Possibilities for improving the pulping process

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ABSTRACT

This paper summarizes the main findings from the Swedish research program "The Eco-cyclic Pulp Mill" which has been in operation between 1996 – 2002. An important part of the program is the comparison between a theoretical state-of-the-art bleached softwood kraft pulp mill and different possible future techniques in theoretical model mills. Compared to most normal mills in operation, the theoretical reference mill has a significantly better performance regarding the environment, energy, costs and pulp quality. The performance can be significantly improved by leaching of chips before cooking, removal of excess lignin, process heat integration and pressurized black liquor gasification with power generation or production of methanol. Removal of excess lignin-fuel and chip leaching before cooking are being studied in the FRAM-program during 2002 – 2004. A long-term alternative to the kraft process may be alkaline sulfite pulping using a recently proposed low temperature gasification process.

INTRODUCTION

This paper presents the summary of the main results of the research program "The Eco-cyclic Pulp Mill", (1996-2002), financed by MISTRA, the Swedish Energy Agency and the Swedish industry. The total budget has been equivalent to about 13 MUSD (8.2 SEK/USD). A comprehensive final report has been released in June 2003 [1]. A number of companies, universities and institutions have been offered to purchase the report. The work carried out until 1999 has been published in a comprehensive report [2] and [3]. General program information is available on the Internet [4].

The program vision is a fully developed ecocyclic system for high quality paper products, with an efficient use of the potential biomass energy. One aim of the program was the development of realistic and environmentally optimal solutions for the production of high-quality pulp and paper products which minimize the use of non-renewable resources and efficiently utilize the potential biomass energy. Another aim has been the education of research scientists (resulting in 21 licentiates and 4 PhD's). The focus has been on the bleached kraft process. The key issues were:

- Mineral balances (soil, pulp mill, solid residuals)
- Minimizing solid residues by process internal measures
- Reduced energy consumption
- Utilization of surplus energy
- High degree of water closure
- Alternatives to the kraft process
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The program has utilized a wide range of competences from academic disciplines (organic chemistry, inorganic chemistry, analytical chemistry, process modeling, chemical engineering, energy systems) to industrial Research, Development & Engineering. All pieces of developed knowledge have been carefully evaluated, together with available external knowledge, in a comprehensive synthesis. The main tool in the synthesis work has been the theoretical model mills. In total 18 Model Mills cases have been evaluated.

Model mills are a useful method to quantitatively estimate and illustrate the potential of new process technologies integrated into a complete generic mill system. The emphasis may be on energy [5], economics [6] environmental parameters [7] or resource utilization [3]

THE REFERENCE MILL YEAR 2000 –THE MOST RECENT AVAILABLE TECHNOLOGY

A theoretical reference case, with respect to resource-efficiency (including economy) and environmental impact, has been defined, called the "Reference Mill". The Reference Mill represents a theoretical, bleached softwood kraft market pulp mill in which the most recent technology used in commercial operation in Finland and Sweden year 2000 is implemented in all process departments. Key data for the Reference Mill is given in Table I. The Reference Mill has a significantly better performance than an average of existing mills as shown in

Table II. Considering the fact that the massive investments in kraft mills are depreciated in at least 20 years, it is evident that the improvements that are possible will take time.

The studies of the Reference Mill show that the kraft process has technical potential to be further developed. The fiber line has a significant potential to become more efficient by modifications in kraft cooking and oxygen delignification, including process machinery that minimizes fiber deformations, in order to produce pulp with higher strength potential and improved bleachability. Combining this with new findings on efficient ways to manage non-process substances originating from wood [1, 2, 8, 9, 10] and to remove high molecular weight lignin from cooking circulations, enhances the possibilities to delignify and bleach pulp even more effectively. This may be achieved while at the same time reducing operating costs, through better conditions for increased system closure and improved energy efficiency.

