BioRegional MiniMill Technology – report on UK Demonstration Mill

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Abstract

Straw and other agricultural crops can make good paper but as they are bulky it is only economic to pulp locally on a smaller scale than traditional wood pulp mills. To date, there has been no commercially viable technology to recover energy and chemicals from black liquor effluent on a small scale. Consequently, the use of straw for paper is declining as new mills cannot be opened for environmental reasons and existing straw mills either cause water pollution or are closed down. Since 1997, BioRegional MiniMills UK Ltd have carried out a series of trials at a laboratory and pilot scale to develop new technology for small-scale energy and chemical recovery from pulp mill black liquor effluent and a new method of pulping using a twin screw extruder. A demonstration plant comprising a feed system, twin screw pulper and black liquor system was installed in Manchester, UK in January 2006 and a testing and development program is in progress for both straw and abaca black liquor treatment and straw pulp for printing and writing paper. The test programme is expected to be completed in Summer 2007. Interim results are reported within this paper.

1. Introduction

The BioRegional MiniMill Technology has been developed as both a “bolt-on” technology for small pulp mills with no black liquor effluent treatment and in order to facilitate manufacture of paper pulp from agricultural residues around the world, reducing pressure on the world’s forests. Since 1997 a development programme, in a partnership between environmental organisations and paper companies, has developed new technology and tested it on a large pilot scale in the UK and the Netherlands. The technical and economic feasibility has been demonstrated and international patents applied for.

The MiniMill innovates in two key areas,

1. Preparation, feeding and pulping of straw in a twin screw extruder to reduce energy use and produce pulp in a shorter time
2. A small-scale black liquor effluent chemical and energy recovery system

The black liquor effluent treatment is the key new technology. Typically in large pulp mills, black liquor is evaporated and conveyed to a separate processing stage for recovery of the digestion chemicals and energy content. The most common process for the treatment of the black liquor is high temperature combustion in an apparatus known as a Tomlinson (or Kraft) recovery boiler. The disadvantages of the Tomlinson process include the requirement to use large and complicated furnaces making them uneconomic at small throughputs (<60,000 TPA), the corrosive nature of the recovered smelt product and the risk of explosions between the smelt and water.

In the MiniMill design, a new process making use of existing technology has been designed and tested. It is a chemical process that liberates organic chemicals derived from the straw present in the black liquor for use as fuel and recovers sodium hydroxide for re-use in pulping. The process takes place at relatively low temperatures in a type of fluidised bed. This fluidised bed has been on the market for 20 years and is used in many industries including food and industrial waste processing. It avoids the problems with agglomeration associated with previous attempts to use fluidised beds for this purpose as it has fast throughput, precise temperature control and good mixing. .

2. Twin Screw Extruder Pulping Process

The new pulping process takes place in a twin screw extruder, technology which is widely used in many industries and allows good mixing, fast throughput and high pressure operation. The MiniMill pulper has been developed and designed to make a quality printing and writing paper pulp but it can also be used to make fluting or other paper grades.

The new process is physically small for its capacity and consequently carries a lower capital cost than competing technologies.

An additional advantage is that the pulping is conducted with low amounts of water, making the production of black liquor at higher concentrations possible. This is beneficial in the black liquor treatment stage, as it reduces or removes the need for evaporation.

The twin screw used is co-rotating, which is beneficial in giving the fibre less mechanical treatment and thus minimising damage to the fibres. The material in the barrel travels in a figure of eight shaped path and thus takes a longer route than if the screws were counter rotating.

It was hoped that a fully digested pulp could be produced in the twin screw without any additional cooking. This would enable rapid response times (under two minutes) to be achieved. The quick response of the twin screw will make it much easier to control pulp quality than is possible with current technologies.

2.1 Pulping Trials at Brunel University, UK using 40mm Twin Screw

A series of practical trials were carried out between 1997 and 2003 at Brunel University, UK using a 40 mm diameter twin screw extruder (Figure 1). These trials have given the research team a deeper understanding of the twin screw pulping process and significant advances have been made in the degree of pulping achieved in this unit, with Kappa numbers of around 30 being achieved in under one minute. From these results we have been able to project that when used for pulping, the extruder could reduce energy and water demand by more than 50% compared to traditional pulping systems, and complete the chemical pulping process in much less time than taken in some traditional processes. As described in our patent, the engineers discovered that by re-designing the internal screw and barrel configuration, throughput can be increased by up to four times, reducing the capital and operating costs significantly and helping to make MiniMill cost competitive with pulp mills ten times the scale.

Figure 1: 40mm twin screw pulping unit at Brunel University UK showing internal shafts

In the trials at Brunel University in 2001, straw was pulped in the twin screw unit. The maximum temperature of the twin screw was set to 130°C, caustic was added at an addition rate of 12% to fibre.

