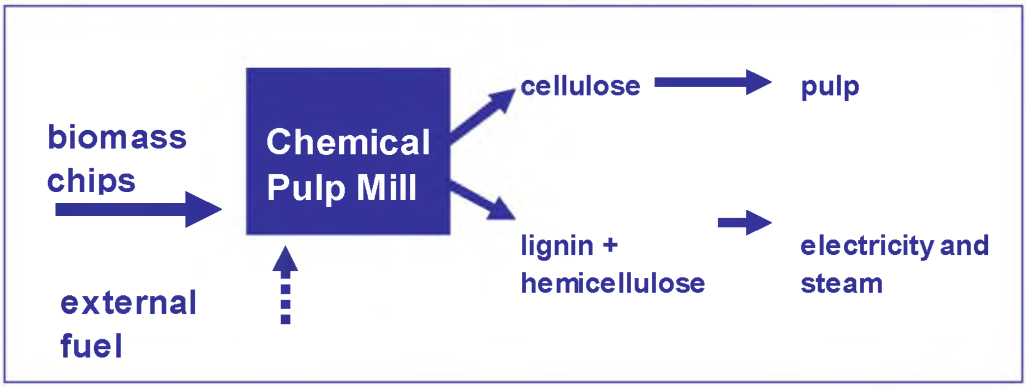


**Figure 1.1 Chemical Pulp Mill**

Integrated chemical mills and mechanical pulp mills have normally not an excess of biofuel. Therefore mill-integrated biorefineries, using internal biomass, are more likely in the future to be applied to chemical market pulp mills when bulk products are produced. Value added specialities can be produced in any kind of pulp mill.

There is a high potential to increase the biofuel excess in future chemical market pulp mills. This has been shown in the energy system oriented studies within the Swedish KAM (The Ecocyclic Pulp Mill) and the FRAM (The Future Resource Adapted Pulp Mill) programs. This can be accomplished by a mixture of measures: New energy efficient components or departments, new energy technologies, more advanced process integration and new system solutions (e.g. process integrated evaporation)

show the potential to create an excess of biofuels in future greenfield market pulp mills compared to current mills using best-available technology (“reference mill”) and average operating technology (“type mill”).

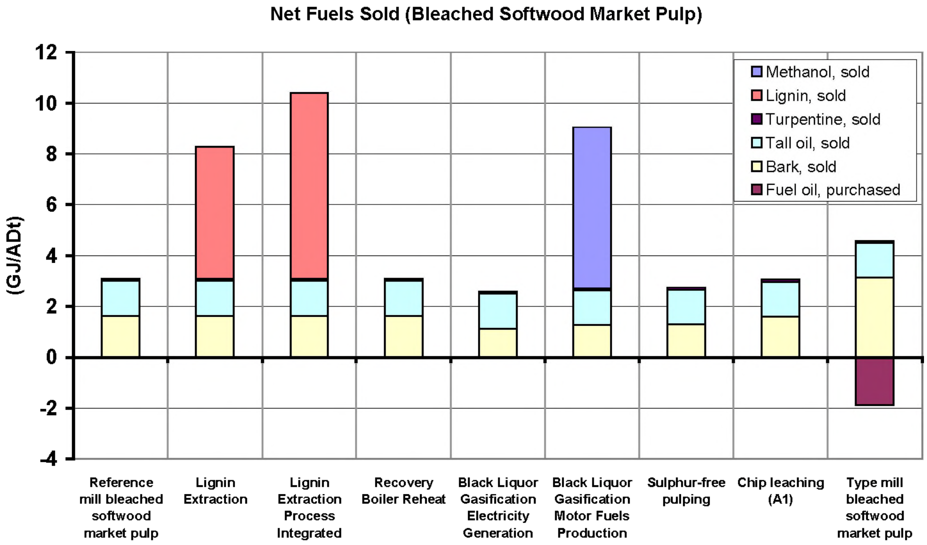


**Figure 1.2 Potential for fuel sales from theoretical model mills producing bleached softwood market pulp. (Purchased fuel oil for the lime kiln is also included for the type mill.)**

## 1.3 Different types of mill integrated biorefineries, using internal biomass

Two major types of mill integrated biorefineries, using internal biomass, can be defined, chemicals/materials oriented and energy oriented, see Figures 1.3 and 1.4. A future biorefinery can of course also be a mix of these two extremes. In such a biorefinery the heat balance can be kept through energy conservation only or through import of fuel (which can be biomass or other fuel).

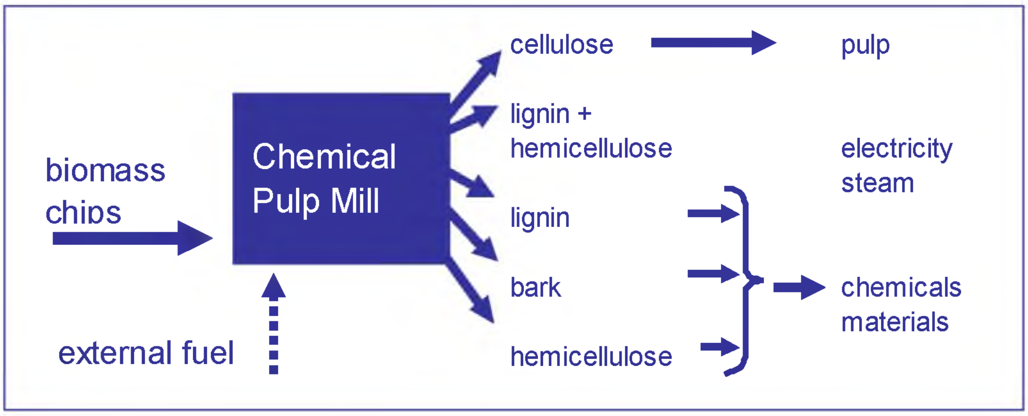


**Figure 1.3 Biorefinery – Chemicals and Materials**

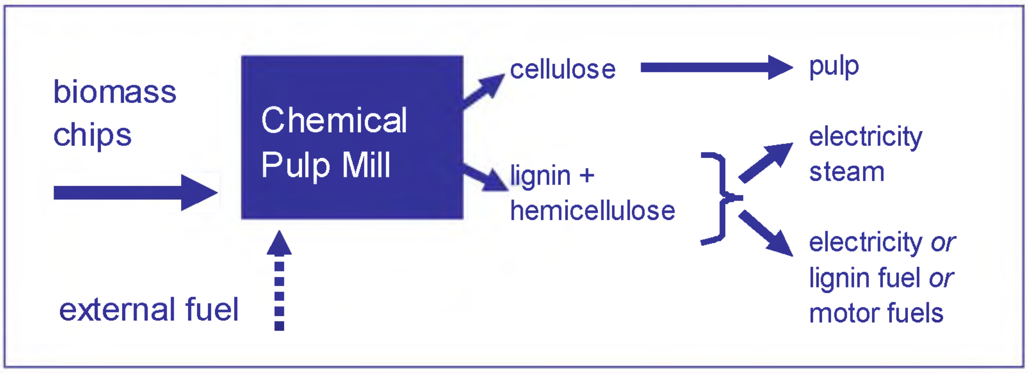


**Figure 1.4 Biorefinery – Energy**

Another type of biorefinery is when a mill and another heat consumer/producer are integrated to achieve synergy effects such as heat cascading. This type is often called Energy Combines. In this case the additional product from the mill is excess heat and/or the products from the plant docked to the mill (e.g. upgraded external biofuel). This type is shown in Figure 1.5.

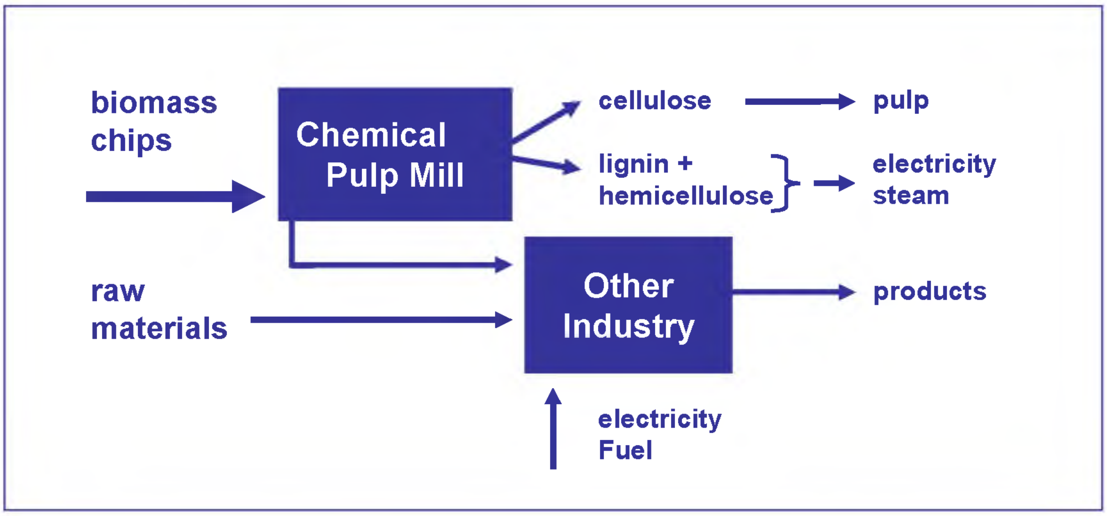


**Figure 1.5 Principles of an Energy Combine**

## 1.4 Biorefinery – Energy

The principles of a biorefinery-energy are shown in Figure 1.4. In such a biorefinery the available lignin and/or hemicellulose is used for production of electricity (in addition to the traditionally one produced in the recovery boiler) and/or biofuels. Due to the complexity of the system, different types of biorefinery-energy can be identified: electricity or lignin production as well as upgraded biofuels, or electricity production using gasification. Typical biofuel products from a gasification type of refinery are methanol or dimethyleteher (DME).

- In the KAM- and FRAM-programs lignin separation from black liquor using the LignoBoost method developed by STFI-Packforsk in cooperation with Chalmers. The LignoBoost process offers the possibility to off-load a capacity limiting recovery boiler for increased production and may supply future lime kilns with fuel.

In the FRAM-program the general conclusions compared with using the excess lignin for increased electricity production in a condensing turbine are:

- There is a high potential for steam savings in current Swedish kraft pulp mills (~ 25 %) making lignin removal more feasible
- Power generation from steam surplus is profitable with current high Swedish power prices due to power certificates
- Lignin extraction is profitable when the lignin value is high (e.g. when replacing mineral oil) or when off-backing a capacity limiting recovery boiler for increased production.

### *Black liquor gasification*

For the gasification type of refinery, more electricity can be produced due to the fact that the produced syngas can be used in a BLGCC plant. The electricity production can be approximately doubled with a BLGCC plant.

A principle scheme for the production of methanol through gasification is shown in Figure 1.6. As is shown there if a large part or all the black liquor is gasified for methanol production, external biofuel must be imported in order to keep the energy balance of the mill.

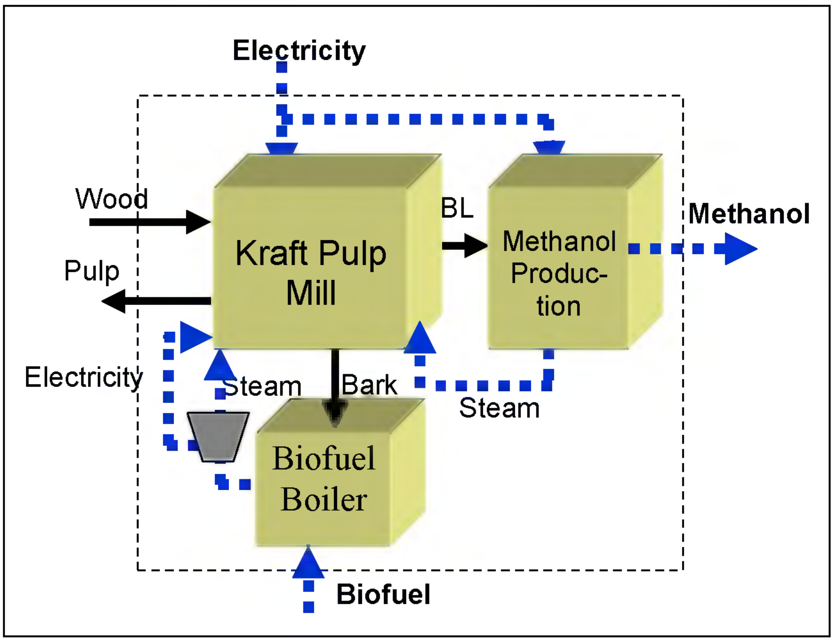


**Figure 1.6 Black liquor gasification with methanol production**

The potentials for producing electricity and motor fuels, respectively, are shown in Figures 1.7 and 1.8

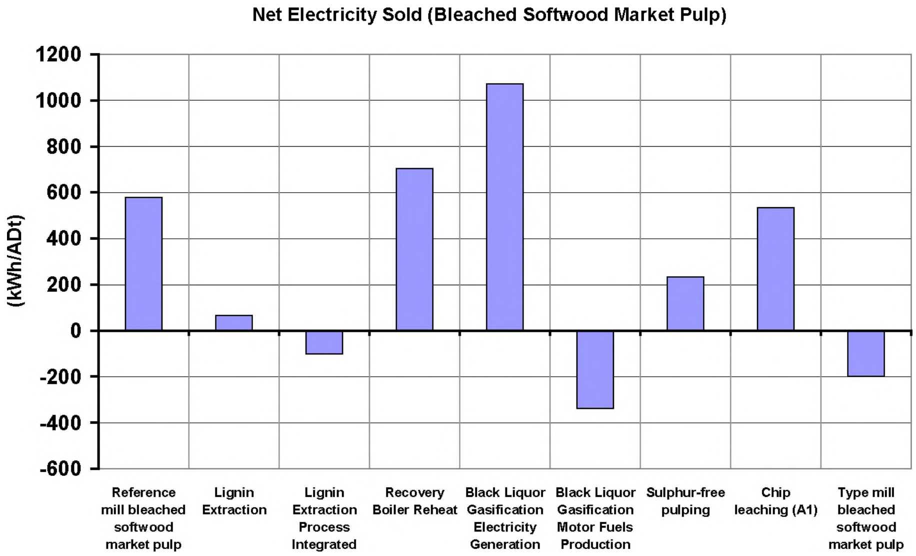


**Figure 1.7 Potential for electricity sales from mills producing bleached softwood market pulp. (Reference mill = hypothetical pulp mill which represents the existing best available, commercially proven, Nordic technology at the time of writing. Type mill = representing typical mill of today in Nordic countries)**

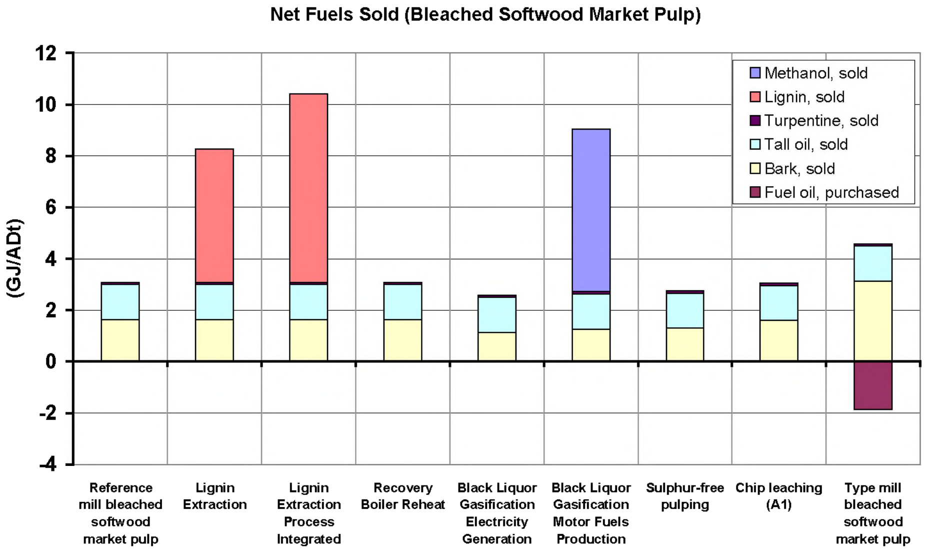


**Figure 1.8 Potential for fuel sales from mills producing bleached softwood market pulp. (Purchased fuel oil for the lime kiln is also included for the type mill.) (Reference mill = hypothetical pulp mill which represents the existing best available, commercially proven, Nordic technology at the time of writing. Type mill = representing typical mill of today in Nordic countries)**

## 1.5 Biorefinery-Energy combines

The principles are shown in Figure 1.5. Cascading of heat between a mill and another industrial plant is done in order to have energy synergy effects.

### *Background*

There is today an increasing interest for energy combines and ecocyclic industrial parks cooperation in terms of e.g. energy between two or more industries and/or society. One example of such cooperation is heat cascading, i.e. where heat for one plant is satisfied by excess heat from another one.

Different opportunities for heat cascading and other energy cooperations in which the pulp and paper industry is one part, are discussed in this chapter. The main aspects included are:

- Drying of biomass (e.g. forest residues, bark)
- Pelletizing in connection with drying and forest residues leaching
- Energy combine with ethanol production
- Energy combines with other industries

Studies of Process Integration between a pulp mill excess heat and drying/pelletizing of biomass have shown that large amounts of excess heat 1-1.5 GJ/ADt can be used for drying and that different ways for integration can be identified. The economy for such an energy combine depends to a high extent on future energy prices and policy instruments. This should be studied further.

Acid leaching could make forest residuals more attractive as fuel in limekilns and power plants. The content in bark, branches and tops of elements that cause environmental or incineration problems can be decreased down to the level of “pure” wood fuels based on stem wood. Less ash content and reduced smell make the fuels more interesting for residential heating as well. Reductions of ashes contents up to 50 % can be achieved. Also reductions of several metal ions, chlorine, etc can be achieved

In the Swedish research programme “Ecocyclic Pulp Mill – KAM”, co-location of an ethanol plant and a pulp mill was studied [KAM 2003]. The pulp mill was a “state-of-the-art” kraft mill and had a considerable fuel surplus (as bark and lignin). One main research area was how to use this surplus in the most efficient and economical way. In the reference case (the Reference Mill), the fuel surplus was used to raise steam for electricity production. One of the studied alternatives was to use it for production of ethanol from cellulose. The studies were done at some special conditions and more studies must be done before general conclusions for this alternative can be drawn. It should also be of interest to identify opportunities for a combine between a mill and another type of industry in order to achieve energy synergy effects. One opportunity is to use the excess heat from a mill for heating another type of industry. This requires a type with need for low temperature heat, e.g. food industry. One problem is that food industries are in most cases relatively small compared to the amounts of excess heat from e.g. a pulp mill.

## 1.6 Carbon dioxide precipitation

One interesting future opportunity for pulp and paper mills is $CO_2$ precipitation. It is included in this report in spite of the fact that it is not generally considered a biorefinery. It is, however, an opportunity for this industry to produce a new valuable product, i.e. $CO_2$.

A large chemical market pulp or pulp and paper mill produces a large amount of $CO_2$. For a market pulp mill of 1 500 ADt the annual production is approximately 860 000 tonne annually. This can be compared with the total annual Swedish production from fossil fuels, approximately 60 Mtonne. Like in large coal condensing plants and natural gas combined cycles, $CO_2$ can be separated from the flue gases from the recovery boiler (and the lime kiln), transported to e.g. an aquifer and stored there. The separation can be done in different ways, e.g. using mono ethanol amine (MEA) in an absorber/desorber system. In such a system additional heat (e.g. biofuel, natural gas combined cycle) must be supplied for the desorption. The profit for a large mill can be very high at future high costs for $CO_2$ emissions. Annual profits can be nearly on the same order as today's electricity certificates, for a large mill on the order of 7-14M€/year.

## 1.7 Production of chemicals and new fibre materials

The utilisation of wood-based side-streams from pulp mills has better economic prerequisites than most other biomass raw materials;

Firstly, the scale of the industry means both large volumes of bio-feedstock in total and large production units with good scale economy.

Secondly, some by-product streams, e g. black liquor, are already partly processed in the pulp production and can be more suited for further refining than wood waste, agro fibres or other natural-fibre feedstock. Biomass is more complex raw material than petroleum, and utilising such partly processed streams therefore means a very efficient resource use.

Thirdly, location of the new valorisation industry by the pulp mill means excellent process integration opportunities (waste heat and other energy, waste and effluent handling, water, general infrastructure etc.).

Another advantage of wood over annual crops is that the wood can be transported to the pulp mill biorefiney during the whole year whereas annual crops have seasonal variations.

The broad spectrum of organic compounds in pulp mill streams such as black liquor and bark could, instead of being incinerated in the recovery boiler and the bark boiler, be processed to high-value chemicals whose raw material today is oil or to completely new products.