The Reference Mill's positive energy balance can be significantly improved by pressurized black liquor gasification (Model Mills 3 and 4) and by removing excess lignin from the process (Model Mill 2) for more efficient external use, see Table II. Process heat integration, including the utilization of low-grade heat, makes it possible to evaporate considerably larger amounts of process water [10], which allows a higher degree of system closure. A critical condition for these developments is to maintain, or preferably to lower, operating costs and to utilize capital more efficiently.

MODEL MILLS

In order to illustrate alternative ways of improving the efficiency of the kraft process from the level of the Reference Mill, in-depth studies have been performed on hypothetical "Model Mills", in which the technology applied in at least one of the sub-processes has not yet been commercially tested. The Model Mills have been evaluated and compared with the Reference Mill with respect to energy-efficiency, capital requirement, operating costs, pulp properties, discharge to water, solid waste generation and the effect on the emission of fossil-fuel derived carbon dioxide. An overview of some of the evaluated Model Mills, and how they differ from the year 2000 Reference Mill, is shown in Table II. Model mills based on 100 % borate autocausticizing, soda-AQ pulping, ASAM and the alkafide processes have been published earlier [2, 3].

REMOVAL OF MINERALS FROM CHIPS – CHIP KIDNEY

One promising concept, developed in the program, for removing non-process elements is chip leaching within a "chip kidney" [1, 2, 4, 9, 10]. A significant part of the non-process elements, such as Cl, K, P, N, Mn, Ba and Ca, can be removed from the wood by leaching the chips with an acidic solution at 80-100 ºC before cooking. The potential for implementation is large. One alternative to take advantage of chip leaching is to close up the water circuits in the bleach plant with the same scaling risk for calcium oxalate and calcium carbonate as in the Reference Mill (Model Mill 1). The basic requirements of chip leaching have been largely clarified [1 and 8]. Mill trials are planned in the near future. A schematic outline of a process for chip leaching in a continuous cooking system is shown in Figure 1.

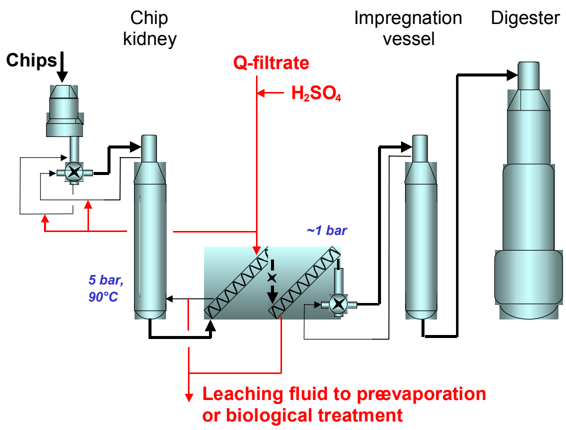

Figure 1. *A schematic outline of a process for chip leaching prior to kraft pulping.*

It has been estimated that the application in a typical existing bleached kraft pulp mill can increase the production and decrease the process steam and chemical demand. The possibilities to further close the bleach plant due to less Ca-related scaling [9] may give lower costs for wastewater treatment. Another interesting development is to lower and control the content metal ions in the product.

ENERGY EFFICIENCY

Direct and avoided emissions of carbon dioxide from the different phases in the life cycle of the Reference Mill are shown in Table III. The negative sign for avoided emissions of carbon dioxide means that society's net emission of fossil CO_2 is reduced as a result of the pulp production. For comparison, data for the Swedish average softwood bleached kraft pulp mill in 2000 is presented. The Swedish average in 2000 is based on weighted averages of data from all softwood bleached market kraft pulp mills in Sweden.

In contrast to the 2000 Swedish average mill, the Reference Mill has a negative net emission of fossil CO_2. The main reason is that the Reference Mill has a surplus of bark and black liquor fuel. The bark is sold, while the surplus black liquor based on present conditions in Sweden – is best suited for the generation of condensing power at about 540 kWh /ADt. This surplus power is assumed to be used to replace power from a natural gas combined cycle power plant.