After treating in the twin screw, the samples were cooked in a digester at either 4 bar or 1.5 bar pressure. The results from this work are summarised in Table 1 below:

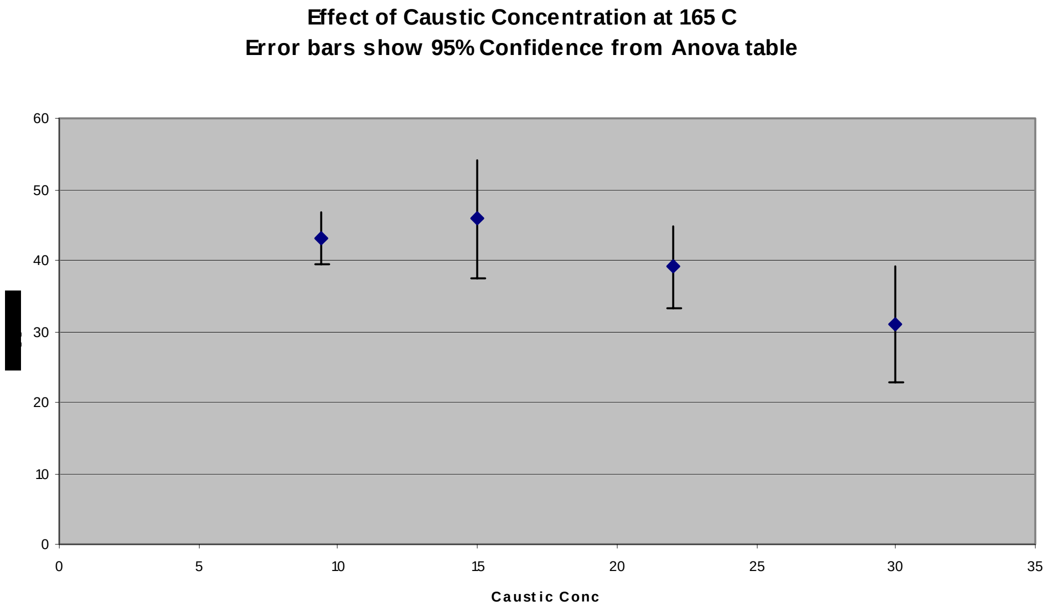
Table 1 – some results of 2001 pulping trials

Sample				
Secondary digestion Time Mins	20	30	30	30
Digestion Pressure bar g	1	1.5	4	4
Kappa No.	54.2	41.4	37.6	35.3
Screened Reject	22.5	14.5	29.1	30.7
Weighted Length	0.65	0.55	0.60	0.63
Lab Sheets Prepared				
Grammage g/m2		64.1	64.7	
ISO-brightness (after bleaching) %		86.2	90.5	
Light-scattering coefficient m2/kg		33.9	46.5	
Light-absorption coefficient m2/kg		0.16	0.10	
Tensile Index (Nm/g)		49.8	27.1	
Stretch %		5.1	3.6	
Tensile energy absorption J/g		2.0	0.8	
Modulus of elasticity N/mm2		4370	1780	

In trial work carried out at Brunel University in 2003 temperatures of 165°C were tested, the highest possible in the 40mm unit. To achieve some statistical probabilities that there is a significant difference between these results, the data was analysed using analysis of variance techniques. By using all the results, at 165°C, to estimate the experimental error it was possible to establish a 95% probability that the caustic addition has an effect on Kappa Number.

The results for the effect of speed and caustic are shown in figs 2 and 3 together with the error bars showing the 95% confidence limit for each point.

Figure 2 Effect of caustic concentration



The results shown above in figure 2 appear to show a fairly linear relationship between Kappa number and caustic concentration in the 15% to 30% range. This relationship appears not to hold true at concentrations below 15%. These results indicate that the optimum caustic concentration in the twin screw may be around 10% addition on fibre.