### *Lignin*

Lignin, which can be recovered from black liquor, is currently used in several applications for example as binder, surfactants, batteries, road additives etcetera.

Much research is performed with the purpose to increase the use of lignin. The focus is either on increasing the performance of the lignin by modifying its structure, or on finding new applications like carbon fibres (CF).

In a future lignin could be used in a more extensive way both in applications where the lignin structure is remained but modified, e.g. as sequestrant for metal ions, and in applications like carbon fibres, one of the most important materials by itself and in advanced composites. Besides of CF intended for structural applications, activated carbon fibres (ACFs) can be produced. They are a special type of CF where surface characteristics are the most important property. ACFs can be used for removal of impurities from gases and liquids, including adsorption of micro-organisms.

An interesting possible product from degraded lignin is phenols, a raw material today for e.g. polymers like formaldehyde resins.

### *Hemicelluloses*

Hemicelluloses are polysaccharides that can be recovered from wood or black liquor. Both xylans and glucomannans can be employed as fibre additives improving the beatability and strengthening the fibre-to-fibre bonding ability of the treated pulps. This means that they improve some of the properties that are especially important for packaging grades e.g., tensile and bursting strength and the folding endurance. Derivatives of hemicelluloses have also been investigated for applications as sizing-additives and adhesives in papermaking, hemicelluloses from wood have a great potential to become very attractive alternative renewable raw materials for packaging coatings and barrier film applications.

Hydrogels - polymeric materials that swell in water but do not dissolve – is another potential product. Hydrogels can be useful as matrices for controlled release of bioactive molecules, in particular pharmaceutical proteins and for encapsulation of living cells

Furfural is an interesting intermediate that can subsequently be converted into a large number of valuable furan compounds which can serve as starting materials for different kinds of plastics.

Degraded hemicelluloses can be transformed into e.g. xylitol and mannitol that can be used as non-cariogenic sweeteners for diabetics.

### *Extractives and fatty acids*

Wood extractives contain a broad variety of organic compounds that are interesting for high-value products like pharmaceuticals and functional foods.

Turpentine, fatty acids and resin acids from cooking liquors are already utilized today for different chemical products. Except for betulin from birch, bark components are little exploited so far. Birch bark consists to a large extent of fatty acids suited for tailor-made polyesters or grafting onto cellulose for bio based composite materials.

## 1.8 Visions for and need for further R&D in Sweden

*Export of energy from the pulp and paper industry to society*

- Opportunities for energy saving in chemical pulp and paper industry in order to identify potentials upgrading of internal biomass to electricity, lignin for sale, motor biofuels, etc
- Opportunities for energy saving in the mill when black liquor gasification is used in the future in order to identify potentials increasing the share of internal biomass of the total fuel consumption
- Increase knowledge of most suitable end products for expert under different future scenarios
- The Swedish lead in several key areas connected to upgraded fuel export should be used for establishing Sweden as a foremost biorefinery Country. Examples of such lead areas are:
    - Process integration in pulp mills (Chalmers)
    - Pressurized gasification of black liquor and conversion into electricity or motor fuels (ChemRec, Nykomb, ETC)
    - Separation of high-quality lignin from black liquor through the LignoBoost process and further upgrading of the lignin (STFI-Packforsk)
    - Chip, bark, etc leaching kidney (STFI-Packforsk, Chalmers)

*Energy Combines*

- Biomass upgrading in connection with pulp and paper mills is future area of high interest in Sweden. Further work on possible synergy effects and on new technologies, e.g. low-temperature drying, should be performed
- More high-quality biomass fuel can be produced through upgrading of e.g. forest residues and bark via leaching of metals and other elements. Technical and economic opportunities should be performed. This could be a highly interesting way to produce high-quality biofuel in Sweden
- Synergy effects of connecting ethanol production to a pulp or pulp and paper mill could improve the economy for this biofuel. Future conditions for this to come true should be explored.

*Separation of $CO_2$ from the process*

- Although most R&D efforts in this area are directed towards $CO_2$ sequestration in coal and natural gas systems, removal of $CO_2$ from pulp and paper mills through $CO_2$ sequestration from recovery boiler flue gases, black liquor gasification systems, lime kiln gases, etc should be of high interest for Sweden and create a win-win situation, i.e. with good profiles for industry and $CO_2$ mitigation with comparatively low cost for society

- The R&D in this field has recently started and there is therefore a need to further explore the different aspects of this technology/system solution. Examples of important further R&D areas are:
  - Investment cost/system solutions and operability aspects for the MEA type of system
  - Pilot plant for testing of the technology real pulp mill flues gases
  - New absorption media at e.g. higher temperature levels
  - Studies in infrastructure aspects for transport of $CO_2$
- In this area Sweden could be a leading nation due to the ongoing research, many pulp mill candidates, and good storage capacity (e.g. in Skåne).

### *Production of chemicals and new fibre materials*

The future kraft pulp mill has a large potential to supply chemicals and materials, in addition to the present fibre products.

Sweden has several advantages that motivate that we should be active in the research and development towards pulp mill biorefineries producing chemicals and new materials.

# 2 Introduction

## 2.1 Background

The background for this project is the rapidly increasing interest for biorefineries, both in Sweden and internationally. There are several reasons for this growing interest. There is an increasing competition from mills in e.g. South America and Asia and from other types of wood-based industry which have both a low cost for raw material and production. Furthermore the market price for pulp has decreased over several years, see Figure 2.1. Other important factors, partly related to the above ones, are:

- The pulp and paper industry is striving at more valuable products
- The energy efficiency and hence the excess of biomass, is increasing/can be considerably increased in pulp mills
- Increased energy prices and new policy instruments

The products from a biorefinery are environmentally important (non petroleum based materials, renewable, biodegradable chemicals, $CO_2$-neutral fuels and electricity, etc).

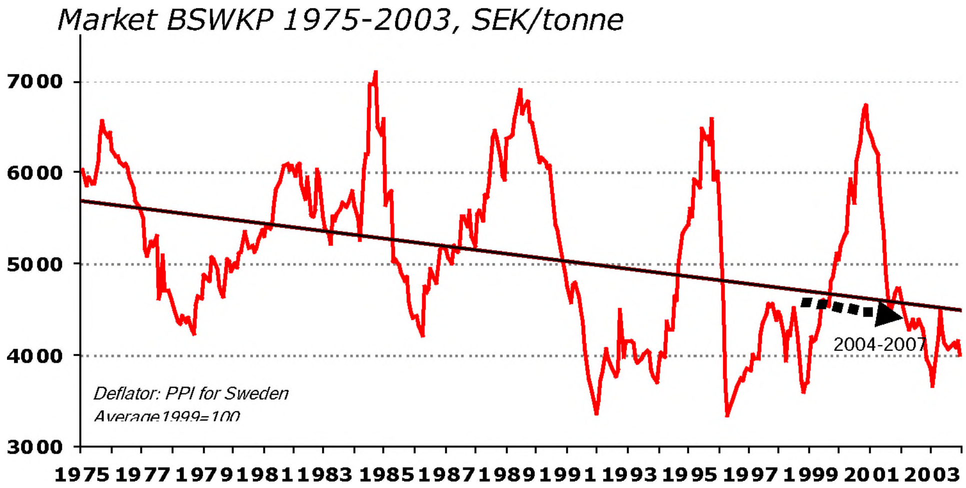


**Figure 2.1 Steady drop in market pulp prices…**

Several countries have started or are planning large programs /projects in the biorefinery area. The conditions in Sweden should be excellent for biorefinery developments. This is discussed in this report.

The project has been carried out jointly by Chalmers University of Technology (Thore Berntsson) and STFI-Packforsk (Peter Axegård, Niklas Berglin, Åsa Samuelsson, Karin Lindgren, Birgit Backlund). The way of working has been to compile and evaluate already existing information and not to develop new knowledge. Therefore, some parts in the text are direct quotations from earlier work of the authors or of others, of course with references in all cases.

## 2.2 Biorefinery – definition and different types

### *Definition*

There is no "scientific" definition of a biorefinery. The general objective of a biorefinery is of course to upgrade biomass to different kinds of more valuable products. A biorefinery can be a "standalone" unit for upgrading biomass or integrated in a pulp or pulp and paper mill. This report deals with biorefineries integrated with a pulp or pulp and paper mill.

Our definition of an integrated biorefinery is:

- Upgrading of biomass to other products or higher amounts of traditional products from pulp and paper industry:
  - Chemicals and Materials (Phenols, adhesives, carbon fibres binders etc.)
  - Biofuels (Pellets, Lignin fuel, methanol, DME etc)
  - Electricity (BLGCC, condensing power etc.)

The new or increased amounts of traditional products can be made from internal and/or external biomass. Three different levels can be identified:

- A high degree of energy saving in future mills, especially chemical pulp mills, will lead to large amounts of excess internal biomass which can be transferred to products mentioned above.
- Components in e.g. the black liquor can be upgraded to more valuable ones and the energy balance of the mill is kept through fuel import, wholly or partly depending on the level of mill energy efficiency. This imported fuel can be biomass or other types.
- External (imported) biomass (in some cases together with excess internal biomass) can be upgraded using synergy effects of docking this upgrading to a pulp or pulp and paper mill.

Electricity has been included as one of the possible biorefinery products. The electricity production in a mill can be increased in several ways which cannot be directly considered as biorefineries, e.g. recovery boiler high efficiency, and intermediate superheating. In this report only measures for increased electricity production which are direct alternatives to other biomass upgrading measures have been included.

### *Background for the interest of biorefineries*

The interest for biorefineries has increased tremendously during recent years. The main reasons are:

- The pulp and paper industry is striving at more valuable products due to the increased competition from pulp and paper producers in South America and Asia that have a low cost for the raw material as well as the operating cost.

- The energy efficiency and hence the excess of biomass, is increasing/can be considerably increased in pulp mills
- Increased energy prices and new policy instruments (non petroleum based chemicals and materials, renewable materials etc.)

Backgrounds for this are the increasing competition from mills in e.g. South America and Asia and the decreasing price for e.g. market pulp.

*Opportunities for excess internal biomass*

As discussed above, a mill integrated biorefinery can use both internal and external (imported) biomass. Below one important aspect is discussed, i.e. possible availability for internal biomass in the future.

The three major parts of wood are cellulose (45 %), hemicellulose (30 %) and lignin (25 %). In a typical chemical pulp mill they are used to produce fibres (cellulose) and electricity/steam (hemicellulose and lignin), as shown in Figure 2.1. In a biorefinery some of the lignin and/or hemicellulose (sometimes also cellulose could be used for other products than pulp) must be available for other products. The energy balance of such a mill must therefore enable an excess of internal biofuel. Modern chemical pulp mills have a slight excess of biofuel and no fossil fuel except for the lime kiln but several use the internal bark.

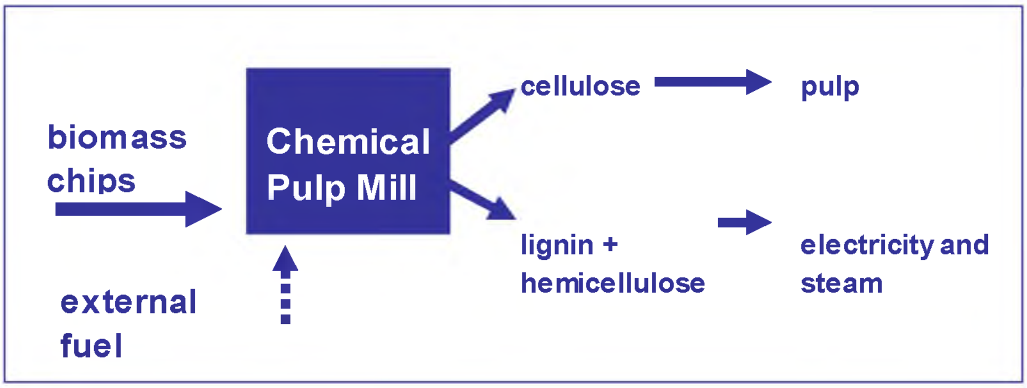


**Figure 2.2 Chemical Pulp Mill**

Integrated chemical mills and mechanical pulp mills have different situations and have normally not an excess of biofuel. There fore mill integrated biorefineries, using excess internal biomass, will in future be more applied to chemical market pulp mills

There is a high potential to increase the biofuel excess in future chemical market pulp mills. This has been shown in the energy system oriented studies within the Swedish KAM (The Ecocyclic Pulp Mill) and the FRAM (The Future Resource Adapted Pulp Mill) programs. This can be accomplished by a mixture of measures: New energy efficient components or departments, new energy technologies, more advanced process integration and new system solutions (e.g. process integrated evaporation), see Chapter 4.

*Different types of mill integrated biorefineries, using internal biomass*

Two major types of mill integrated biorefineries, using internal biomass, can be defined, chemicals and materials oriented and energy oriented, see Figures 2.2 and 2.3. A future biorefinery can of course also be a mix of these two extremes. In such a biorefinery the heat balance can be kept through energy conservation only or through import of fuel (which can be biomass or other fuel).

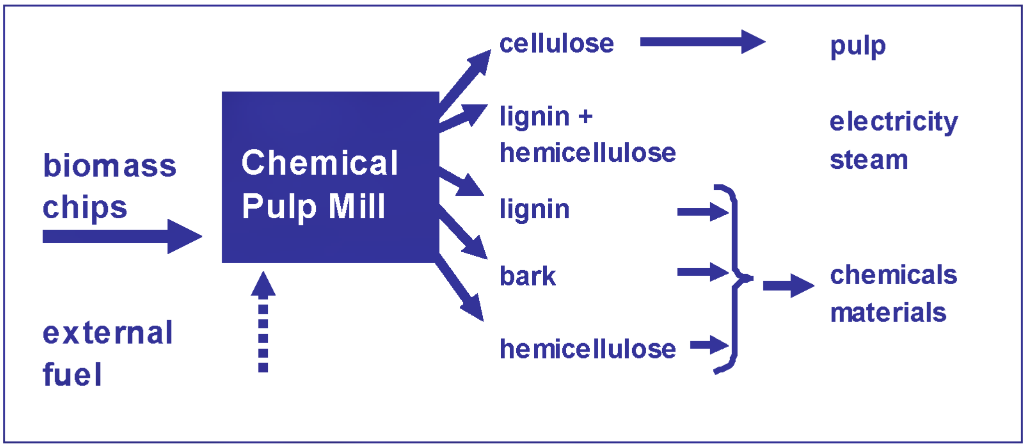


**Figure 2.3 Biorefinery – Chemicals and Materials**

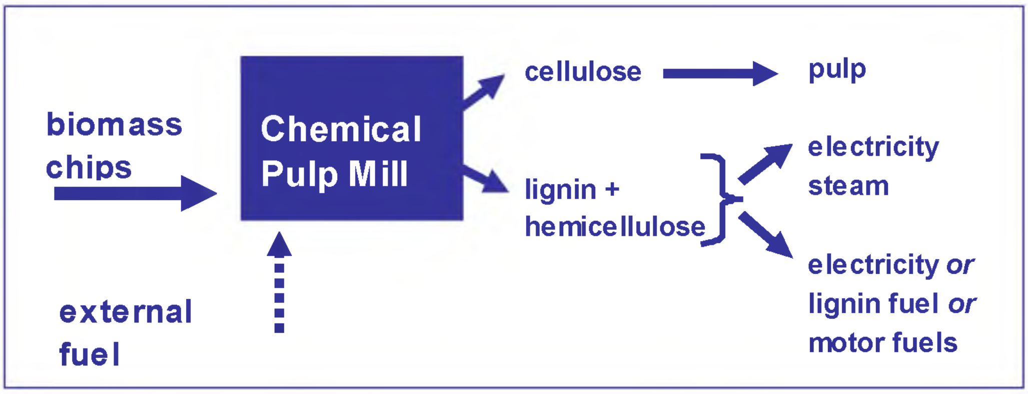


**Figure 2.4 Biorefinery – Energy**

Another type of energy biorefinery is when a mill and another heat consumer/producer are integrated to achieve synergy effects such as heat cascading. This type is called Energy Combines. In this case the additional product from the mill is excess heat and/or the products from the plant docked to the mill (e.g. upgraded external biofuel). This type is shown in Figure 2.5.

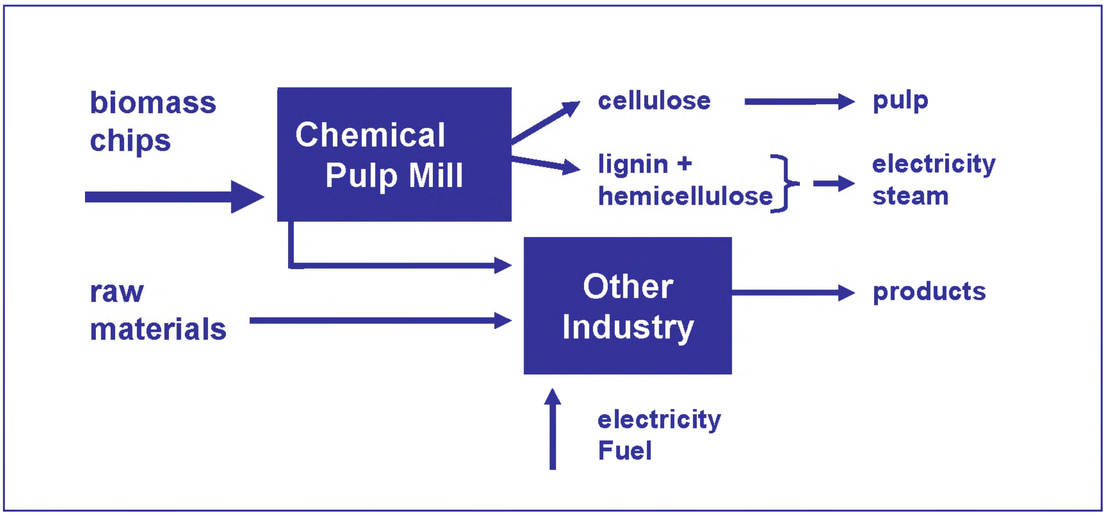


**Figure 2.5 Principles of an energy Combine**

One interesting future opportunity for pulp and paper mills is $CO_2$ precipitation. It is included in this report in spite of the fact that it is not generally considered a biorefinery. It is, however, an opportunity for this industry to produce a new valuable product, i.e. $CO_2$.

A large chemical market pulp or pulp and paper mill produces a large amount of $CO_2$. For a market pulp mill of 1 500 ADt the annual production is approximately 860 000 tonne annually. This can be compared with the total annual Swedish production from fossil fuels, approximately 60 Mtonne. Like in large coal condensing plants and natural gas combined cycles, $CO_2$ can be separated from the flue gases from the recovery boiler (and the lime kiln), transported to e.g. an aquifer and stored there. The separation can be done in different ways, e.g. using mono ethanol amine (MEA) in an absorber/desorber system. In such a system additional heat (e.g. biofuel, natural gas combined cycle) must be supplied for the desorption. The profit for a large mill can be very high at future high costs for $CO_2$ emissions. Annual profits can be nearly on the same order as today's electricity certificates, for a large mill on the order of 7-14M€/year.

## 2.3 Potentials for biomass in Sweden for possible use in biorefineries

In 2001 the Swedish consumption of biomass was 97 TWh/year. Today it is around 105 TWh/year. The situation in 2001 is shown in Table 2.2:

The available amount of biomass in Sweden in future depends on several parameters, e.g. price levels, ash reversal and nitrogen festilization. Different studies have come to different results. The variation is between 20 and 120 TWh/year more than is used now. A typical level mentioned often is 30-60 TWh/year more.

**Table 2.1 Use of biomass 2001, [TWh]**

| | | |
|---|---|---|
| **Industry** | Pulp and paper industry, black liquor | 35,5 |
| | Pulp and paper industry, Wood fuel | 7,7 |
| | Saw mill industry | 8,3 |
| | Other industry | 0,7 |
| **Building** | District heating | 30 |
| | Small houses | 9,3 |
| **Electricity production** | | 4,4 |

In one of the projects within the Swedish Energy Agency Program EUFORI, some estimations of potentials based on results from several different projects/programs have been done. No detailed calculations were carried out, instead the estimations were based on results from these other programs. The work was performed by Peter Axegård, STFI Packforsk, Thore Berntsson, Chalmers and Nippe Hylander, ÅF Process. The main results were:

For kraft pulp based mills:
Two scenarios were looked at, one with maximisation of electricity production and one with maximisation of biomass fuel export from the mill.

In the maximal electricity scenario 5-8 TWh/year were electricity can be produced and 1.5-5.5 TWh/year biomass fuel can be exported.

In the maximal biomass fuel scenario 7 TWh/year biomass fuel can be exported and 2.5 TWh/year more electricity can be produced.