Table II indicates that an even higher energy efficiency, and hence, a larger effect on the emission of greenhouse gases, can be obtained with pressurized black liquor gasification (BLG) with power generation (Model Mill 3) or BLG with methanol generation (Model Mill 4).

Similar or better energy efficiency seems to be attainable by removing excess lignin fuel. Removal of lignin from black liquor evaporation seems to be an attractive option for existing mills that are severely recovery boiler limited. Excess lignin can in principle be removed from the black liquor evaporation between 30 and 40 % black liquor dry solids (Model Mill 2), or more futuristic from a cooking liquor circulation. In the latter case, besides the energy efficiency, improvements in cooking efficiency, chemical consumption and bleachability could be expected. The recent development of modern ceramic membranes with good performance is crucial for this development. Laboratory and mill pilot studies on both applications for lignin removal will carried out in the near future.

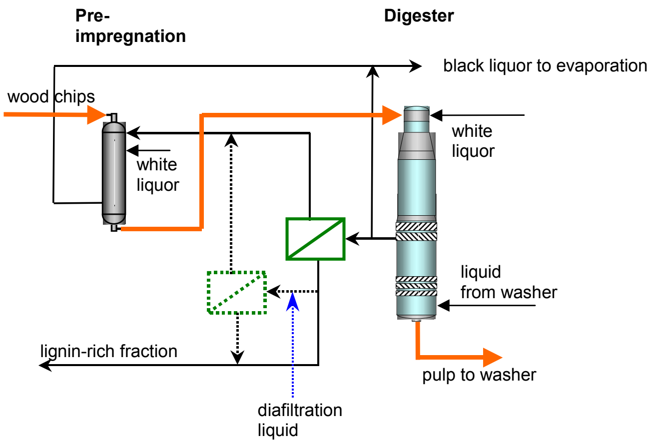

Figure 2. *Lignin fractionation of kraft black liquor by ultrafiltration, integrated in a continuous kraft cooking system.*

The current incentives for increased energy efficiency as outlined above are limited as the capital market's demand on capital efficiency has to be satisfied. However, the kraft pulping industry is in a much better position than many other industries to play a future role as a significant supplier of biobased energy.

ALTERNATIVE TO KRAFT

The most promising alternative to the kraft process that seems to be able to provide equivalent or better pulp properties is the ASAM process [3, 13]. However, with conventional chemical recovery, the complicated energy and chemical recovery system and inferior energy efficiency must be dealt with before this process can be of industrial interest [1, 2, 3, 13].

By replacing the conventional chemical recovery with a low temperature gasification-based process, alkaline sulfite pulping is equivalent to or better than kraft also regarding investment costs and energy efficiency [13, 14] (Model Mill 5). The process is called AS-KAMGASRec. The process would become even more competitive if methanol could be avoided. Recent findings indicate that this may be possible [15].

Another new promising process called NovaCell is in the development stage. This process is based on a new pre-treatment technique before a cooking operation without the addition of sulphur. NovaCell shows a great potential to become a cost efficient alternative with interesting environmental performance for unbleached qualities such as liner [16]. The next step in development is focused on bleached softwood and hardwood qualities.

CONCLUSIONS – "INDUSTRIAL IMPLEMENTATION"

An important initial step is to approach the performance of the Reference Mill in existing mills and in future greenfield mills. Removal of excess lignin-fuel and chip leaching before cooking may be of interest in future mill up-grades and in future greenfield mills. These two applications are being studied in the FRAM-program during 2002 – 2004 with a budget corresponding to about 6.5 MUSD.

The kraft process, and its present chemical recovery system, still has a considerable development potential and a good chance to be competitive for a very long time. Alternative cooking processes, like an alkaline sulfite process, preferably combined with a modified chemical recovery based on low temperature black liquor gasification, are, however, also of future interest due to improved pulp yield/pulp strength, lower investment costs and good bleachability.