In mechanical pulping 2 TWh/year and in paper production 3 TWh/year electricity can be saved.

The overall total potential is therefore:
10-13 TWh/year electricity
1.5-4.5 TWh/year biomass fuel export

Or

7.5 TWh/year electricity
TWh/year lignin fuel
1.5- 4.5 TWh/year fuel export

It shall be noted that some of the measures may not be additive and therefore the total potentials can be slightly exaggerated. Other conditions have been that no biofuel import to the mills and no use of gasification have been assumed.

## 2.4 Aims of this project

The general aims with this report are to describe principles, opportunities and where possible, Swedish potentials for different kinds of biorefinery, to describe the ongoing development in some countries, to give the authors´ visions of developments for Swedish biorefineries and, finally, suggest possible further work in different biorefinery areas.

In accordance with the commission from the financer, the Swedish Energy Agency, the emphasis is on energy related aspects of biorefineries. Therefore production of chemicals is not covered in such detail as the energy related parts. This area, however, is also of high importance and is therefore included in Chapter 7, in which different possible future chemicals and materials are discussed but state-of-the-art, future opportunities, etc for technologies and processes for their production are not covered in detail.

# 3 Biorefinery activities in different countries

## 3.1 Introduction

In this chapter some major activities in other countries and in Sweden are presented briefly. More information can be found in the references given in the chapter.

## 3.2 US

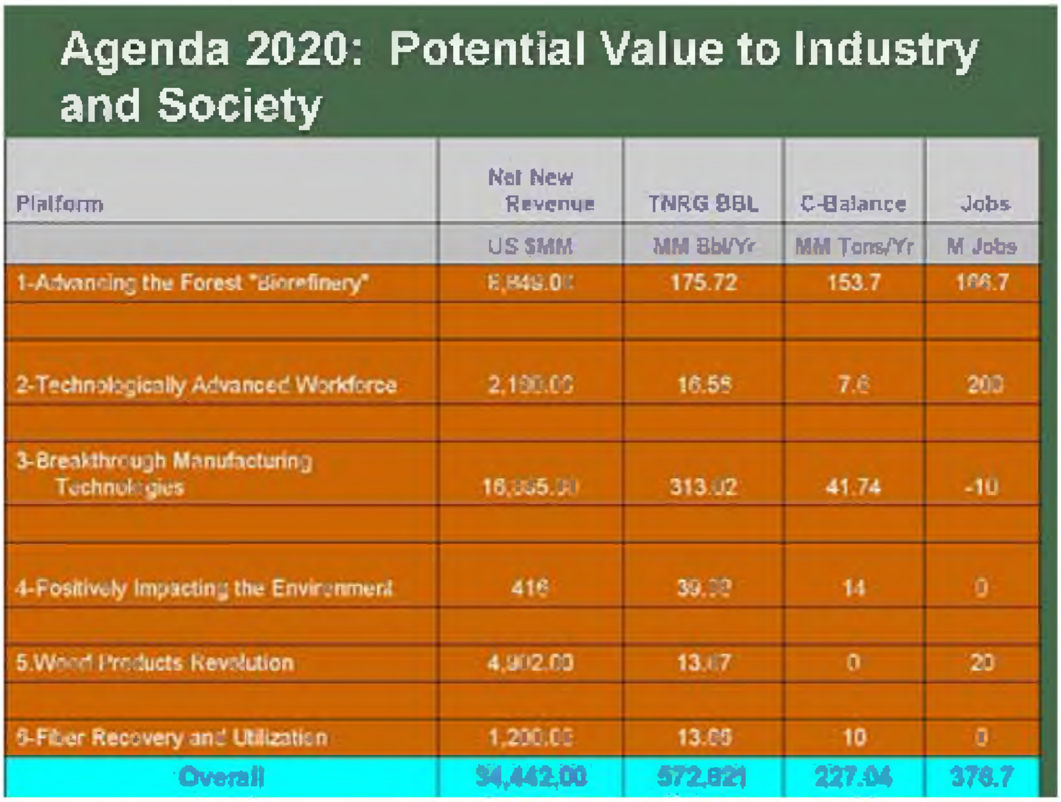
In US there exists a large programme which is to a high extent directed towards biorefinery principles. It is called Agenda 2020 Technology Alliance and main financing bodies are Department of Energy (DOE), USDA/Forest Service and National Science Foundation together with the pulp and paper industry in the US. It was initiated in 1994 and it has seven major R&D platforms:

- Advancing the Forest Biorefinery
- Nanotechnology for the Forest Product Industry
- Breakthrough Manufacturing Technologies
- Next Generation Fibre Recovery and Utilization
- Positively Impacting the Environment
- Advancing the Wood Products Revolution
- Technologically Advanced Workforce

These Forest Bio energy Platform includes growing and harvesting forests to increase biomass potentials in the US in special plantations, producing boards, panelling etc, extraction of hemi cellulose from a pulp mill for upgrading to ethanol, acetic acid, chemical intermediates etc, black liquor gasification for producing electricity or liquid fuels and energy integration between pulp mill, recovery power plant and paper/board/other mills. More information is given in http://www.agenda2020.org/Tech/port_eval.htm. As is shown there, the main activities in the pulp mill biorefinery are black liquor gasification and extraction of hemicelluloses prior to pulping.

The potential value for US industry and society of the Agenda 2020 programme is:

**Table 3.1 Agenda 2020 Value to Industry and Society**



Agenda 2020: Potential Value to Industry and Society

| Platform | Net New Revenue | TNRG BBL | C-Balance | Jobs |
|---|---|---|---|---|
| | US $MM | MM Bbl/Yr | MM Tons/Yr | M Jobs |
| 1-Advancing the Forest "Biorefinery" | 8,849.00 | 175.72 | 153.7 | 166.7 |
| | | | | |
| 2-Technologically Advanced Workforce | 2,190.00 | 16.55 | 7.6 | 200 |
| | | | | |
| 3-Breakthrough Manufacturing Technologies | 16,885.00 | 313.02 | 41.74 | -10 |
| | | | | |
| 4-Positively Impacting the Environment | 416 | 39.[illegible] | 14 | 0 |
| | | | | |
| 5.Wood Products Revolution | 4,902.00 | 13.07 | 0 | 20 |
| | | | | |
| 6-Fiber Recovery and Utilization | 1,200.00 | 13.66 | 10 | 0 |
| Overall | 34,442.00 | 572.821 | 227.04 | 376.7 |

## 3.3 Canada

There is no national or industrial programme ingoing in the biorefinery area. In addition, no larger R&D projects have been started so far. The biorefinery concept, however, has been identified as of vital importance for Canadian pulp and paper industry. This is evident from the shortlist of Canadian scientific papers dealing with this area.

At a recent Canadian biorefinery workshop called "Capturing Canada´s Natural Advantage, one important consensus reached was that before mills can implement the forest biorefinery, they need to increase their energy efficiency, eliminate fossil fuels and maximize carbon availability for the forest biorefinery. This statement is of course true for pulp and paper mills worldwide but is more applicable for Canada than for e.g. Sweden, due to the higher shore of fossil fuels used there.

According to available papers (see below) the ideas of a forest biorefinery concept in Canada are very much the same as in Sweden, i.e. to produce energy (electricity, lignin or upgraded biomass fuels, e.g. methanol, DME, hydrogen) and/or chemicals/materials (the same end products as discussed in Sweden).

*Some papers of interest from Canada are:*

Van Heinigen, A. " Converting a kraft pulp mill into an integrated forest products biorefinery" PAPTAC 92nd Annual Meeting 2006.

Wising, U., Stuart, P. "Identifying the Canadian forest biorefinery", PAPTAC 92nd Annual Meeting, 2006.

Mabee, W., Saddler, J. "The potential of bioconversion to produce fuels and chemicals", PAPTAC, 92nd Annual Meeting, 2006.

Pervaix, M., Sain,. "Biorefinery: Opportunities and barriers for petro-chemical industries", PAPTAC, 92nd Annual Meeting, 2006.

Mabee, W., Gregg, D, Saddler, J. "Assessing the emerging biorefinery sector in Canada" Applied biochemistry and biotechnology, 2005 Spring.

## 3.4 Finland

There are a number of on-going pulp mill biorefinery research project in Finland. The main research groups are VTT Processes, VTT Biotechnology and Åbo Akademi (Wood and Paper Chemistry). As regards chemicals the main focus is on specialty chemicals from bark and wood. The financing comes mainly from TEKES, Finska Akademin and EU. As regards energy VTT is the main actor. The main focus is on pyrolysis of wood and forest residues.

There seems to be no research on extraction of chemicals from black liquor. Here the Swedish efforts are unique.

### *Chemicals from the pulp mill biorefinery*

The main part of the Finnish projects here are a part of the WoodWizdom-programme, which is a Swedish-Finnish cooperation between TEKES och Vinnova. (*www.woodwisdom.fi*)

*The following projects are identified:*

*NanoCell* (2004 – 2006) studies cellulose nanoparticles extracted from pulp fibres for use in various composites. Partners: Helsinki University and STFI/KTH.

*NewCell* (2004 – 2006) studies production of cellulose derivatives for a wide range of potential applications. Partners: Helsingfors University, Tampere University and KTH.

*WoodBiocon* (2004 – 2006) studies extraction and modification of substances from bark for use in glues, tensides, antioxidants etc. One of the main leads is fatty acids from birch bark. Partners: Åbo Akademi, VTT Processes, VTT Biotechnology, STFI-Packforsk.

*Other projects:*

*Nanox* in which Åbo Akademi studies extraction of antioxidants from softwood knots and *Cerberus* in which Åbo Akademi studies extraction of bioactive substances from wood and bark. The main finacing comes from TEKES.

Åbo Akademi initiated 2005 a project on extraction of glucomannans from TMP white water for potential use as oxygen barrier in liquid board. The project is a copy of the Swedish NovHemi-project finaced by Vinnova.

## 3.5 Sweden

There are many projects in the area of the pulp mill biorefinery in Sweden. The projects in the Finnish Swedish *WoodWisdom*-program are shortly described under Finland above.

*Chemicals from the pulp mill biorefinery*

The EU project *WaCheUp* 2005-2008 studies by-products from production of pulp and cork. The partners are in Sweden (LTH, Chalmers STFI-Packforsk which is the coordinator), Finland (VTT, Åbo Akademi) and Portugal (U. Aveiro, U. Minho, Amorim) and the budget is 2.8 MEuro. The main intermediates are lignin, hemicelluloses and suberin (from bark/cork). Both biochemical and chemical methods are included. (*www.stfi-packforsk.se/wacheup*)

STFI-Packforsk has a Biorefinery Cluster project 2005-2008 in the industrial research program. The total budget is about 18 MSEK. The cluster focuses on extraction and up-grading of lignin, hemicelluloses and bark and includes evaluation of the technical and economical feasibility.

*The main activities:*

- Develop methods to isolate suitable lignin fractions from kraft-pulping black liquors. Residual lignin from production of dissolving pulp, from the “sulphur-free” NovaCell process and from production of ethanol from wood might also be included.
- Produce phenols, chelating agents, binders, dispersion agents and carbon-fibre intermediates from selected lignin fractions.
- Develop methods to recover non-degraded hemicelluloses from black liquor CTMP/TMP filtrates and “chip kidney” treatment of pulpwood chips and forest residues.
- Develop hemicellulose derivatives suitable as e.g. thickeners, food additives, emulsifiers, gelling agents, adhesives or adsorbents and use xylan for fibre modifications.
- Investigate how residual degraded sugar acids could be used as e.g. specific chelating agents.
- Valorise fatty acids from bark suberin into building blocks for “green” polymers, composites and specialty chemicals.

- Investigate possibilities to valorise extractives — recovered from bark and other pulp mill streams — into value-added fine chemicals, especially polymer additives.
- System analysis of the integration of the above technologies with the pulp mill, including the effects on waste-product streams, energy surplus and waste-water treatment etc.

Products from hemicelluloses are also studied within the Vinnova programs NovHemi and Hemigels. *NovHemi* (2003-2006) (coordinator STFI-Packforsk) has barrier films for packaging as end product. *Hemigels* (2004-2007) (coordinator KTH) is focused on hydrogels as product.

Sweden participates in the above mentioned *WoodBiocon* (2004 – 2006) with studies on extraction and modification of fatty acids from birch bark.

A commercial production of resin acids, fatty acids and lipofilic extractives started up in spring of 2006 in northern Sweden under the name *SunPine*. The process is based upon a new method for separation of fatty acids and resin acids by using $CO_2$. Compared to tall oil acidulation with $H_2SO_4$ the separation with respect to resin acids and fatty acids is improved.

### *Energy from the pulp mill biorefinery*

There are two major Swedish programs in the area. The BLG-program 2004-2006 and the FRAM2-program 2005-2008.

The Swedish BLG (Black liquor Gasification)Program 2004-2006 has two parts, a research program with eight sub-projects and the construction of a 20 ton/day gasifier in Piteå with an associated test run program. A summary of the sub-projects in the BLG Program 2004-2006 is shown in Table 3.2.

The FRAM2-program 2005- 2008 focuses on development of the Lignoboost-process developed in the KAM/FRAM-programs 1996-2005. FRAM2 has budget of about 53 MSEK the main part of which comes from STEM and the rest from the industry. (Industrial partners; ÅF-Process Stora Enso, Södra Cell, Weyer-haeuser, Eon and Fortum). The overall objective of FRAM2 is to develop a cost efficient process for production of lignin from kraft black liquor and to create a new biofuel from the lignin. FRAM2 comprises four sub-projects:

1 Wood species & pulp process
2 Development LignoBoost process
3 Lignin refining & evaluation
4 System analysis

In parallel to FRAM2 a lignin removal development plant is planned to start up in the fall of 2006. The planned production is 4000 t of lignin per year.

**Table 3.2 Projects in the BLG Program 2004-2006**

| Project name | Project leader | Description |
|---|---|---|
| 0. Synthesis of results and project coordination for the BLG Program | Prof. Rikard Gebart, ETC | Coordination of sub projects, participation in the IEA Annex 15 Technical Review Committee, synthesis and dissemination of project results, workshops for technology transfer. |
| 1. Modelling, simulation and optimisation of a black liquor gasification reactor | Rikard Gebart, ETC | Development and validation of a computer model for the hot parts of the gasifier. The model shall be validated by comparison to the DP1 reactor and then be used for studies of scale-up effects. |
| 2. Validation of models for the quench and the counter current condensor in a black liquor gasifier | Ass.prof. Lars Westerlund, Luleå University of Technology | Development and validation of a computer model for the quench cooler and counter current condenser. The model shall be validated by comparison to the DP1 reactor and then be used for studies of scale-up effects. |
| 3. Gas phase reactions, smelt formation and green liquor quality in pressurized black liquor gasification | Prof. Anders Nordin & prof. Björn Warnqvist, Umeå University | Detailed studies of reaction kinetics for the inorganic reactions between smelt, water spray and syngas. Determination of fundamental thermo-chemical data that are needed as input to computer models. |
| 4. The kinetics of the gasification of black liquor | Ass. prof. Tobias Richards, Chalmers | Detailed studies of reaction kinetics for the gasification reactions (drying, pyrolysis and char gasification). Theoretical and experimental studies of swelling of black liquor droplets during gasification. Determination of fundamental data and reduced models that can be implemented in computer models. |
| 5. Borate autocausticizing and chemical recovery of sulphur-free pulping processes | Dr Ingrid Nohlgren, ETC | Evaluate possibilities for borate autocausticization during black liquor gasification conditions. Borates follow the pulping liquor through the pulping cycle. The objective is to eliminate the need for increased causticization capacity, and thereby the demand for redesigning the existing lime kilns when introducing black liquor gasification in the pulping process. |
| 6. Pulps produced with liquors from new recovery systems | Dr Leelo Olm, STFI | The increased control of process chemistry, which is made possible by introduction of black liquor gasification, opens the possibility to implement modified pulping processes. This project is focused on investigation of the yield increase with so called ZAP pulping when combined with black liquor gasification. |
| 7. Kidneys in a kraft pulp mill with a pressurized black liquor gasification system | Tekn. Lic. Niklas Berglin, STFI | In the recovery boiler process there is a natural purging mechanism for non-process elements through the electrostatic precipitator dust. No natural purging mechanism exists in the black liquor gasifier. Alternative methods for control of accumulation of non-process elements will be studied in this project. |
| 8. Material investigation in green liquor | Dr Lars Troselius | In the recovery boiler, green liquor is produced with a temperature that is controlled by the boiling point of the green liquor. In pressurized black liquor gasification the green liquor temperature will be increased with more than 100ºC, which will severely increase the corrosion rate of the materials in contact with green liquor. The knowledge of the impact on the materials is very limited since the process is new. In this project, materials suitable for contact with hot green liquor will be identified by experimental studies of stress corrosion. |

## 3.6 Norway

### *Chemicals from the pulp mill biorefinery*

Two projects based on cellulose are on-going at PFI within the *Nanomat* program (2004-2006):

- Development of chelating agents, thickeners and cellulose derivatives from cellulose through nanotechnology.
- Cellulose nanoparticles as a basis for barrier materials in packaging.

### *Energy from the pulp mill biorefinery*

Production of liquid biofuels are studied within a project co-ordinated by PFI with partners in Norway and Sweden. The end-product is bio diesel from rosin- and fatty acids and pyrolysed lignin via steam explosion treatment of wood. (The carbohydrates are supposed to be used for ethanol production).

# 4 Export of energy from the pulp and paper industry to society

## 4.1 Background

Overall energy use in Sweden is on the order of 400 TWh annually. Industrial use is about 157 TWh and the pulp and paper industry uses close to 50 % of this (Swedish Energy Agency 2005). The pulp and paper industry is different from most other industries in that most of its energy use is met with fuels that are generated internally as by-products of the pulping process. In chemical pulp mills, 40-60 % of the wood entering the mill is used as a fuel. Black liquor, which is the most important internal fuel, is generated in the kraft pulping process, the dominant process for pulp production in Sweden and worldwide.

Black liquor contains most of the organic substances that must be dissolved in order to free the wood fibres. In addition, the major part of the chemicals used in the cook is recovered in the black liquor. It is essential for the economy of the pulping process that these chemicals can be regenerated and recycled to the process. These demands of the recovery process to be an efficient chemical reactor while also being able to convert the energy contained in the black liquor to useful heat and power. The long-standing practice has been to perform these tasks simultaneously in one piece of equipment, the recovery boiler, sometimes referred to as the Tomlinson boiler after its inventor.

As interpreted in this report, energy export from a pulp mill biorefinery focuses on production of fuels for use in other sectors rather than on the production of electric power or heat for district heating. These are, however, important ways of utilising excess energy today, and are therefore included for comparison.

### 4.1.1 Reference and type mills

In the KAM program the focus of the system analysis was on a theoretical *"reference mill"*, a hypothetical pulp mill which represents the existing best available, commercially proven, Nordic technology at the time of writing. It was assumed to be built as a greenfield mill. The reference mill has been updated and reference mills for other product grades have been added. In addition to the reference mills, *"type mills"* have been included representing typical mills of today in Nordic countries. The resource utilisation in the type mills is at about the same level as the average in Nordic countries.

The reference and type mills studied in the FRAM program are:

- Bleached market pulp mill operating in campaigns with hardwood and softwood
- Integrated fine paper mill, pulp mill as above
- Kraftliner mill

Detailed descriptions of each of these reference and type mills with process layout and key operating data are available as specific FRAM reports. Full mill models have been created in the process simulation program WinGEMS including mass (fibre, flow, Na, S, Cl, K, Ca, Mg etc.) and energy balances (steam and secondary heat).

These reference and type mills have been used for technical and economical assessment of the different new technologies developed in the FRAM program – chip leaching, lignin separation, and energy-efficient evaporation – as well as some other new technologies developed outside the FRAM program. The term *"model mill"* is used to describe a case where the reference mill or the type mill has been modified to include a new process.

## 4.2 Technical and economic potentials

There are currently 21 kraft mills in operation in Sweden, black liquor being fired in 33 recovery boilers. In 1997, the total kraft pulp production amounted to 6.3 million tons (FAO, 1999). In order to estimate the amount of electricity that could be generated from black liquor in the future, it is desirable to attempt a prediction of how much black liquor will be available and at which rate existing recovery boilers could be expected to be replaced, either with new boilers or with gasifiers.

Production of unbleached kraft pulp has been relatively constant throughout the last two decades, and production of unbleached pulp would be expected to remain at close to 2.4 million tons per year. As a consequence, the entire growth in production would be expected to fall on bleached pulp, leading to an estimated production rate of approximately 7 million tons per year of bleached kraft pulp in the year 2025.

Figure 4.1 contains an estimate of black liquor production rates based on the pulp production estimates. The specific black liquor production rate (expressed as tDS/ADt) can vary widely between different mills, but for the simplified analysis here was assumed to be a constant for each pulp category. The values used were 1.7 tDS/ADt and 1.2 tDS/ADt for bleached and unbleached pulp, respectively. The error introduced by these assumptions is estimated to a maximum of 15 %. The corresponding energy content was estimated by assuming a lower heating value of 12 MJ/kgDS for all the black liquor produced, which should fall within 5 % of the actual value. Based on these assumptions, the 1997 black liquor production was about 10 million tonnes of dry solids, corresponding to an energy content of 120 PJ (33 TWh), which is close to the value based on information from the mills (NUTEK, 1998).

The total global production of black liquor has been calculated based on statistics for kraft pulp production to be about 190 million tonnes (as dry solids) per year (Berglin 2005), corresponding to an energy value of more than 2 EJ (Figure 4.1).

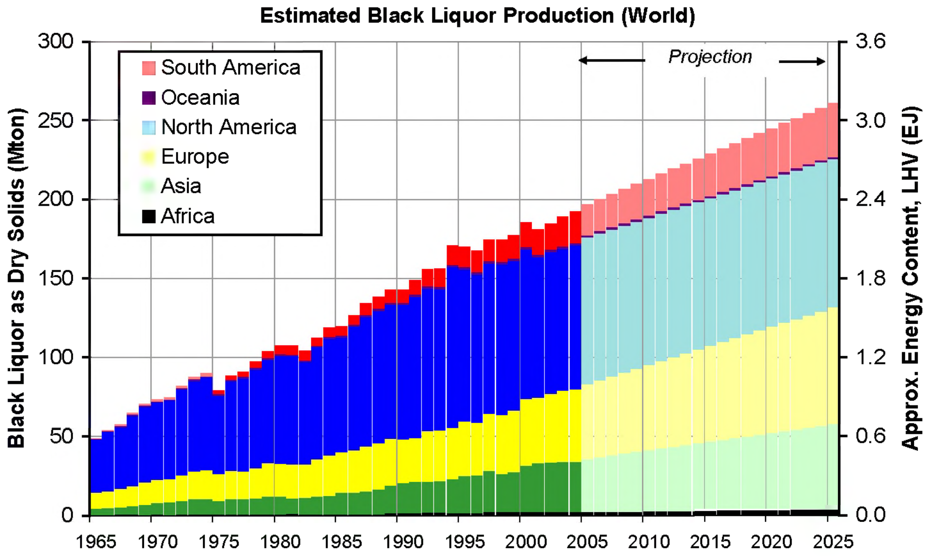


**Figure 4.1 Global kraft black liquor production calculated from data on kraft pulp production compiled by FAO, 2005. Extrapolations are based on linear trends for each market.**

### 4.2.1 Potential for energy saving in pulp mills

Within the FRAM programme, two models of average Scandinavian mills producing bleached market pulp have been analysed from an energy perspective. The aim was to explore the opportunities for heat integration in order to create a steam surplus. The steam surplus gives opportunities for increased power generation or lignin extraction. The technical and economic consequences of using the steam surplus in this way are explored in a continuation of this project.

Two different approaches for creating a steam surplus have been investigated: 1) conventional measures and 2) process-integrated evaporation (PIvap). The former approach includes improved heat integration and new equipment. The latter approach means that excess heat from the mill is used for evaporation to partly replace live steam.

The two model mills created within FRAM differ in the level of water usage, since it is expected that the amount of excess heat for PIvap will increase with decreasing water usage. They are called HWU (high water usage) and LWU (low water usage).

Conventional measures consist of the following ones: Solving pinch violations (deleting heat exchange with very high DT, heating at low temperatures or cooling at high temperatures), new equipment (e.g. shoe press in the dryer and increasing the dry solids content of the heavy liquor from 73 % to 80 % and compiling the surplus, blow out steam. The resulting total steam surplus and associated investment costs are shown in Table.4.1.

**Table 4.1 Resulting steam surplus and investment costs for conventional measures**

| Steam saving measure | Steam surplus [MW] | [GJ/ADt] | Inv. cost [M€] | Spec. inv. [€/W] |
|---|---|---|---|---|
| Pinch violations | 17.4 | 1.51 | 4.3 | 0.25 |
| New evap. plant | 21.8+6.0 | 2.40 | 6.4 | 0.23 |
| Shoe press | 6.2 | 0.53 | 5.2 | 0.85 |
| Blow off | 8.2 | 0.71 | 0 | 0 |
| **Total** | 59.6 | 5.15 | 15.9 | 0.3 |

This Table is approximately valid for both the HWU and LWU case.

When using PIvap for creating a large steam surplus the amount of water, as the amount of available excess heat above 95°C in the plant the PIvap solution) is influenced. To collect the excess heat for the evaporation a new hot and warm water system (HWWS) must be designed. The resulting steam savings and associated investment cost are shown in Table 4.2, where different number of evaporation effects is included (Convap 7+ is the conventional design):

**Table 4.2 Steam surplus and costs for the approach with PIvap**

| | Steam surplus [MW] | | | | | | |
|---|---|---|---|---|---|---|---|
| **Steam saving measure** | **PIvap6 HWU** | **PIvap6 LWU** | **PIvap7 HWU** | **PIvap7 LWU** | **PIvap8 HWU** | **PIvap8 LWU** | **Con-vap7+** |
| Evap. plant | 17.1 | 23.1 | 25.0 | 30.9 | 30.3 | 33.6 | 21.7 |
| Increased DS | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 | 6.0 |
| hw/ww prod | 6.4 | 6.4 | 6.4 | 6.4 | 6.4 | 6.4 | 6.4 |
| Wood yard | 1.6 | 1.6 | 1.6 | 1.6 | 1.6 | 1.6 | 1.6 |
| *Blow out* | *8.2* | *8.2* | *8.2* | *8.2* | *8.2* | *8.2* | *8.2* |
| **Total surplus** | **39** | **45** | **47** | **53** | **52** | **56** | **44** |

| | Costs [M€] | | | | | | |
|---|---|---|---|---|---|---|---|
| Evap. plant | 2.7 | 3.9 | 5.7 | 7.0 | 8.0 | 9.3 | 6.4 |
| New HWWS* | 2.5 | 2.2 | 2.5 | 2.2 | 2.5 | 2.2 | 0.6 |
| **Total** | **5.3** | **6.2** | **8.3** | **9.3** | **10.5** | **11.5** | **7.0** |

* New HWWS solves pinch violations (and gives excess heat for PIvap)

To summarize, by investing 11 M€ in conventional measures it is possible to create a steam surplus of 53 MW (about 26 % of the total consumption), independent of the level of water usage. For the PIvap approach, the level of water usage matters, since there is more excess heat for PIvap in the mill with lower water usage. As a result, the total steam surplus with the PIvap approach differs in the two mills: up to 52 and 56 MW, respectively. Hence, the steam savings for the PIvap approach are similar to those in the approach with conventional measures; and so are the investments needed (10-12 M€). Even though the two approaches give approximately the same savings with the same investment, the PIvap approach might be easier to implement in an existing mill.

### 4.2.2 Export of electricity or lignin

Here a comparison between increased power generation and lignin export is discussed. In the FRAM programme, lignin separation has been investigated by ultra filtration in the digester plant (Wallberg 2005) and acid precipitation in the evaporation plant (Öhman 2006). In the present study, lignin is assumed to be precipitated from a black liquor stream that is diverted from the evaporation plant, where the DS content is about 30 %; see Figure 4.2. By injecting $CO_2$, the pH is lowered, which causes an agglomeration of lignin molecules. At pH 9, about 70 % of the lignin molecules precipitate (Öhman 2006). The precipitated lignin is separated and then washed with acidified condensate from the evaporation plant ($H_2SO_4$ is used as acidifier). The final lignin cake has a DS content of 70 %. The filtrates from the lignin separation plant are recirculated to the evaporation plant.

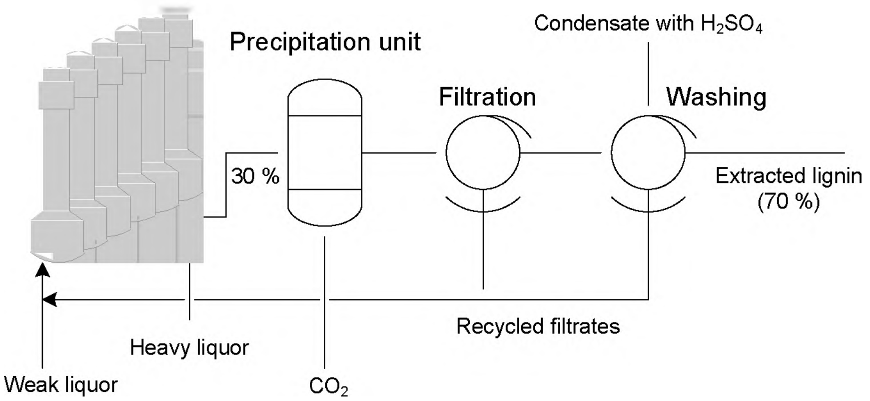


**Figure 4.2 A lignin separation plant integrated with the evaporation plant. In this work, the filtrates are assumed to be recycled to the evaporation plant.**

*Lignin extraction versus condensing power generation*

Energy efficient market pulp mills are self-sufficient in steam production from the liquor alone. In the reference mill the energy surplus from the black liquor is used for production of electric power in a condensing turbine. An alternative to this, especially with a pulp production limiting recovery boiler, can be to extract lignin from the black liquor corresponding to the energy surplus.

A lignin extraction process which can produce lignin suitable for combustion has been studied and developed. It has been successfully tested in a pilot plant employing the same type of automatic filter as proposed for the full scale process.

With the present power prices and Swedish electricity certificates, the value of power production from black liquor is however high and the lost revenue of power production highly affects the cost for the lignin production. However, this implies a recovery boiler with no production limiting problems. Another important factor is the cost for $CO_2$ used for precipitating lignin. With the assumed market prices, the cost to produce lignin *in the reference mill* would be about 200 SEK/MWh. Without electricity certificates, whose duration is not known, the cost drops to about 125 SEK/MWh. However, it is important to state that this process not is optimised and has potential to lower production costs considerably.

Two ways of using excess fuel, emanating from saved steam, have been investigated. These are 1) increased electricity production through a condensing turbine and 2) lignin extraction for sale. The amounts of additional electricity production or lignin extraction depend on the measures used for steam saving, but can be up to 120 GWh/a electricity production or 451 GWh/a lignin extraction, in the case of process-integrated evaporation. The economy for the two different ways depends to a high extent on the electricity and lignin values. For high electricity value (about 500 SEK/MWh) steam savings in combination with new turbines have a payback period of about 4 years and annual profits up to 4 million euro for an annuity factor of 0.1. With a low electricity value (about 270 SEK/MWh) and a lignin value of about 135 SEK/MWh, the payback period for lignin extraction is about 6 years. The annual profit for lignin extraction is relatively low, however, below approximately 1 million for an annuity factor of 0.1. This means that the future interest for lignin extraction in this case will be relatively low. On the other hand, at future high electricity values condensing power production through process integration should be an interesting option.

The economy for increased electricity production depends on the measures for steam saving taken. Process-integrated evaporation is as good or, normally, better than only advanced evaporation in terms of both payback period and annual profit, especially at high electricity values.

#### *Lignin extraction versus recovery boiler expansion*

In existing mills a promising alternative is to use lignin extraction as a means to reduce the load on the recovery boiler. A comparison with a larger expansion of the recovery boiler shows that lignin extraction can be a competitive way to increase the pulp production. An additional attractive possibility is to replace oil in the lime kiln with lignin fuel.

Two different ways for accomplishing a pulp production increase of 25 % have been studied:

- Debottlenecking for the increased capacity; this means that the recovery boiler, the evaporation plant and the turbine system are upgraded.
- Steam saving through process integration, so that the existing recovery boiler and turbine can be used, combined with lignin extraction for sale.

The investment cost for the first case is typically 35-40 M€ and for the second 20-25 M€. The operational profits in the two cases are the income for the additional electricity production (in the upgraded backpressure turbine) and for the lignin sales, respectively. The net annual profit for the two cases depends on the electricity and lignin values and the annuity factor. With a high value of electricity the two cases show similar profitability for a lignin value of 10 to 17 €/MWh, depending on $CO_2$ cost and annuity factor. With a low power value lignin extraction is economically preferable.

Even if the type mill with low water consumption has a 6 effect evaporation plant from start, sufficient steam savings for lignin can be accomplished. In this case, however, an 8 effect process-integrated evaporation plant is needed.

With a high power value for the mill, e.g. due to policy instruments, there is a good profitability for steam savings that can be used for electricity production through a condensing turbine. In this case lignin extraction cannot compete economically with electricity production. With a low power value, lignin extraction is a better alternative than electricity production. The annual profit, however, is low.

In the case with increased production, lignin extraction in combination with energy savings that enable lignin selling can be an interesting alternative to upgrading the recovery boiler. The reason is that the lignin extraction alternative has a considerably lower investment. With reasonable ratios between lignin and power values the annual profit is comparable for the two alternatives, although depending on price levels and annuity factors.

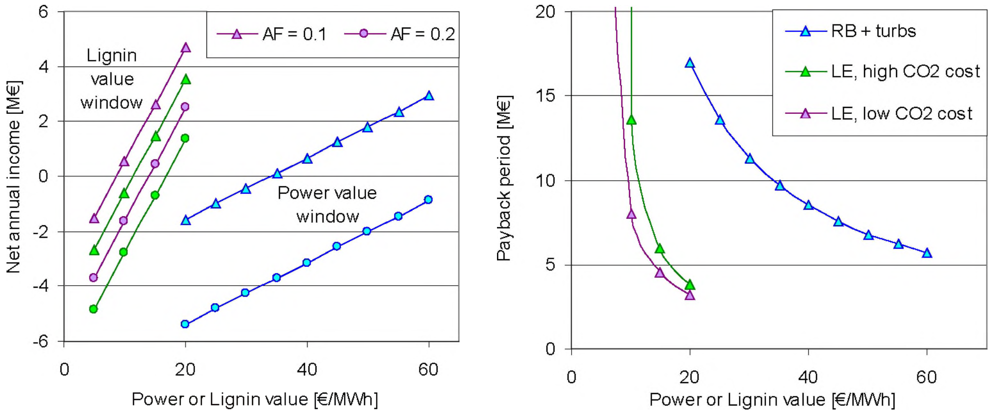


**Figure 4.3 Net annual income and payback period for lignin extraction (with a conventional 8 effect evap.) and rebuilding recovery boiler (and adding new turbines) for increased production in a type mill for bleached softwood market pulp. Net annual income is shown for annuity factor 0.1(triangles) and 0.2 (circles).**

In contacts with potential users (existing pulp mills) of the LignoBoost-process the following conclusions can be drawn:

- LignoBoost offers a cost efficient unloading of a capacity limited recovery boiler. One example is a kraft pulp mill with an annual capacity of 250.000 tonnes per year in which the capacity is increased 25 % to 320.000 tonnes per year. This corresponds to a production of 50.000 tonnes of lignin per year. Compared to a recovery boiler investment the investment is reduced 140 MSEK.
- If the lignin is sold for use outside of the pulp mill for 175 SEK per MWh and the energy deficit is covered by import of forest residues for 120 SEK per MWh all variable costs for producing the lignin will be fully covered by the sales of lignin.
- If the lignin is sold for 275 SEK per MWh the annual reduction in variable costs are 40 MSEK.

LignoBoost offers a cost effective replacement of fuel oil in the lime kiln. At USD 65/bbl the payback is in less than 3 years even if no extra pulp is produced.

### 4.2.3 Synthetic fuels

In this alternative the recovery boiler is replaced with a gasification plant. The evaporated black liquor is gasified in a pressurised reactor under reducing conditions. The generated gas is separated from the inorganic smelt and ash. Hydrogen sulphide is separated from the gas phase in a pressurised absorption stage. The resulting gas is then used to synthesize motor fuel (hence the acronym BLGMF, Black Liquor Gasification - Motor Fuels), e.g. methanol as shown in Figure 4.4. In principle, other fuels than methanol – for example, dimethyl ether (DME), synthetic diesel (Fischer-Tropsch) or hydrogen – can be produced in the same way. Methanol has the advantage that it can easily be blended into gasoline and used in conventional engines, which simplifies distribution.

The gasification process is shown in Figure 4.4 and comprises pressurised oxygen-blown black liquor gasification in an entrained flow reactor with a quench primary cooler, green liquor handling and gas cooling in a countercurrent condenser. These units are identical in the power generation (BLGCC) and the methanol (BLGMF) production schemes.

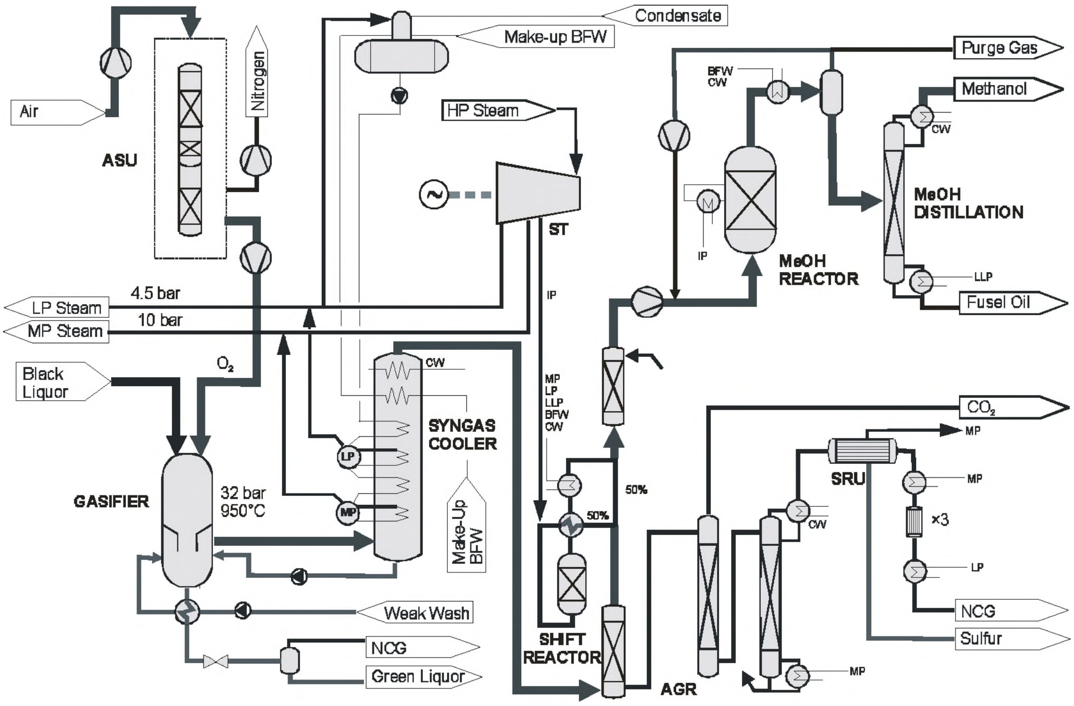


**Figure 4.4 Chemical and heat recovery by pressurised black liquor gasification, followed by conversion of the synthesis gas to methanol. The acid gas removal system (AGR) is different from that in the BLGCC concept. The gas turbine is replaced by a methanol, DME, Fischer-Tropsch or hydrogen plant.**

Because a large amount of the sulphur can be separated from the smelt the possibility to generate liquors with different sulphidities increases. This is of interest to be able to further optimise the kraft cook.

In order to determine when these schemes could be profitable, a production cost of electricity was calculated. All extra capital costs and operating costs (including changes in wood consumption) were thus allocated to the electricity produced, and the resulting electricity production cost was 0.28 SEK/kWh and 0.11 SEK/kWh, respectively.

### *Methanol/DME*

In a second alternative the synthesis gas produced by the black liquor gasification plant is used to synthesize methanol for use as a motor fuel. The methanol plant thus replaces the combined cycle. In principle, other fuels than methanol – for example, dimethyl ether (DME) or hydrogen – can be produced in the same way. Methanol has the advantage that it can easily be blended into gasoline and used in conventional engines, which simplifies distribution.

For comparison with other methods of producing carbon-neutral motor fuels, a production cost of methanol was calculated by allocating the incremental capital and operating costs for the BLGMF model mill to the methanol produced. The calculated cost, expressed as SEK per litre of gasoline equivalent, is similar to that of gasoline, indicating that methanol from black liquor could be competitive with gasoline even if the $CO_2$ tax were lower than today.

### *Fischer-Tropsch diesel*

Production of synthetic diesel via the Fischer-Tropsch (FT) process, using syngas from black liquor gasification is described by Berglin (2005) and Ekbom et al (2005).