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Table I. Key data from the theoretical year 2000 Reference Mill, employing dry debarking (bark press water to black liquor evaporation), cooking to kappa number 27, selective slot screening and extensive washing before and after two-stage oxygen delignification to kappa number 10. ECF-bleaching to 89 % ISO with Q(OP)(DQ)(PO). A TCF alternative uses Q(OP)(ZQ)(PO). Alkaline bleaching filtrates are recycled to the brown stock washing; acid bleach filtrate to the biological treatment. The chemical recovery is conventional. The recovery boiler, with steam data 80 bar(a) and 490°C, receives black liquor at 80 % DS content. Spill liquors are efficiently recovered. The lime kiln uses pyrolysis gas from gasified bark, while surplus bark is sold. Excess steam is used for condensing power.

	ECF	Deviating data, TCF
Pulp yield, incl. wood and fiber losses, % of wood	43.7	43.5
Surplus energy in the form of steam, GJ/ADt	4.7	4.4
Surplus bark, kg/ADt	102	
Emissions		
Sulphur to the atmosphere, kg S/ADt	0.2	
NO_x to the atmosphere, kg NO_2/ADt	1.0	
Total process water effluent flow, m^3/ADt	16	15
Bleach plant water effluent flow, m^3/ADt	10	9
Process water COD after effluent treatment, kg/ADt	7	
Process water AOX after effluent treatment, kg/ADt	<0.1	(0)

Table II. Key data for theoretical green field Model Mills compared with the theoretical year 2000 Reference Mill with ECF bleaching. All Model Mills have a kappa number of 27 after cooking. For comparison, data for the average year 2000 Swedish softwood bleached kraft pulp mill is included.

Case	Sold fuel GJ/ADt	Sold power kWh/ADt	Net operating costs 1) %	Capital invest-ment %	Emission of ”fossil” CO_2 kg/ADt	COD to recipient kg/ADt
Reference Mill with ECF-bleaching	**3.1**	**540**	**100**	**100**	**-260**	**7**
Reference Mill with TCF-bleaching	**3.1**	**490**	**98**	**99**	**-270**	**7**
Swedish average 2000	**-0.6**	**-140**	**120**	**n.a.**	**+320**	**26**
Model mill 1. Chip kidney with advanced bleach plant water closure	3.0	490	98	103	-250	<1
Model mill 2. Export of excess lignin from black liquor evaporation	7.3	70	102 2)	99	-450	7
Model mill 3. Pressurized BLG with conv. lime cycle and power generation	2.4	1040	94	109	-390	7
Model mill 4. Pressurized BLG with conv. lime cycle and methanol production	8.9	-370	78	109	-400	7
Model mill 5. AS-KAMGASRec	3.6	510	102	100	-290	7

1) Includes costs for wood, chemicals and energy, minus sold power, bark, lignin and tall oil.
Power 0.20 SEK /kWh (0.0024 USD/kWh), bark and lignin 0.1 SEK/kWh (0.0012 USD/kWh)
2). Green certificates that currently are discussed in Europe will increase the lignin value

Table III. Direct and avoided carbon dioxide emissions for different phases in the life cycle of the pulp production, "from plant seedling to pulp bale", for the year 2000 Reference Mill with ECF bleaching [11]. The incineration of fibers in the paper products corresponds to an additional amount of 1400 kg avoided CO_2/ADt.

Phase in life cycle	Emissions of fossil based CO_2, kg/ADt	
	Reference Mill	Swedish average 2000
Forest operations	60	60
Transportation of wood	40	40
Production and transportation of chemicals	100	120
Pulp mill, mineral oil	0*)	50
Pulp mill, power	0	50
Sum direct emissions	**200**	**320**
Avoided mineral oil	-260	0
Avoided power (natural gas combined cycle)	-200	0
Sum avoided emissions	**-460**	**-100**
Sum direct minus avoided emissions	**-260**	**320**

*) < 5 CO_2