The results show that up to about 500 tonnes of FT products can be produced per day in the reference 2000 ADt/d mill. Approximately two thirds of the FT products can be used as a high quality diesel fuel.

A comparison with earlier studies of methanol and DME production in a market pulp mill show that the amount of biomass that needs to be purchased to maintain the steam balance in the FT case is smaller. The main reason for this is that the FT reactions are more exothermic than for example the methanol synthesis. Only a relatively small biomass boiler (about 2 GJ/ADt or 50 MW) is required, alternatively the recirculation around the FT reactor can be decreased and the boiler fired with residual gas from the synthesis only.

The change from electricity generation to fuels production results in a need to purchase almost all electricity used in the mill. To indicate a correct system efficiency, the whole decrease (including the surplus) in electricity generation is included. For the base case the biomass-to-diesel efficiency becomes 43 % compared to approximately 65 % for methanol and DME production.

If the naphtha fraction is included, the total biomass-to-FT-products efficiency is also about 65 %, although it should be noted that a more advanced recycling scheme has been assumed in the calculations for the FT synthesis than for methanol and DME synthesis.

FT synthesis also opens up a possibility to produce specialty chemicals, e.g. lube oils, from waxes that may be extracted from the process instead of recycled. Wax production in the reference mill could be on the order of 100 tonnes per day.

#### *Hydrogen*

Hydrogen production from gasified black liquor was studied by Andersson et al (2004, 2005). Their calculations indicate that the market pulp reference mill requires import of 140 000 tonnes of biomass for steam production, if all the black liquor is used for hydrogen production. That is the same size as large production units for densified biomass. 0.6 TWh of electric power must also be imported. If all market pulp mills in Sweden were to produce hydrogen from their black liquor the biomass demand would be 3.3 TWh or 3.4 % of the total biofuel use today in Sweden, and the power demand would be 3.4 TWh or 2.6 % of the demand in 2002. But the $CO_2$ emissions will still be substantially reduced if hydrogen is produced and used in the transportation sector to replace gasoline.

If the produced hydrogen replaces gasoline in the transportation sector it will reduce the $CO_2$ emissions by 1100 ktonnes$CO_2$/year. If all market pulp mills in Sweden were to produce hydrogen from their black liquor the reduction of $CO_2$ would be equal to 10 % of the $CO_2$ emissions in Sweden. With $CO_2$ sequestration the reduction would correspond to 19 % of Sweden's $CO_2$ emissions. This reduction is calculated based on pulp production in an energy efficient mill such as the KAM-mill, not in an average mill today. If hydrogen production from gasified black liquor was implemented in existing mills the reduction will be even larger.

### 4.2.4 Summary of potentials for the chemical pulp mill

The potential for selling excess energy, as electricity or as fuels, from a mill producing bleached softwood market pulp is summarised for the reference, type and model mills in Figure 4.5 and Figure 4.6.

In the near term scenario the role of the electricity certificates is important. The value of these is at present about 200 SEK/MWh, which adds about 70 % to the potential income of sold electricity from the mill. Cases that allow an increased amount of electricity to be sold would therefore be strongly favoured in the near term. The reference mill itself with a condensing steam turbine is a strong case since it is a net seller of electricity. This is not surprising as the system with electricity certificates has been established to encourage new investments in electricity generation from renewable energy sources. In the short term there is a considerable deficit of electricity certificates and the price will therefore be high until the new investments in electricity generation begin to have an effect on the amount of electricity generated. In principle, this will also increase the value of biofuels that can be sold by the mill, an effect that is noticeable, but in the near term has not fully been priced into the market. The first round of investment decisions following the introduction of the electricity certificates in 2003 has to a great deal focused on the utilisation of "hidden" opportunities where the electricity generation can be increased without any large increase in fuel consumption (e.g. by expanding steam turbines to eliminate blow-off steam).

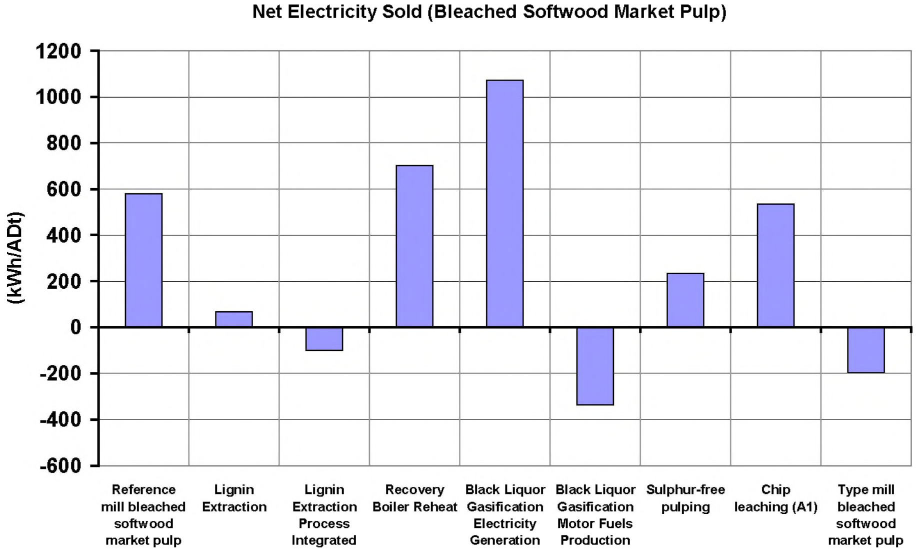


**Figure 4.5 Potential for electricity sales from mills producing bleached softwood market pulp. (Reference mill = hypothetical pulp mill which represents the existing best available, commercially proven, Nordic technology at the time of writing. Type mill = representing typical mill of today in Nordic countries)**

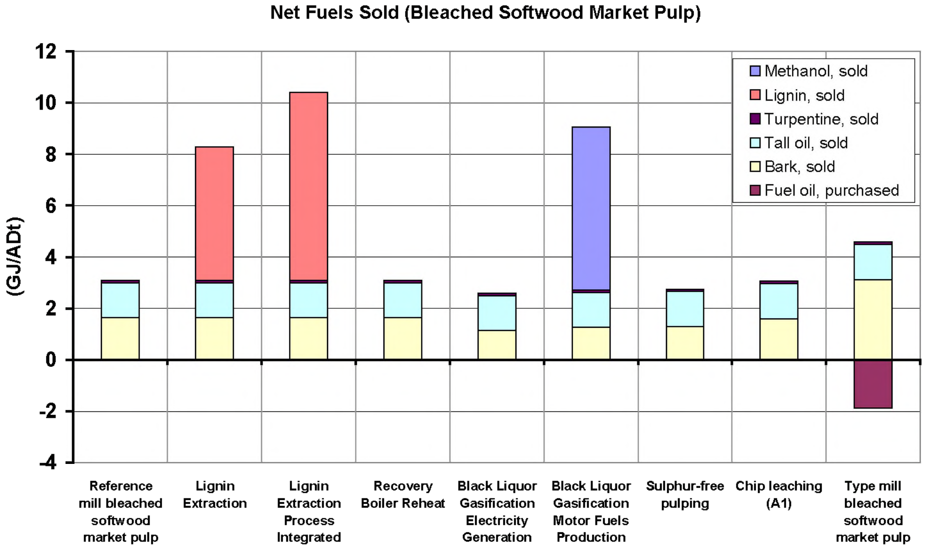


**Figure 4.6 Potential for fuel sales from mills producing bleached softwood market pulp.(Purchased fuel oil for the lime kiln is also included for the type mill.) (Reference mill = hypothetical pulp mill which represents the existing best available, commercially proven, Nordic technology at the time of writing. Type mill = representing typical mill of today in Nordic countries)**

A summary of the most important differences between the model mills and the reference mill is given in Table 4.3.

**Table 4.3 Key numbers for the model mills based on the reference mill for bleached softwood market pulp. Energy costs and revenues evaluated under a near-term scenario.**

| Model Mill | Pulp quality | Wood (sub) | Sold power | Sold fuel[2] (net) | Oper. cost, excl. energy | Oper. cost, incl. energy | Invest-ment | Devel. status[1] | Efflu-ent COD | Direct minus avoided $CO_2$ emiss-ions |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  | $m^3$/ADt | kWh/ ADt | GJ/ADt |  |  |  |  | kg/ADt | kg/ADt |
| FRAM Reference Mill, Bleached Softwood Market Pulp | 0 | 4.93 | 579 | 3.10 | 100 % | 100 % | 100 % | 5 | 7 | -147 |
| Lignin fuel | +/-0 | +/-0 | -512 | +5.2 | +2.6 % | -6.9 % | 0 % | 3 | +/-0 | -168 |
| Lignin fuel + heat integration | +/-0 | +/-0 | -679 | +7.3 | +3.8 % | -10.1 % | -2 % | 3 | +/-0 | -278 |
| Recovery boiler with reheat | +/-0 | +/-0 | +124 | +/-0 | +0.1 % | -1.9 % | -1 % | 4 | +/-0 | -45 |
| Black liquor gasification with power generation | +/-0 | +/-0 | +494 | -0.5 | +1.3 % | -5.6 % | +9 % | 3 | +/-0 | -130 |
| Black liquor gasification with motor fuels production | +/-0 | +/-0 | -916 | +6.0 | +1.1 % | -33 % | +9 % | 3 | +/-0 | -140 |
| Sulphur-free pulping | lower | -0.28 | -346 | -0.3 | +2.7 % | +9.4 % | +2 % | 2 | +1 | +186 |
| Chip leaching | +/-0 | +/-0 | -45 | +/-0 | +0.7 % | +1.6 % | -1 % | 3 | -3 | +21 |
| FRAM Type Mill, Bleached Softwood Market Pulp | +/-0 | +/-0 | -777 | -0.4 | -1.8 % | +15 % | N/A | 5 | +4 | +314 |

[1] Scale 1-5, from limited tests in the laboratory (1) to industrial application of unit processes (5).

[2] Includes 1.48 GJ tall oil and turpentine per ADt.

### 4.2.5 Other products form the pulp mill

The two major fuel products from the pulp mill today are bark and tall oil.

Some mills that have a surplus of bark for steam production use bark to replace part of the fuel in the lime kiln, either by gasifying the bark and firing the fuel gas in the kiln, or by direct use of pulverised bark.

One mill has a pelletizing plant for production of bark pellets.

The tall oil is normally sold as raw material for chemicals production, but the distillation residue, tall oil pitch, can be used as a fuel in lime kilns.

**Table 4.4 Amount of bark available for export from a market pulp mill (FRAM 2005)**

| | Reference mill | | Type mill | |
|---|---|---|---|---|
| | Softwood | Hardwood | Softwood | Hardwood |
| **Bark balance, DS t/ADt pulp** | | | | |
| Bark from woodyard | 0.19 | 0.24 | 0.19 | 0.24 |
| Bark to lime kiln | 0.09 | 0.08 | 0.00 | 0.00 |
| *Remaining bark* | 0.10 | 0.16 | 0.19 | 0.24 |
| Sold bark | -0.10 | -0.16 | -0.19 | -0.21 |
| *Bark to bark boiler* | 0.00 | 0.00 | 0.00 | 0.03 |

## 4.3 Visions for Sweden

As has been stated in Section 2.2 one important type of biorefinery is where incoming biomass to a mill is utilized better than in traditional mills for increased production of biofuels and/or electricity. In Section 2.3 and in this chapter possible future potentials for energy saving and thereby opportunities for increased biofuel/electricity production have been discussed. It can be concluded that these potentials are high, in spite of the fact that the energy efficiency standard in Swedish mills is good. By using process integration and best available technologies, large amounts of steam could be saved in future chemical market pulp and pulp and paper mills, at least 25-40 % depending on conditions and original energy status. This means a considerable improvement of the economy of mills (given reasonable future energy prices and policy instruments) and also a significant influence on the energy system in Sweden and Northern Europe.

The further work in this area should be to explore the opportunities for energy saving in even more detail and for identify practical obstacles, operability, investment costs, dynamic behaviour, etc of future systems with new technologies and more process integrated.

The potentials for energy export from a mill can be increased by import of additional biomass for keeping the energy balance when using e.g. black liquor gasification for producing high quality products (electricity, upgraded biofuels). This means that substantially more electricity or biofuels can be produced and the imported biomass is thereby “transformed” into more valuable products for society.

The amount of imported biomass needed for a certain “valuable product” production level depends to a high extent of the degree of energy efficiency in the mill. In the 90´s studies on process integration in connection with black liquor gasification were performed (Niklas Berglin, “Pulp Mill Energy Systems with Black liquor Gasification – a Process Integration Study”, Licentiate Thesis) but recent findings of energy efficiency potentials (discussed above) have so far not been connected with black liquor gasification for electricity production or methanol, etc production. Such studies should therefore be performed. They will most certainly show that considerably lower amounts of imported biomass, than discussed today and shown in this chapter, are needed. This will, in turn, identify opportunities for achieving a more competitive economy for black liquor gasification. Other important R&D areas for further development of the black liquor gasification technology is discussed in the Swedish BLG (Black Liquor Gasification) programme and in the international cooperation project IEA, IETS (Industrial Related Technologies and Systems Implementing Agreement, Annex VI). This is therefore not discussed here.

As has been discussed in this chapter the biofuel from a mill can be transferred into different types of more upgraded fuels. The lignin in the kraft black liquor can be precipitated using e.g. the Liquor Boost process and be used for e.g. replacing oil in the lime kiln and/or for reducing the recovery boiler load when increasing the pulp production. With the aid of gasification syngas can be produced from the black liquor, which can be used for methanol, DME, synthetic diesel or hydrogen (in future) production (or, of course, for electricity production). This gasification can also be performed together with other biomass or even fossil fuels.

There is a need for further R&D work on system aspects of upgraded fuel production. In addition to process integration aspects for black liquor gasification, discussed above, the type or types of upgraded fuel (or the competition electricity that should be produced at different future scenarios) and how this could compete with other techniques for transport biofuel production. Some of these aspects have recently been included in the research activities within the Swedish Programme Energy System.

Sweden has an international lead in several of the areas discussed above, e.g.:

- Process integration in pulp mills (Chalmers)
- Pressurized gasification of black liquor and conversion into electricity or motor fuels (ChemRec, Nykomb, ETC)
- Separation of high-quality lignin from black liquor through the LignoBoost process and further upgrading of the lignin (STFI-Packforsk)
- Forest residues leaching kidney (STFI-Packforsk, Chalmers)

The opportunities discussed above should be of interest also in other pulp and paper producing countries. The knowledge being developed in Sweden could therefore lead to new markets for technology and knowledge export.

# 5 Energy combines

## 5.1 Background

There is today an increasing interest for energy combines and ecocyclic industrial parks cooperation in terms of e.g. energy between two or more industries and/or society. One example of such cooperation is heat cascading, i.e. where heat for one plant is satisfied by excess heat from another one.

Different opportunities for heat cascading and other energy cooperations in which the pulp and paper industry is one part, are discussed in this chapter. The main aspects included are:

- Drying of biomass (e.g. forest residues, bark)
- Pelletizing in connection with drying and forest residues leaching
- Energy combine with ethanol production
- Energy combines with other industries

Visions in these areas for Sweden and suggestions for further work are given in the end of this chapter.

## 5.2 Drying of biomass + pelletizing

Upgrading of biomass is done in order to get a homogenous fuel with high heat content per weight. This means advantages both in transportation and in combustion. Dried biomass can be upgraded to solid fuels (pellets, briquettes, powder) or liquid fuels (pyrolysis oil, ethanol etc) or gaseous fuels via e.g. gasification (syngas to be converted to methanol, DME, hydrogen, etc).

Today only approximately 5 % of biomass fuels used in Sweden is upgraded.

### 5.2.1 Drying of biomass in pulp and paper industry - Technologies

The majority of biomass used for production of pellets in Sweden today is spill from sawdust, shavings and other by-products from the sawmill industry. (Olsson, 2001). There are 18 companies in Sweden producing pellets in 22 plants (Olsson, 2001). Different kinds of combines are done in four plants, two connected to heat and power plants (Skellefteå Kraft AB and Bioenergi i Luleå AB), one connected to a sawmill (Forssjöbruk AB) and only one connected to a pulp mill (Södra Cell Mönsterås AB).

In the following opportunities for energy combines between pellets and pulp production, using internal bark and/or imported biomass for pellets production, is discussed. First different kinds of drying plants, possible for use in pellets production, are described briefly. The presentation is based on Wimmerstedt and Linde (1998) and Andersson et al (2003).

### Technologies for Drying of Biomass

There are three main types of dryers, namely:

*Rotary dryer:* The most common dryer in Sweden today for drying biomass is a rotary dryer where the biomass is dried with flue gases in direct contact with the wet biomass. There are also indirect rotary driers. The rotary dryer is a rotation drum where the wet material and the hot flue gases pass the dryer in the same direction. Rotary dryers are popular due to high operability factor and flexibility. Rotary dryers can be used for material with variation of moisture content and size.

*Pneumatic conveying dryers:* In a pneumatic conveying dryer the velocity of gas, flue gases or steam, will transport the material through the dryer and separate dry material in a cyclone. Some pneumatic dryers have a mill to reduce the particle size of the biomass. The pneumatic dryer can be direct or indirect depending on if the gas has contact with the material or not.

*Fluid bed dryer:* In a fluid bed the heating media passes through the material with a flow that lifts the bed of wet biomass. The heating media is circulated and reheated externally with steam in a heat exchanger.

Dryers can also be categorized by heating medium, namely steam dryers, flue gas dryers and vacuum dryers. They work in different temperature ranges, which is of interest when considering integration with a mill.

For a steam dryer all three types mentioned above can be used. All steam dryers are indirect. Superheated steam, typically 10-26 bar, is used as heating medium. The contaminated steam has typically a pressure of 3-5 bar. The net heat to evaporate 1 kg of water is approximately 500 kJ (550MJ/tonne pellets), if the heat of condensation in the contaminated steam is used in an energy combine. The electricity consumption is approximately 40 hWh/ton pellets at high pressures and increased at low pressures.

### Flue gas dryers

In these types hot flues gases are used as heating medium. The heating can be direct or indirect, with the direct type being the by far most common one. The flue gas temperature must be below approximately 400°C due to the fire risk and the lowest possible is approximately 160°C. The exit temperature of the flue gases should be above 110°C to avoid condensation. The most common type is the drum dryer but at low flue gas temperatures the pneumatic dryer is also used.

In a direct type, the heat needed is at least 2 800 kJ/kg evaporated water (3 000 MJ/ton pellets). The electricity consumption is approximately 30 kWh/ton pellets for drum dryers and 80 kWh/ton pellets for pneumatic dryers.

In an indirect flue gas dryer the extra investment compared with the direct one can only be justified if the energy in the contaminated exit steam can be utilized. In that case the net heat needed is 500 kJ/kg evaporated water (550 MJ/ton pellets). The electricity consumption is the same as for the direct type.

*Vacuum dryer*

In a vacuum dryer the evaporation is done below atmospheric pressure so that e.g. industrial excess heat (for example very low pressure steam or warm water) can be used. The steam evaporated is condensed within the plant and pumped out as water.

There is so far no commercial vacuum dryer on the market. Torkapparater AB have shown that it should be possible to dry biomass of 0.2 bar with water of 60_70°C as heating medium. The heat needed is 2 500 kJ/kg evaporated water (2 780 MJ/ton pellets). The electricity consumption should be high (no data available) and cooling is needed at 30-60 °C.

*Heat Pumping*

Via a heat pump the heat in the exit flue gases can be upgraded and reused for drying. This technology is mainly interesting for stand-alone units and therefore not discussed further in this report.

*Pelletizing of Biomass*

After drying the dry biomass is grounded before pelletizing, which is done in a pellet press. The pelletizing is conducted at high pressure and temperature is 60 °C-90 °C and is normally cooled by outdoor air. The electricity consumption is 100 kWh/ton pellets, which is 2 % of the heating value of the pellets.

### 5.2.2 Process integration of drying and pelletizing

The energy situation in the model mill in KAM2 was used in a study by Andersson et al (2003) on integration between a pulp mill and a drying/pelletizing unit. The heat need/excess in that mill is shown in Figure 5.1 in a so called Grand Composite Curve, which shows the temperature levels of the heat need (above 140 °C) and heat excess (below 140 °C), respectively. This means that the curve below 140°C shows the net amount of heat available (when all necessary heating has been satisfied) at different temperature levels.

From the figure the conclusion can be drawn that there is an excess of heat above 95°C of approximately 0.9 GJ/ADt and a need of heat at 140-150 °C of 7 GJ/ADt. Three in principle different ways of integrating a drying/pelletizing plant to a pulp mill are:

- Integration below the “pinch”, i.e. to use the excess heat above 95 °C for drying in a low temperature dryer
- Integration above the “pinch” i.e. to use a steam dryer driven by high pressure steam and producing low pressure steam above 140 °C, to be used for heating the mill
- To use the heat in the flue gases (not included in Figure 5.1) for drying the biomass.

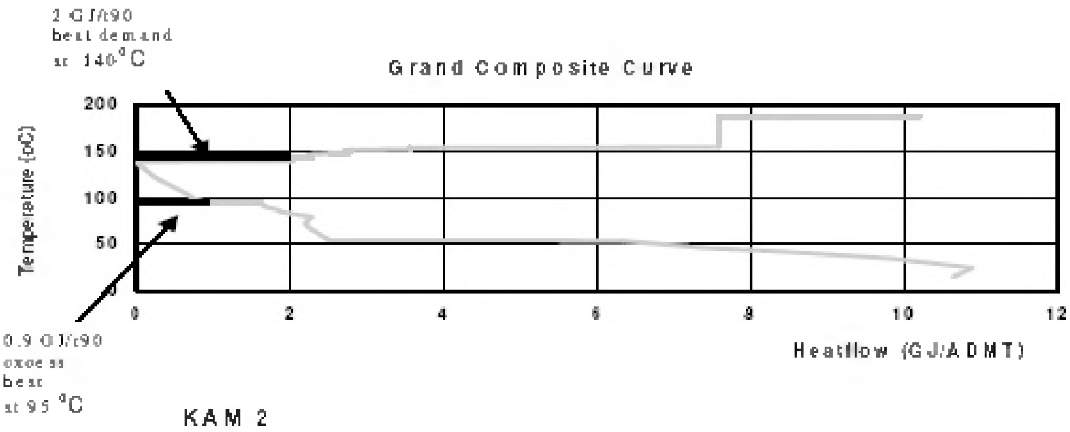


**Figure 5.1 Grand Composite Curve for KAM 2**

Calculations and evaluations of the three alternatives were done in Andersson et al (2003)
The results were:

*Integration below the Pinch*

With a vacuum dryer, using hot water heated by the mill from 50-90°C and then recirculated, 8 kg/s water can be evaporated in the KAM2 mill, corresponding to 209 000 ton pellets per year.

*Integration above the Pinch*

Three cases have been evaluated:

- Case 1: The steam dryer is driven by 26 bar steam and the size of the dryer is chosen so that all 4.5 bar steam to the mill is produced by the dryer
- Case 2: All bark, produced internally in the mill, is dried, using 26 bar steam
- Case 3: The limiting size for a pellet plant is in many cases the amount of biomass available at reasonable distance. Typical sizes of today's pellet plants in Sweden are 40 000 ton/year or less. Therefore 110 700 (including the bark) ton/year was chosen as a reasonable size. The biomass was dried in a steam drier driven by 26 bar steam. The results from the three cases are summarized in Table 5.1.

**Table 5.1 Results for steam dryers**

| | **Case 1** | **Case 2** | **Case 3** |
|---|---|---|---|
| Steam level bar | 26 | 22 | 26 |
| Annual pellet production, (tonne/year) | 1 675 000 | 70 700 | 110 700 |
| Decrease in electricity production (MW) | 48 | 2.0 | 3.2 |

*Flue gas dryer*

The fluegases in the KAM2 mill have a temperature of 160 °C (12 % moisture) and the flow is 115 kg dry gases per second. A pneumatic conveying dryer is assumed for the calculations. With an exit temperature of the flue gases of 110 °C 2.33 kg dry solids/s, corresponding to 70 500 ton pellets per year can be produced.

*Economy*

For the economic attractiveness of the different alternatives, the following aspects must be taken into consideration:

- In the alternatives with integration above the pinch, the electricity production capacity is reduced as the amount of steam through parts of the turbine is reduced
- Costs for the different types of dryer are highly dependent of e.g. temperature and pressure levels of the heating media

The economy is therefore highly dependent on future energy prices and policy instruments (e.g. cost of emitting $CO_2$). These aspects should be studied more in the future.

### 5.2.3 Uppgrading of forest residues

Acid leaching could make forest residuals more attractive as fuel in limekilns and power plants. The content in bark, branches and tops of elements that cause environmental or incineration problems can be decreased down to the level of "pure" wood fuels based on stemwood. Less ash content and reduced smell make the fuels more interesting for residential heating as well.

Biofuels like forest residues and bark would get more attractive incineration properties through decreased contents of metal ions and other elements that disturb the process or cause discharges that are harmful to health and environment. Bark in particular has considerably higher contents than stem wood of potassium and other elements that cause deposits, sintering and corrosion. In limekilns can potassium, sodium, silicon and aluminium cause additional problems with decreased lime reactivity, increased dead load and ring formation. Furthermore do biofuels generally form more nitrogen oxides in the smoke gases, due to high nitrogen contents.

A first trial has been carried out in order to get an idea of how acid leaching – according to STFI-Packforsk´s method for pulpwood chips – works for three types of wood fuels: chipped forest residues, bark and knot rejects from kraft cooking. The chips were steamed in a compression screw and leached with 6 kg $H_2SO_4$/t wood in 30 minutes at 80-100 °C to pH ca 2.6. The procedure was repeated in a washing stage with water.

The method seems to have the potential to decrease the content of problem substances in forest residues and bark to the level of the cleanest forest fuel quality today. The best reduction of the ash content, ca 50 %, was obtained with forest residues. In bark, with its more than three times as high ash content (2.8 % of wood), was 35 % of the ash removed. Ca 60 % of the potassium was leached out in the acidic stage. After the washing stage, about 85 % had been removed in total. The treatment was also efficient on sodium which occurs in high levels in kraft pulping reject. Other metal ions were removed to varying degrees up to ca 50 % without washing stage. Some phosphorus and nitrogen were also leached out – 30 and 25 % respectively from bark; 45 and 10 % respectively from forest residues. The reduction of chlorine was estimated to 50 % in forest residues and 80 % in bark. The sulphuric acid used for leaching doubled the sulphur content of the fuels. This added sulphur was washed out in the subsequent washing stage.

The leachate could be discharged after passing the biological treatment of the pulp mill or taken to the bark boiler after evaporation. Of three applications that have been evaluated briefly, the alternative where leached bark replaces oil in the limekiln and the leachate is discharged after treatment has the best economic potential.

The leaching process needs development regarding process conditions and apparatus. The handling of leachates needs to be investigated further from economic and environmental points of views.

## 5.3 Co-location of ethanol plant and pulp mill

In the Swedish research programme “Ecocyclic Pulp Mill – KAM”, co-location of an ethanol plant and a pulp mill was studied [KAM 2003]. The pulp mill was a “state-of-the-art” kraft mill and had a considerable fuel surplus (as bark and lignin). One main research area was how to use this surplus in the most efficient and economical way. In the reference case (the Reference Mill), the fuel surplus was used to raise steam for electricity production. One of the studied alternatives was to use it for production of ethanol from cellulose.

The KAM Ethanol Plant
Ethanol production via fermentation needs carbohydrate as raw material. This means that the ethanol plant in this Model Mill receives energy, but not raw material, from the pulp mill processes. The ethanol plant is dimensioned so that it uses the entire steam surplus in the Reference Mill.

The raw material consists of wood logging residues and thinnings; softwood mixed with small quantities of hardwood. The cellulose and hemicellulose can be converted to fermentable sugars by hydrolysis. The dilute acid hydrolysis process chosen (NUTEK 1995) is shown in Figure 5.2. The process conditions and yields are slightly modified.

The hydrolysis takes place in two stages. The first stage operates under milder conditions (175°C, 0.7 % sulphuric acid), which maximizes the yield from the hemicellulose. In the second stage, the cellulose is hydrolysed under harsher conditions (225°C, 1.6 % sulphuric acid). A wash water flow rate of about 3 times the weight of dissolved solids in the hydrolysis steps is used. The washing loss is 2 %.

The hydrolysis yield for cellulose is assumed to be 49 %. With an overall ethanol yield of 90 % of the six-carbon sugars (hexose), the ethanol yield is 0.14 t/t DS in wood. No pentose fermentation is assumed. The yield is 10 % lower than in the study from 1995 (NUTEK 1995) due to a more technically and economically realistic raw material. (The NUTEK study used sawmill residue as raw material.)

### 5.3.1 Comparison of processes and equipment with the reference mill

The steam and electricity needed in the ethanol plant are supplied by the pulp mill. The wood residue (lignin) and distillation residue from the ethanol plant are sold. The lignin is assumed to be mechanical dewatered to about 70 % and sold without any further drying. The distillation residue is processed in a plant for production of pelletized fuel together with the bark surplus from the pulp mill. To match the fuel (steam) surplus in the Reference Mill, without a condensing turbine, the ethanol plant needs to be supplied with a raw material feed of 706 000 t DS/year. The corresponding ethanol production is 97 000 t/y. This is such a big plant that this amount of wood residues might be difficult to obtain locally. For comparison; Agroetanol in Norrköping produces about 40 000 t/y from crops and EtanolKemi in Örnsköldsvik produces about 15 000 t/y from spent sulphite liquor.

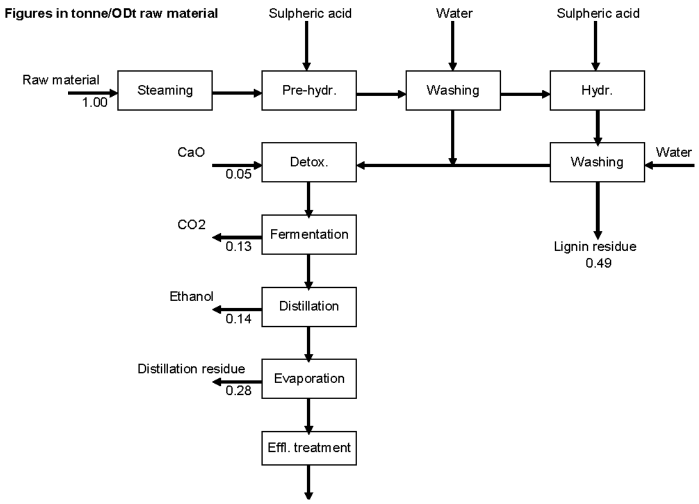


**Figure 5.2 The dilute-acid process for ethanol production according to (NUTEK 1995). The included detoxification process is from (Fransson 2000). The figures correspond to the ethanol yield used in this study.**

About 75 % (DS) of the raw material becomes solid by-products (distillation and wood residue) while less than 15 % is converted to ethanol. A rough energy balance for the ethanol plant is shown in Figure 5.3.

The wood residue consists mainly of lignin and could be expected to have a higher market value than forest residues. Here it is assumed to be 33 SEK/GJ (120 SEK/MWh) or about 670 SEK/t DS. The distillation residue is a poorer fuel and the selling price is assumed to equal that of bark, i.e. 22 SEK/GJ (80 SEK/MWh) or about 310 SEK/t DS.

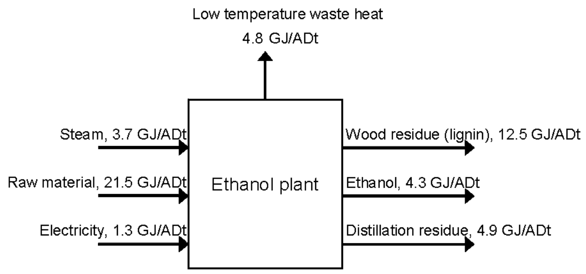


**Figure 5.3 A rough energy balance for the co-located ethanol plant. The energy content in the biomass streams are based on the lower heating value for the dry substance.**

Besides sharing utilities for steam and electricity, the ethanol plant and pulp mill share raw water and effluent treatment facilities. As opposed to the mill in (NUTEK 1995), facilities to produce 99.8 % ethanol (dehydration) and pelletized fuels are included in the ethanol plant.

It is estimated that the investment cost synergies for amounts to about 50 MSEK. This figure does not include the avoided cost for a steam boiler. A stand-alone ethanol plant would require a boiler for steam production and the corresponding investment cost could be expected to lie in the range 150–200 MSEK for a plant of this size.

The large raw material demand for the ethanol production leads to long average transportation distances for the raw material, and this is reflected in the raw material cost, 535 SEK/t DS or 32 SEK/GJ (115 SEK/MWh). Lime is used for detoxification in the ethanol plant. It is assumed that the lime kiln provides the lime necessary for this purpose. Besides a larger kiln, it also means a larger bark gasifier and thus a smaller bark surplus in the pulp mill. The need for purchased $CaCO_3$ is increased with by 13 000 t/year, or 21 kg/ADt. The $CaSO_4$ produced in the detoxification stage is sent to landfill.

### 5.3.2 Investment and operating costs

The investment cost for the ethanol plant is substantial, about on third of the investment for the pulp mill.

The operating costs are high and dominated by the cost of raw material. There is also a substantial loss in electricity sales. Since most of the raw material becomes by-product fuels, the economic result is very sensitive to the market price for the by-products.

An economic evaluation and comparison with the Reference Mill show that the cost to produce ethanol is 4 910 SEK/tonne ethanol. This corresponds to 3.9 SEK/l ethanol or 5.7 SEK/l gasoline equivalents. The investment costs are mainly based on (Fransson 2000).

### 5.3.3 Conclusions

Compared to other Swedish studies, there does not seem to by any advantage in integrating ethanol production with a pulp mill. This is not entirely true. For a plant of this size the investment cost synergies amounts to 200–250 MSEK. The results could instead be explained by different assumptions.

- The ethanol yield is lower due to:
  - The ethanol plant in KAM is based on the more mature dilute acid hydrolysis method while many other studies are based on enzymatic hydrolysis.
  - No pentose fermentation is assumed in the KAM ethanol plant.
  - A more technically and economically realistic raw material: wood logging residues and thinnings instead of sawmill residuals.
- The large raw material demand for the ethanol production in "KAM Ethanol" leads to long average transportation distances for the raw material, and this is reflected in the high raw material cost.
- The investment costs in "KAM Ethanol" reflect present costs and does not account for anticipated cost reductions in the future.

It must also be emphasised that the one of the aims of the programme "Eco-cyclic Pulp Mill" was to examine the best ways to use the fuel surplus in the pulp mill, not to examine if integration of a pulp mill and an ethanol plant is the best way to produce ethanol.

## 5.4 Energy combines with other Industries

The use of excess heat from pulp and paper mills for district heating is a traditional system solution, which is used in several places in Sweden. This is well known and therefore not discussed further in this report.

Some of the excess heat used or possible to use for district heating is in fact at such high temperatures that it is useful for process integration within the mill (see section 4.2). There will therefore probably be a conflict between internal use and use for district heating in future situations, when enhanced process integration is considered. The knowledge of this conflict and optimal use of excess heat is today rather poor. In a few projects at Heat and Power Technology, Chalmers, studies of different options for excess heat have been carried out (see Cecilia Bengtsson: "Applied studies of possibilities for process integration in the pulp and paper industry", Ph. D. Thesis). The results in these studies indicate that excess heat in most cases should be used internally if it is at temperature levels above approximately $90^0$C. However, these aspects should be studied further. In two new Ph. D. projects within the Swedish Programme Energy System these aspects will be studied.

It should also be of interest to identify opportunities for a combine between a mill and another type of industry in order to achieve energy synergy effects. One opportunity is to use the excess heat from a mill for heating another type of industry.

This requires a type with need for low temperature heat, e.g. food industry. One problem is that food industries are in most cases relatively small compared to the amounts of excess heat from e.g. a pulp mill. The synergy effects would in such cases be relatively marginal. Another possibility would b e to develop ecocyclic industrial parks in the future, i.e. several industries are built close to each other and have at least partly, a common energy system. Such ecocyclic industrial parks exist in e.g. Kalundborg, Denmark. This option should be studied further and evaluated technically and economically. Such solutions must of course be seen in a long term perspective.

## 5.5 Visions for Sweden

Although biomass upgrading in connection with the energy system in market pulp or pulp and paper mill is done today, more R&D of opportunities and possible synergy effects should be performed. One of the important areas is further research on new temperature drying technologies and system solutions.

Forest residues and bark could be upgraded to high-quality biofuel through leaching of metals and other elements that cause incineration or environmental problems. The leached material could then be pelletized with black liquor lignin as binder in order to increase the energy density and facilitate the handling. Also here, the technical and economic opportunities should be explored in further work. This could be a highly interesting way of producing upgraded biofuel in Sweden.
Further R&D on opportunities and possible synergy effects for ethanol production in connection with a mill should be performed. The study referred to in this chapter was done using other conditions and assumptions that may be the case in future situations. This will be studied in a newly started Ph. D. project within the Swedish Programme Energy System.

Possibilities for larger Ecocyclic industrial parks should be explored in further R&D work.

# 6 Separation of $CO_2$ from the process

## 6.1 Background

Today $CO_2$ capture from flue gases in e.g. coal condensing plants transport and long-term ground formation (e.g. aquifer) is considered to be one of the most interesting and economic ways for future $CO_2$ mitigation. Lately work to investigate opportunities for applying this way of $CO_2$ mitigation also connected to flue gases from recovery boilers in pulp and paper industries. Also lime kiln flue gases could be of interest. The reasons are that modern and, not the least future, mills are big enough to justify the investments for $CO_2$ capture, the large amounts of $CO_2$ in the flue gases and that the economy for this (according to existing studies) looks very attractive at probable future high $CO_2$ trading prices. Therefore, this technique could mean a cost-effective way for society to leanly reduce future GHG emissions.

In this chapter state-of-the-art techniques for $CO_2$ capturing from pulp a mill flue gases is presented and need for future work as well as opportunities in Sweden are discussed.

## 6.2 Principles

There exist different techniques for separating $CO_2$ from other gases in e.g. exhaust gases. For chemical pulp or pulp and paper mills this means that $CO_2$ can be separated from the exhaust gases from the recovery boiler. Also lime kiln gases can be cleaned in this way, although the size would then be much smaller and therefore in itself less economically interesting. (A combination between recovery boiler and lime kiln gases could maybe be possible in the future, although this option has so far not been studied.)

Black liquor gasification is today discussed and studied as an alternative to recovery boiler. In such plants $CO_2$ can be removed already in the gasification process stage and can probably therefore be done much cheaper.

## 6.3 Techniques and systems for $CO_2$ capture, transportation and storage

### *$CO_2$ Capture*

There are several types of techniques for capturing $CO_2$ from gas streams used or discussed. The conditions regarding gas pressures, $CO_2$ concentration, etc. decided which technique should be chosen in each case. For $CO_2$ capture from recovery boiler flue gases (possibly combined with lime kiln flue gases) in the pulp and paper industry, chemical absorption should be suitable (low pressure, low $CO_2$ concentration). This is proven method and is used today in e.g. North

Sea offshore plant for capturing $CO_2$ from natural gas, transferred back and stored in the aquifer below the natural gas.

The normally used absorption medium is monoethanolamine (MEA). In this technique there is a rather high heat demand due to heat consumption during desorption for regeneration of the solvent.

Although there are commercially available technologies for $CO_2$ capture, the efficiency and economic performance of biomass energy with $CO_2$ capture can be improved through integrated process configurations and the development of new technologies. This is being studied in a Swedish project for $CO_2$ capture from pulp mill recovering boiler flue gased, see Hektor and Berntsson (2006).

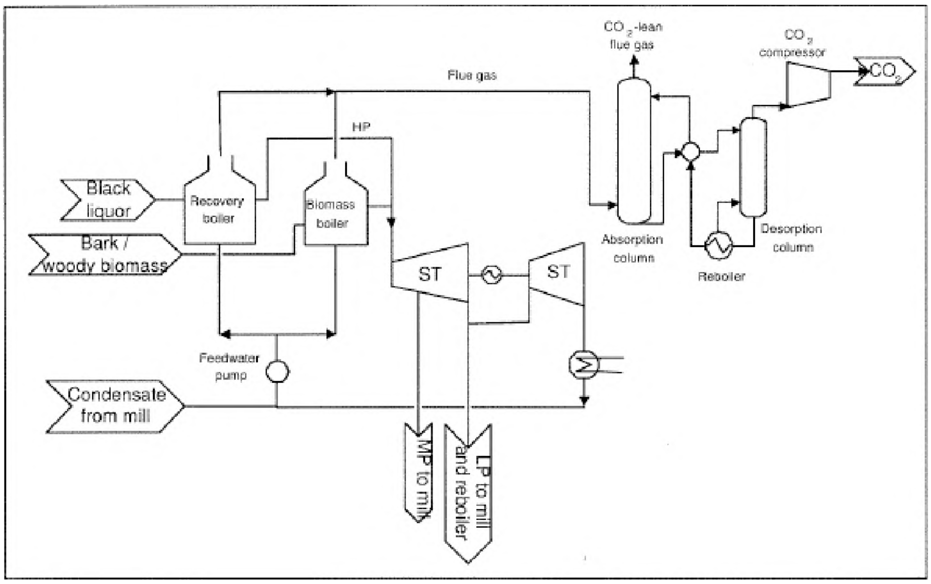


**Figure 6.1 CHP system based on boiler and steam turbine technology. The CHP system in the figure includes post-combustion $CO_2$ capture.**

With future black liquor gasification systems, the $CO_2$ produced can be removed in the gasification stage. In a Chemrec type of gasification unit, producing e.g. electricity or Methanol/DME, a part of the $CO_2$ (25-30 % approximately) can be removed after the quench,

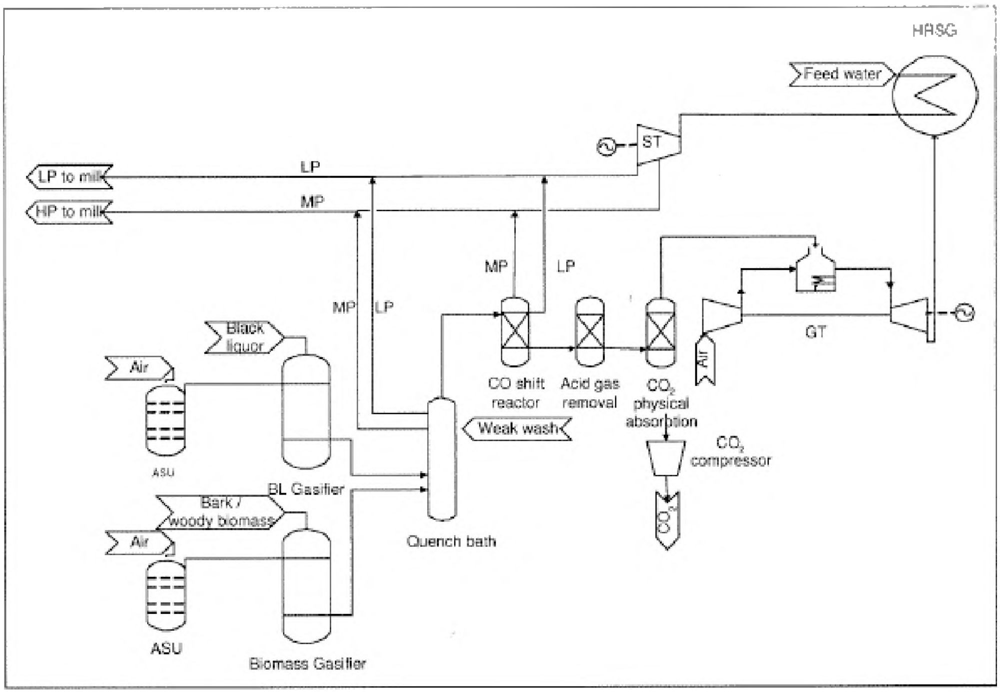


**Figure 6.2 CHP system based on gasification and combined cycle technology. The CHP system in the figure includes pre-combustion CO2 capture.**

If hydrogen is produced from black liquor gasification in the future, practically all of the $CO_2$ can be removed after gasification (as there is no carbon in the final product). Such a removal can therefore be done without large costs and can be one of the driving forces for a future "hydrogen society".

### *$CO_2$ Transportation*

Because of the large volumes involved, pipelines are requested for the transportation of $CO_2$ to a storage location once it has been captured (IEA, 2002). Transport of $CO_2$ can best be done at high pressure in the range of 80 to 140 bars. Compression and pipeline transport of $CO_2$ is feasible and technically proven. In addition, the use of large tankers might be economically attractive for long-distance transportation of compressed/liquefied $CO_2$ over water (Ekström et al., 1997). This means that $CO_2$ Capture also in pulp and paper plants in parts of the world, where storage opportunities are small, can be of interest in the future.

### *$CO_2$ Storage*

A key issue is where $CO_2$ should be stored. The discussion on $CO_2$ storage covers the injection of supercritical-state $CO_2$ into underground geological formations or the deep oceans and technologies for conversion to stable carbonates or bio carbonates. Much further work is required to investigate the permanent storage of $CO_2$. Deep underground disposal is regarded as the most mature storage option today according to Lindeberg (1999). Suitable candidate underground $CO_2$ storage locations are exhausted natural gas and oil fields, not exhausted oil fields (so-called enhanced oil recovery), unminable coal formation, and deep saline aquifers (water-containing layers). Lindeberg (1999) points out that the advantage of underground disposal compared with other storage options (such as ocean storage) is that it gives minimum interface with other ecological systems and can provide storage for very long periods of time. International monitoring of current disposal projects will help to evaluate whether underground storage is a safe mitigation option.

## 6.4 Different system configurations

For end-of-pipe solutions the Amine based system has been more studied than other alternatives. It contains mainly two unit operations, absorption of $CO_2$ in e.g. ethanoldiamine and desorption at a higher temperature. The desorption operation is endothermic, which means that heat is needed for this system. In fact the increase of the total heat needed in the pulp mill is, substantial and this is an important part of the total cost for the $CO_2$ precipitation, transport and storage.

Several different systems and fuels can be used for the additional heat needed. Möllersten et al (2003) have studied import of biomass fuel which is burnt in a biomass boiler. Hector and Berntsson (2005) have studied different alternatives, biofuel, boiler, natural gas boiler and natural gas combined cycle (NGCC). More alternatives are currently evaluated in Figure 6.1 one of the alternatives, NGCC, is shown.

## 6.5 Economy

In the studies of Hektor and Berntsson (2005) the cost of capturing the $CO_2$ and then transporting and storing it has been calculated for different alternatives. But the key question before evaluating the result is of course the price that the governments, EU etc put on emitting $CO_2$. Although the $CO_2$ comes from biofuel it is still a decrease in total emissions and therefore it should be credited and valued in the same way as $CO_2$ from fossil fuel. It is unlikely with a future price of $CO_2$ in the neighbourhood of 400-500 SEK per tonne. Then a profit of around 100-200 SEK per tonne could be achieved in some cases. The amount of $CO_2$ that is avoided in the recovery boiler of a mill producing 1500 ADt/day is roughly 700 000 tonne per year. This means that the net profit could be as high as 70-140 MSEK per year for one big mill. The results have also shown that the use of natural gas for the desorber regeneration can be a better future alternative both economically and environmentally than using it in e.g. a CHP plant.

## 6.6 Visions for Sweden

Sequestration and storage of $CO_2$ is considered one of the most important measures for Greenhouse Gas Emissions mitigation. Within EU this area is highly prioritized and IEA has now more or less officially stated that there are two main areas globally for the necessary $CO_2$ mitigation, energy efficiency measures and $CO_2$ sequestration and storage. All other measures and new technologies will, according to IEA, have considerably lower impacts on $CO_2$ mitigation up to at least 2050.

R&D work in this area is mainly directed towards $CO_2$ sequestration from flue gases in coal condensing plants and natural gas combined cycles ("downstream") and coal and natural gas liquefaction ("upstream"). Recently R&D work for other plants with large flue gases have started, for example the studies reported in this chapter. When using this technique in large chemical market pulp or pulp and paper mills, biomass fuel can be turned into a fuel with negative $CO_2$ emissions, which is highly interesting. As has been indicated in the studies discussed above, $CO_2$ precipitation in these types of mills could in the future be done with very good profits for a mill, given probably future high costs for $CO_2$ emissions. This technology can therefore be of high interest for pulp and paper industry and mean a win-win situation, i.e. with good profits for industry and $CO_2$ mitigation with comparatively very low costs for society.

The R&D in this field has recently started and there is therefore a need to further explore the different aspects of this technology/system solution. Examples of important further R&D areas are:

- Investment cost/system solutions and operability aspects for the MEA type of system
- Pilot plant for testing of the technology real pulp mill flues gases
- New absorption media at e.g. higher temperature levels
- Studies in infrastructure aspects for transport of $CO_2$

In this area Sweden could be a leading nation due to the ongoing research, many pulp mill candidates, and good storage capacity (e.g. in Skåne).

- A great amount of birch, which is excellent as raw material for both the hemi-cellulose xylan and the bark substances suberin and betulinol.
- Modern, efficient kraft pulp mills that would be well suited for development into biorefineries
- The LignoBoost process for separation and purification of high-quality lignin from black liquor (STFI-Packforsk et al).
- A method under development for isolation of non-degraded xylan from black liquor (STFI-Packforsk)
- A method under development for isolation of hemicelluloses from wood or forest residues (STFI-Packforsk et al)
- A lead in the development of hemicellulose-based gas-barrier materials for e.g. packaging. (Chalmers et al)
- Research in the forefront regarding enzymatic modification of wood polymers (KTH)
- Research in the forefront regarding wood chemistry and materials (polymers and composites) in general (KTH, Chalmers, STFI-Packforsk)

Forest residues and bark can be up-graded to high-quality biofuels. There are also possibilities to extract compounds that can serve as raw material for value-added specialty chemicals. Suberin fatty acids from birch bark can be transformed into tailor-made polymers. Hemicelluloses extracted from forest residues can be upgraded towards numerous applications such as oxygen barriers in food packaging and hydrogels for controlled release of specific substances in e.g. pharmaceutical applications.

Black liquor can be used as source for hemicelluloses and lignin. The hemicellulose xylan can be upgraded to e.g. fibre additives for high paper bulk, thickeners, food additives, emulsifiers, gelling agents, adhesives and adsorbants. Lignin can be used as a substrate for value-added chemicals and products such as phenols, carbon fibres and adsorbing carbon structures.

# 7 Production of chemicals and new fibre materials

## 7.1 Background

The pulp mill processes today represent a sub-utilisation of the incoming biomass. The broad spectrum of organic compounds in the pulp mill streams such as kraft mill black liquor and bark could instead of incineration in the recovery boiler and bark boiler respectively be processed to valuable “green” chemical products within pulp mill biorefineries. The main incentive is to improve the economic performance of the mill while the pulp mill expands to a multi-output biorefinery with advanced utilisation of the incoming biomass and other raw materials, for simultaneous production of fibres for paper products, chemicals and energy.

The idea to increase the value of the by-products has been studied by several authors earlier. (Kringstad, 1976, Katzen, 1996). Wood-based side-streams from pulp mills have better economic prerequisites than most other biomass raw materials: Firstly, the scale of the industry means both large volumes of bio-feedstock in total and large production units with good scale economy. Secondly, some by-product streams, e. g. black liquor, are already partly processed in the pulp production and can be more suited for further refining than wood waste, agro fibres or other natural-fibre feedstock. Biomass is a more complex raw material than petroleum, and utilising such partly processed streams therefore means a very efficient resource use. Thirdly, location of the new valorisation industry by the pulp mill means excellent process integration opportunities (waste heat and other energy, waste and effluent handling, water, general infrastructure etc).

In table 7.1 below are some of the chemicals that could be produces from a pulp mill biorefinery summarized.

**Table 7.1 Potential and existing chemicals from a biorefinery including the processes needed for the separation from raw material and refining processes. The development status varies largely from idea to existing process.**

| Raw material | Primary processes | Intermediate Product | Refining Processes | End product | Use | Development status |
|---|---|---|---|---|---|---|
| *Black liquor* | | | | | | |
| | Separation, fractionation | Lignin fractions | Supercritical oxidation?<br>Catalysed hydrogenation? | Phenols | Phenolic resins | Laboratory |
| | Separation, fractionation | Lignin fractions | Spinning, carbonisation, activation | Carbon fibres | Construction, sporting goods, adsorbents, Catalyst | Idea/Laboratory |
| | Separation | Lignin fractions | | Active carbon | | Laboratory |
| | Separation | Lignin fractions | Purification | Lignin fuel | Fuel | Pilot plant |
| | Separation | Lignin fractions | Purification, sulfonation | Road additive, binder, battery additive, dispersant, plant nutrition, soil treatment etc | Binder, dispersant, emulsifier, | Commercial process |
| | Gasification | Syngas | Synthesis | MeOH, DME, FT-diesel | Chemicals/fuel | Pilot plant |
| | Separation | Tall oil | Distillation | Fatty acids | Paint, plastics. lubricants | Commercial process |
| *TMP water or black liquor* | | | | | | |
| | Separation | Hemicellulose | Cross linking | Hydrogels | Hydrogels | Laboratory |
| | Separation | Hemicellulose | Purification | Polymers | Packaging films oxygen-barrier | Laboratory/Pilpot scale |
| | Separation | Glucomannan | Acid Hydrolysis<br>Catalysed hydrogenation | Mannitol | Sweetener | Commercial process |
| | Separation | Hemicellulose | Purification and/ or derivatization | Xylan, xylan – derivatives | Paper additives | Laboratory |
| | Separation | Saccharinic acids | | | Complexing agent | |
| | Separation | Saccharinic acids | | | Polymers | Idea/laboratory |
| | Separation | Xylan | Acid hydrolysis<br>Catalysed hydrogenation | Xylitol | Sweetener | Commercial process |
| *Wood* | | | | | | |
| | Leaching, sc extraction? | Hemicellulose extractives | Separation | | | Idea |
| *Forest residues* | | | | | | |
| | Leaching, sc extraction? | Hemicellulose extractives | Separation | | | Idea |
| *Birch outer bark* | | | | | | |
| | Separation | Suberin | Purification, polymerization | Functional polymer | | Idea |
| | Super critical extraction | Extractive | | Betulin | Pigments and coatings | Commercial process |

## 7.2 Technical and economic potentials

Lignin and hemicellulose could be a bio-based feed-stock for several chemicals where oil is the raw material used today. The economical feasibility is depending both on the scale of the production unit but is also dependent on the oil price. The changeover to a bio based feedstock will be gradually where some products will reach the feasibility point compared to oil based products at a lower oil price than other products.

## 7.3 Lignin used for production of chemicals

The production of lignin chemicals from sulphite and kraft pulp mills is approximately 1 million tonnes per year, where about 10 % origins from kraft pulp. Lignin is currently used in several applications for example as binder, surfactants, batteries, road additives etcetera.

Much research is performed with the purpose to increase the use of lignin. Either the focus is on increasing the performance of the lignin by modifying its structure or the focus is to find new applications like carbon fibres and other carbonaceous products.

In a future lignin could be used in a more extensive way both in applications where the lignin structure is remained but modified and in applications like carbon fibres and in the production of for example phenols.

### 7.3.1 Binder

Lignin is used as binder in several applications; concrete, road binder, ceramics, fertilisers, animal feed etcetera. The use of lignin as a binder is the largest lignin application with the use of lignin in concrete mixture is standing for the majority of the lignin use when used as binder. Lignin is also used for dust control on unpaved roads. A surface with a high content of moisture helps fines to adhere to each other and the breakdown of road will slow down. This is the lignin application with the lowest market value, assumed to 310 €/ton, the price is assumed to be the same as for calcium chloride (used for road dust control).

### 7.3.2 Surface active chemicals

The surface active properties of lignin are well known. The product group could be separated in two parts; lignin as dispersant and as emulsifier.

Water-soluble lignin derivatives, such as lignosulphonates, are used as dispersants for cements, textile dyes and oil-well drilling muds.

Water reducing agent in gypsum wallboard. Currently, lignosulphonates both from the sulfite process and sulfonated kraft lignin are used in the formulation of gypsum wallboard. The alternative use of dispersant is to use syntetic condensation polymers of sulfonated naphthalene with formaldehyde. The addition is used to reduce the amount of water needed to obtain a slurry. Sulfonated kraft lignins are as good or better than lignosulfonates from sulfite process. The low cost of the lignosulfonate allow these products to compete on the market even though they are not as dispersing as syntetic alternatives and they retard the setting of the board. (Northey, 2002). The market price for lignin used as dispergent could be about 850 €/ton.

### 7.3.3 Sequestrant

Lignin can tie up metal ions, preventing them from reacting with other compounds and precipitate in insoluble form. Metal ions sequestered with lignins stay dissolved in solution, keeping them available to plants and preventing scale deposits in water systems. As a result, they are used in micronutrient system, cleaning compounds and in water treatments for boilers and cooling systems. If the lignin could be modified to be as effective as sequestrant as EDTA the price for lignin is assumed to be the same; 1200 €/ton

### 7.3.4 Batteries

Lignin is used in batteries to increase the life time for the battery. The lignin is added to the negative pole during the formulation of the battery. The lignosulphonate is modified but the kraft lignin could be used either unsulphonated or sulphonated. (Gargulak 2000) The believed mechanism is that the lignin acts as a crystal growth inhibitor, causing the negative plate to maintain its spongy character, thus optimizing surface area and current discharge. A relatively small amount of lignin, only a few grams per battery is needed to largely increase the life time of the battery. (Gargulak 2000)

### 7.3.5 Phenols

Lignin is an obvious candidate as a source for bio-based phenols. Phenols have a large range of applications, a major application is in formaldehyde resins. The idea to produce phenols from lignin is not new. Goheen (1966) showed how phenols could be produced by catalytic hydrogenation from lignin in a rather complicated process by using the produced phenols as solvent. There are recent published data indicating that it is possible to produce monomeric phenols by supercritical oxidation. (Gaspar et al, 2005). The market price for phenols is 500-700 €/ton.

### 7.3.6 Carbon fibre

The low weight, high resistance to heat and corrosion, high strength and stiffness, makes carbon fibres (CFs) one of the most important materials by itself and in advanced composites.

Besides of CF intended for structural applications, activated carbon fibres (ACFs) are a special type of CF where surface characteristics are the most important property. ACFs are used for removal of impurities from gases and liquids including adsorption of micro-organisms (Chen and Zeng, 2002) as well as for catalysis (Rodríguez-Reinoso and Sepúlveda-Escribano, 2001).

The cost is due to the raw materials used, especially for polyacrylonitrile (PAN), and to the high production cost of CF. In general, the raw material accounts for 45-60 % of the total production cost of CF composites. It is however expected that an increased production of CF will decrease the cost, and thus CF will be possible to use in a broader application area.

In this context lignin should be an attractive precursor for CF production, due to the low cost, great availability as well as its renewability.

There has been commercially produced carbon fibre using lignin as a precursor on the market from 1967 to 1973 when the production discontinued.

The market price for carbon fibres are 18-56 €/kg. If lignin could be used as a precursor the price would probably be similar to that of pitch, marketed for 160-340 €/ton.

## 7.4 Hemicellulose: Functional chemicals

Hemicelluloses are structural polysaccharides that are biosynthesized in large quantities in trees and annual plants. The hemicelluloses are the world's second most abundant family of polymers after cellulose and represent an enormous renewable resource.

The major constituent of the hemicellulose of softwood is glucomannan. In the case of hardwood, the predominant component of the hemicellulose is xylan.

The structural features of hemicelluloses present properties and possibilities which make these polysaccharides very interesting to develop in to value-added advanced polymer products. The side group content and distribution influence the physico-chemical properties of these polysaccharides. Furthermore, the different structural elements present in these polysaccharides enable specific modifications by chemical and enzymatic means and may serve as a raw material source for further processing into low molecular speciality chemicals e.g., furfural, xylitol or mannitol.

Xylans have been recovered in polymeric form and in good yields from kraft black liquors by e.g., precipitation techniques.

In conclusion, large-scale isolation of hemicelluloses from pulp mill spent liquors may develop into a cost-efficient method for obtaining substantial quantities of polysaccharides for further processing into polymers, hydrogels, coatings and films or low-molecular chemicals based on truly renewable forest resources.

### 7.4.1 Fibre and paper additives

Hemicelluloses added during the processing of chemical pulps have a significant influence on the physical properties of the fibres, especially when these polymers are enriched at the fibre surface. It is well known that the properties of paper made from certain chemical pulps can be improved significantly by the addition of kraft or sulfite hemicelluloses during processing of the fibres. Both xylans and glucomannans can be employed as fibre additives improving the beatability and strengthening the fibre-to-fibre bonding ability of the treated pulps. Addition of hemicelluloses thus improves some of the properties that are especially important for packaging grades e.g., tensile and bursting strength and the folding endurance. In addition to application as fibre additives, hemicelluloses can replace starch in the sizing of packaging paper grades. It has been demonstrated that liner and corrugated paper sized using hemicelluloses under mill operation conditions employing an industrial size-press, were stronger than the corresponding paper products sized with starch.

Derivatives of hemicelluloses have also been investigated for applications as sizing-additives and adhesives in papermaking. For example, carboxy-methylxylans have been synthesized and found to have properties similar to the corresponding carboxymethylcellulose (CMC). The market price of CMC is 1150-1300 €/ton.

### 7.4.2 Coatings and films

A development of renewable packaging materials that can be easily recycled or disposed with minimal environmental effects is highly demanded. Hemicellulose-based coatings and films have great potential for replacing many of the synthetic polymers commonly employed today. There are several patents describing various procedures for producing hemicellulose-based coatings and films. Usually, addition of a plasticized (glycerol, sorbitol or mannitol) is needed in order to achieve good mechanical film properties.

Controlled release of packed active agents at a desired site, time, and at a specific rate, has gained considerable attention for different types of packaging application. To protect packed food from the ingress of oxygen an oxygen barrier material is commonly integrated in the food packaging consisting of several layers. Today, aluminium and synthetic polymeric materials, such as ethylene vinyl alcohol, EVOH, are often used as oxygen barriers in food packaging applications. An introduction of biodegradable and renewable hemicellulose-based coatings and films would favour recycling and a sustainable development in this area. However, hemicelluloses from wood have a great potential to become very attractive alternative renewable raw materials for packaging coatings and barrier film applications. The market price of an oxygen barrier (in the price example; EVOH) is less than 1600 €/ton.

### 7.4.3 Hydrogels, emulsifiers and thickeners

The term hydrogel refers to a class of polymeric materials that swell in water but do not dissolve. They include many natural materials of both plant and animal origin. Hydrogels can be useful as matrices for controlled release of bioactive molecules, in particular pharmaceutical proteins and for encapsulation of living cells. In such applications hydrogels of natural polymers, especially polysaccharides, may offer several advantages. Polysaccharides are, in general, non-toxic, biocompatible, biodegradable and abundantly occurring in biological systems. Using polysaccharides for hydrogel preparation often requires chemical or physical cross linking. Dextrans are polysaccharides often used for hydrogel synthesis. Hemicelluloses constitute a much larger raw material reserve, which has not been extensively used in hydrogel and thickener applications so far.

### 7.4.4 Low molecular chemicals

Several chemicals of industrial importance can be derived from hemicelluloses from forest industry wastes or from spent liquors from pulping processes. However, many of these chemicals are today produced from agricultural wastes. Furfural is perhaps the chemical of most industrial importance produced from xylan (via a two-step procedure involving acid hydrolysis and dehydrogenation). The agricultural sources provide higher yields of furfural than do the forest industry wastes. However, in contrast to agricultural wastes, forest wastes are not dependent on seasonal variations and, hence, do not require large storage facilities. Therefore, xylans from spent liquors from kraft pulping have a potential for replacing the agricultural-derived xylans employed today for furfural production. Furfural can subsequently be converted into a large number of valuable furan compounds which can serve as starting materials for different kinds of plastics.

The xylose-rich product obtained by acid hydrolysis (or enzymatic hydrolysis) of xylan can also be converted to xylitol by catalytic hydrogenation, and this is already a commercial process. Xylitol is a very good non-cariogenic sweetener for diabetics with comparable sweetness to glucose. Another polyol is mannitol which can be derived in a similar manner but from wood glucomannan. After acid hydrolysis glucomannans can be fermented to ethanol, whereas xylan-rich wastes can be utilized for production of yeasts. Other chemicals like 2,3-butandiol and butanol can also be produced by combined enzymatic hydrolysis and fermentation of wood hemicelluloses. Xylitol is twice as sweet as sorbitol while mannitol has the same sweetness as sorbitol. The market price of sorbitol is 480-700 €/ton.

### 7.4.5 Conclusions

The hemicelluloses are the world's second most abundant family of natural polymers after cellulose and represent an enormous renewable resource. There are several promising techniques for using the hemicelluloses either for various polymer applications or for production of special chemicals. Although, these applications have not hitherto been fully competitive with oil-derived synthetic products, new hemicellulose isolation and conversion technologies together with substantially increasing prices for crude oil will certainly contribute to increased hemicellulose utilization in the near future.

General reference to hemicellulose:
R. Whistler and C-C. Chen, Hemicelluloses, in Wood structure and composition, Eds Lewin and Goldstein, Marcel Dekker, New York, 1991.

## 7.5 Extractives

Besides the main components, carbohydrates and lignin, wood also contains small amounts of compounds that are extractable with neutral solvents. The total amount is normally only a few percent of the wood, but it can be considerably higher in parts like bark and branches and is normally also increased in wounded wood.

In the kraft process the main part of the wood resin is dissolved in the black liquor and normally incinerated to give energy or in few cases, separated and used as a source for production of specialty chemicals. Especially during kraft pulping of pine trees the gases released from the digester are condensed and a turpentine fraction can be separated from the aqueous distillate. Further, the removal of the sodium salts of fatty and resin acids from the black liquor followed by acidification gives tall oil, which is refined into a number of commercially important products, like paper sizes, adhesives, and ink and paint ingredients.

The phenolic compounds are usually only found in the heartwood and in the bark, where they act as fungicides. Since most of these compounds are water soluble, they are removed in the cooking stage and thus not present in chemical pulps. Together with the resin acids the phenols are responsible for the main toxicity in effluents from mechanical pulping.

### 7.5.1 Turpentine

A turpentine fraction can be separated from the gases after blowing the cook. The kraft turpentine fraction is normally containing also some sulphur compounds which deteriorates the quality. A turpentine of higher quality can be collected from TMP mills.

Unfractionated turpentine can be used as solvent in varnishes and paints and can also be used for production of polyterpene resin, which is a tack ingredient in adhesives.

A main product from the monoterpene hydrocarbons is pine oil. It is used in several products such as e.g. disinfection and cleaning agents to give a “pine” odour.

The terpenes in turpentine can be fractionated by distillation. Beta-pinene is used as an intermediate for making e.g. menthol and linalool (lilac-like fragrance) both used as flavour and aroma compounds. Hydrogenation of alpha-pinene gives camphene, which can be used for synthesis of substances with a sandalwood odour.

Also other monoterpenes, can be used as raw material for production of insecticides, flavours and aroma chemicals.

### 7.5.2 Tall oil

Tall oil soaps, which are dissolved in the black liquor during the cook, will separate in the evaporation plant and can be collected as a soap layer. By acidifying the soap with sulphuric acid, free fatty and resin acids will form. The amount of tall oil is about 25 –50 kg/ton of pulp for softwood kraft. The tall oil can be refined by distillation in a fraction containing mainly resin acids, a fraction containing mainly fatty acids and a fraction called tall pitch oil containing neutral substances. The market price for tall oil is 70-170 €/ton.

### 7.5.3 Resin acids

Major uses are as paper sizing agent. The resin acids may also be esterified and used in pressure-sensitive adhesives and as ink component.

### 7.5.4 Fatty acids

Major uses are for production of soaps, detergents and surfactants or esterified in alkyd coatings (varnishes and paint). Further methylated or butylated fatty acids fractions are used as ingredients in ink. Glycerol ester of selected fatty acids are used as a friction modifier in lubricating systems such as crankcase oils, metal working fluids and hydraulic fluids. They are also used as intermediate chemicals for production of e.g. ethoxylates, polyesters epoxy esters etc.

### 7.5.5 Tall pitch oil

This fraction is mainly used as heavy fuel oil in heat production plants. Since it is classified as a biofuel it is free of carbon dioxide tax. Minor fractions from tall oil are refined by Arizona Chemicals in a US facility to specialty value added products like anti-viral medicine and road paint.

### 7.5.6 Sterols

The neutral fraction of tall oil consists mainly of sterols (sitosterol and campesterol) and triterpene alcohols like betulinol (birch). The sterols can be extracted from the tall oil.

Sitosterol is used (in Finland) for production of a margarine additive used to lower the cholesterol value in human blood. (Product names Becel, Benecol).

### 7.5.7 Tannins

Tannins can be extracted from wood and are widely used in the food (beer/wine making), and leather industries. The only native plant-derived tannins used in the leather industry are oak bark tannins derived from hand-stripped bark (mechanical stripping causes an undesirable increase in red colouring) and demand is unsaturated in this particular sector. The laborious method of collection means that tree-bark-derived tannins are uncompetitive compared with synthetic tannins and imported vegetable-based tannins. The world market for tannins is estimated at 500,000 tonnes per year. Tannins have potential for use in particleboard adhesives where the high reactivity is used. Tannins may be used as insect, mollusk (snails), bacterial and fungal control agents.

### 7.5.8 Flavanoids, stilbenes, etc.

Hundreds of compounds are reported to be bioactive, and used as pharmacologically active metabolites. Examples found in Scandinavian species are catechin, ferulic acid, gallic acid, ellagic acids, estragole.

One example of a product on the market is a bark extract (Barrträdsextraktdryck) containing mainly a stilbene (resveratrol glucoside) and the flavanoid chatechin, sold in Finland as a “nature-cure medicine”. The effect is said to be that of an antioxidant.

### 7.5.9 Lignans (antioxidants)

The lignans (a phenolic compound) from spruce (especially hydroximatairesinol) can be extracted from knots (kvistnötter). A process have been developed at Åbo University (Bjarne Holmbom et al) It is documented that lignans in the food can lower the bad cholesterol and are also effective as “anti tumour agents”. Besides to be used as food additives and pharmaceutical drugs the substances can substitute synthetic antioxidants in products such as cosmetics and food.

### 7.5.10 Birch bark

Bark in general in a pulp mill is used as fuel in a bark boiler. Minor commercial uses are as bark filler in gardens and as soil additives. Another application is the use of suberin in cork from oak for processing e.g. cork stoppers. Generally, the most feasible use of bark is as fuel in a bark boiler, however, bark from birch differs from bark from other species as it contains the interesting compounds suberin and betulin in higher concentrations than in other species.

### 7.5.11 Functional polymers

In birch suberin one interesting epoxy-hydroxyacid dominates; 18 hydroxy 9, 10 epoxyoktadekanoic acid. The content of the acid in birch suberin is about 30 %. The acid could be used to produce high-value epoxy polyester with specialty properties.

### 7.5.12 Antioxidants

Betulin, also called betulinol, is an extractive also common in the outer bark of birch. It is the crystals of betulin that give birch its characteristic white colour. Betulin protects the tree from bacterial and fungal attacks as only few micro-organisms can utilize the bark. Betulin has a high chemical stability and is relatively inactive; however it has a high biological activity. For example, it has shown to be active against cancer, virus and malaria. Preliminary studies have been made of the activity of betulin showing that the toxicity is low and that it has gastric-protective properties (Kuznetsov 2004).

Both betulin and betulinic acid are currently used in the cosmetics industry. Betulin and lupineol are used for their anti-inflammatory activity and the ability to support supple skin. Birch extract has been used in cosmetics since mid-1990s.

*General references to extractives:*

Rowe, J.W. (Editor): “Natural Products of Woody Plants I and II” (1989), Springer-Verlag.

Back, E.L. and Allen, L.H. (Editors): “Pitch Control, Wood Resin and deresination” (2000) Tappi Press.

## 7.6 Black liquor gasification for production of chemicals

In the chemical industry a large number of products are manufactured from synthesis gas (syngas). The production of syngas is describes in chapter 4.2.3.

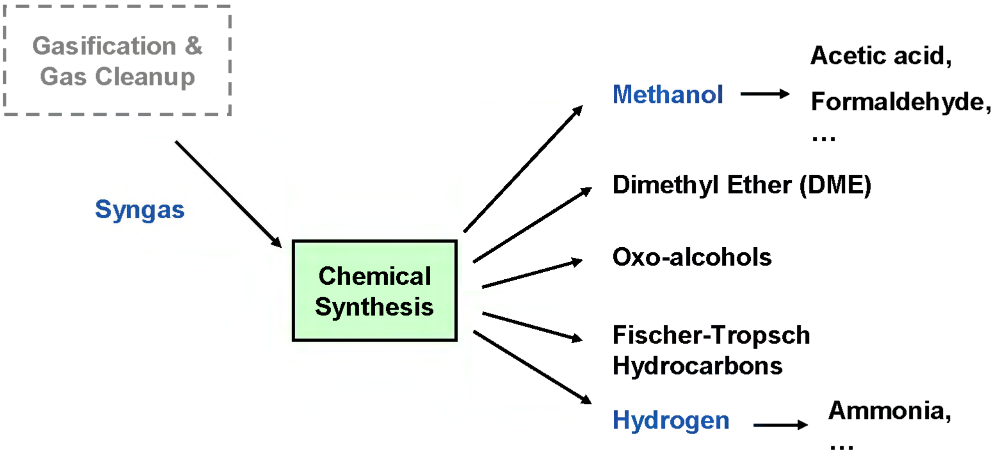


**Figure 7.1 Some examples of possible products from syngas derived from black liquor.**

### 7.6.1 Potential products

Products manufactured via syngas are normally bulk chemicals. The economy of scale favours large plant and the volumes produced are therefore also large. In general, the potential to produce syngas at a pulp mill is on the same order of magnitude as chemical plant operating today, but in the low range.

### 7.6.2 Methanol

The major use of methanol today is as intermediate in the production of other chemicals, with formaldehyde and methyl tertbutyl ether (MTBE) as the most important products. Acetic acid and dimethyl ether (see below) can be produced via methanol. Methanol is also used as a solvent, as antifreeze, and in small amounts as a fuel.

Natural gas is the most common raw material for syngas used for methanol production. Methanol is synthesized over a copper catalyst according to the reaction

$$2H_2 + CO \rightarrow CH_3OH$$

at high pressures (60-80 bar) and temperatures of about 250°C.

The total global production capacity is about 35 million tonnes per year. The largest new plant has a capacity of up to 5000 tonnes per day. The market price for chemical grade methanol is 220 €/ton.

### 7.6.3 DME

Dimethyl ether (DME) can be recovered as a by-product from methanol synthesis, or intentionally manufactured through dehydration of methanol.

$$2\,CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

The most important use of DME today is as a propellant in spray cans where it has replaced freons. The market price for DME chemical grade is 500 €/ton.

## 7.7 Vision for Sweden

The future kraft pulp mill has a large potential to supply chemicals and materials, in addition to the present fibre products,

Forest residues and bark can be up-graded to high-quality biofuels. There are also possibilities to extract compounds that can serve as raw material for value-added specialty chemicals. Suberin fatty acids from birch bark can be transformed into tailor-made polymers. Hemicelluloses extracted from forest residues can be up-graded towards numerous applications such as oxygen barriers in food packaging and hydrogels for controlled release of specific substances in e.g. pharmaceutical applications.

Black liquor can be used as source for hemicelluloses and lignin. The hemicellulose xylan can be upgraded to e.g. fibre additives for high paper bulk, thickeners, food additives, emulsifiers, gelling agents, adhesives and adsorbents. Lignin can be used as a substrate for value-added chemicals and products such as phenols, carbon fibres and adsorbing carbon structures.

Another way to utilize kraft black liquor is to gasify it in its entirety to syngas for production of various hydrocarbons. These could be a source for a wide range of chemicals and polymers in the same way as petroleum is today.

Sweden has, together with other north-European countries, strong motives to strive towards the pulp mill biorefinery vision:

- The political and economic necessity to decrease the dependence on petroleum as raw material.
- Decreasing profitability in birch pulp production, due to competition from countries with fast-growing eucalyptus.
- The global necessity to decrease greenhouse gas emissions from fossil raw material

Sweden has also several advantages that motivate that we should be active in the research and development towards pulp mill biorefineries:

- A great amount of birch, which is excellent as raw material for both the hemicellulose xylan and the bark substances suberin and betulinol. (STFI-Packforsk)
- Modern, efficient kraft pulp mills that would be well suited for development into biorefineries
- The LignoBoost process for separation and purification of high-quality lignin from black liquor (STFI-Packforsk et al).
- A method under development for isolation of non-degraded xylan from black liquor (STFI-Packforsk)
- A method under development for isolation of hemicelluloses from wood or forest residues (STFI-Packforsk et al)
- A lead in the development of hemicellulose-based gas-barrier materials for e.g. packaging. (Chalmers et al)
- Research in the forefront regarding enzymatic modification of wood polymers (KTH)
- Research in the forefront regarding wood chemistry and materials (polymers and composites) in general (KTH, Chalmers, STFI-Packforsk, LTH)

The research and development in Sweden should utilise the lead we have in the research areas mentioned above.

Carbon fibres, for example, are a high-value product with a potentially very big market. Researchers in North America have a lead regarding the actual fibre processing from biomass. Our strength lies in this case in the beginning of the product chain, i.e. development of a suitable lignin raw material.

Hemicellulose is an excellent and abundant raw material for paper mill additives and performance materials like hydrogels and packaging barriers. Sweden should take advantage of the lead we have both regarding some product groups and regarding methods for recovery from the pulp mill.

It is also important to utilize the gathered knowledge in wood chemistry and biochemical methods for basic research on wood constituents in order to identify new high-value applications for wood-processing by-products.

Sweden also has a good basis – both regarding competence and co-operation networks - for continued development of new polymer and composite materials.

# 8 Visions for and need for further R&D in Sweden

This chapter is a summary of the discussions on visions and needs for further work in the preceding chapters.

*Export of energy from the pulp and paper industry to society*

- Opportunities for energy saving in chemical pulp and paper industry in order to identify potentials upgrading of internal biomass to electricity, lignin for sale, motor biofuels, etc
- Opportunities for energy saving in the mill when black liquor gasification is used in the future in order to identify potentials increasing the share of internal biomass of the total fuel consumption
- Increase knowledge of most suitable end products for expert under different future scenarios
- The Swedish lead in several key areas connected to upgraded fuel export should be used for establishing Sweden as a foremost biorefinery Country. Examples of such lead areas are:
  - Process integration in pulp mills (Chalmers)
  - Pressurized gasification of black liquor and conversion into electricity or motor fuels (ChemRec)
  - Separation of high-quality lignin from black liquor through the LignoBoost process and further upgrading of the lignin (STFI-Packforsk)
  - Chip, bark, etc leaching kidney (STFI-Packforsk, Chalmers)

*Energy Combines*

- Biomass upgrading in connection with pulp and paper mills is future area of high interest in Sweden. Further work on possible synergy effects and on new technologies, e.g. low-temperature drying, should be performed
- More high-quality biomass fuel can be produced through upgrading of e.g. forest residues and bark via leaching of metals and other elements. Technical and economic opportunities should be performed. This could be a highly interesting way to produce high-quality biofuel in Sweden
- Synergy effects of connecting ethanol production to a pulp or pulp and paper mill could improve the economy for this biofuel. Future conditions for this to come true should be explored.

*Separation of $CO_2$ from the process*

- Although most R&D efforts in this area are directed towards $CO_2$ sequestration in coal and natural gas systems, removal of $CO_2$ from pulp and paper mills through $CO_2$ sequestration from recovery boiler flue gases, black liquor gasification systems, lime kiln gases, etc should be of high interest for Sweden and create a win-win situation, i.e. with good profiles for industry and $CO_2$ mitigation with comparatively low cost for society

- The R&D in this field has recently started and there is therefore a need to further explore the different aspects of this technology/system solution. Examples of important further R&D areas are:
    - Investment cost/system solutions and operability aspects for the MEA type of system
    - Pilot plant for testing of the technology real pulp mill flues gases
    - New absorption media at e.g. higher temperature levels
    - Studies in infrastructure aspects for transport of $CO_2$
- In this area Sweden could be a leading nation due to the ongoing research, many pulp mill candidates, and good storage capacity (e.g. in Skåne).

*Production of chemicals and new fibre materials*

The future kraft pulp mill has a large potential to supply chemicals and materials, in addition to the present fibre products.

Sweden has several advantages that motivate that we should be active in the research and development towards pulp mill biorefineries producing chemicals and new materials:

- A great amount of birch, which is excellent as raw material for both the hemicellulose xylan and the bark substances suberin and betulinol.
- Modern, efficient kraft pulp mills that would be well suited for development into biorefineries
- The LignoBoost process for separation and purification of high-quality lignin from black liquor (STFI-Packforsk et al).
- A method under development for isolation of non-degraded xylan from black liquor (STFI-Packforsk)
- A method under development for isolation of hemicelluloses from wood or forest residues (STFI-Packforsk et al)
- A lead in the development of hemicellulose-based gas-barrier materials for e.g. packaging. (Chalmers et al)
- Research in the forefront regarding enzymatic modification of wood polymers (KTH)
- Research in the forefront regarding wood chemistry and materials (polymers and composites) in general (KTH, Chalmers, STFI-Packforsk)

Forest residues and bark can be up-graded to high-quality biofuels. There are also possibilities to extract compounds that can serve as raw material for value-added specialty chemicals. Suberin fatty acids from birch bark can be transformed into tailor-made polymers. Hemicelluloses extracted from forest residues can be up-graded towards numerous applications such as oxygen barriers in food packaging and hydrogels for controlled release of specific substances in e.g. pharmaceutical applications.

Black liquor can be used as source for hemicelluloses and lignin. The hemicellulose xylan can be upgraded to e.g. fibre additives for high paper bulk, thickeners, food additives, emulsifiers, gelling agents, adhesives and adsorbants. Lignin can be used as a substrate for value-added chemicals and products such as phenols, carbon fibres and adsorbing carbon structures.

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Energimyndigheten, Box 310, 631 04 Eskilstuna
Telefon 016-544 20 00. Fax 016-544 20 99, www.energimyndigheten.se