Figure 3 – Effect of speed on Kappa number

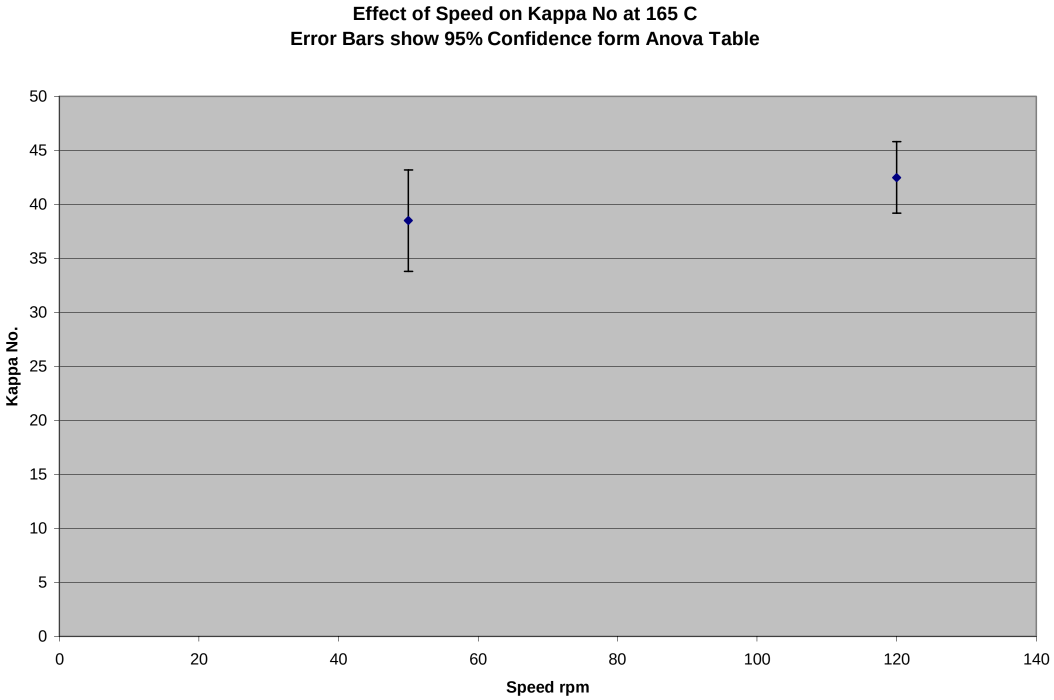


Figure 3 shows a slight improvement in Kappa number from running at the slower speed, which is as expected. However, the improvement is relatively small and more work is required to establish if it is significant. This indicates that the process in not highly time sensitive. This is an encouraging result, since it indicates that the commercial unit will not need to be extended to increase residence time.

The trial results although from a relatively small data set, are reasonably consistent and the results follow predictable trends. This gave an encouraging indication that with further trials in a larger unit it will be possible to achieve a good statistical model, which will enable resulting Kappa Numbers to be predicted for a given set of conditions. This will provide a good framework for the design and specification of commercial twin screw pulping units.

2.1.1 Results for pulp samples in 2003 trials Samples from after the pulping process were sent to KCL in Finland on several occasions. KCL bleached the pulp, made hand sheets and carried out a number of analytical tests. The results from these tests in 2003 (Table 2) show a pulp which was less well draining than previous samples. These results were comparable to a deinked pulp. The variation in freeness from the previous results is not due to a decreased fibre length, as this was very similar to the previous results.

Table 2 - Summary of KCL test results of two pulp samples from 2003 trials.

Sample		Run 10	Run 12
Bleaching no		1510 SO2	1511 SO2
Drainability, CSF, ml	ISO 5267-2	174	112
Drainability, SR-number	EN ISO 5267-1	55.0	66.0
Preparation of laboratory sheets (for physical testing)	EN ISO 5269-1		
Grammage, g/m^2	EN ISO 536 modif.	64.8	64.0
ISO-brightness, %	ISO 2470	88.2	86.9
Opacity (65g/m^2), %	ISO 2471	59.6	59.8
Light-scattering coefficient, m^2/kg	ISO 9416	19.1	18.9
Light-absorption coefficient, m^2/kg	ISO 9416	0.06	0.07
Tensile index, Nm/g	EN ISO 1924-2	72.4	66.9
Stretch, %	EN ISO 1924-2	4.5	4.3
Tensile energy absorption index, J/g	EN ISO 1924-2	2.35	2.11
Tensile stiffness index, kNm/g	EN ISO 1924-2	6.73	6.43

The tensile strength of the sheets produced this time was much higher than in previous trials. This is very encouraging, but requires further work to verify the results and understand the mechanisms involved.

2.2 Pulping Trials carried out at Demonstration Plant in Manchester, UK using 83mm Twin Screw

To fully test the pulping capability of the twin screw extruder a larger unit has been built (Figure 4) and is currently being tested as part of the demonstration plant at a mill in Manchester, UK. It is 83mm diameter internally and 4m long. With this longer unit it has been possible to maintain a plug in the screw and thus maintain cooking pressures of around 7 bar. Initial conclusions of the test program are that Kappa Numbers of around 40 can be achieved in under one minute of digestion, with sodium hydroxide additions below 12%. To achieve a full chemical pulp with a Kappa no 14 additional cooking is required for 90 minutes at 6 bar pressure. This is more or less as expected from previous trial work, and subsequent digestion is included in all projected equipment costings and operating costs. However, there had been a hope that in a larger unit a higher degree of de-lignification would have taken place. The experiments have proved that this is not the case. The research team have determined developments in the feed system that will increase throughput. As previously thought and drawing on the findings of trials with this larger unit, we anticipate that a plant producing 10,000TPA of pulp will need two twin screw pulpers with 160mm diameter flights and modified feeding geometry. The quality of the pulp produced is still being optimized at the time of writing.

Figure 4 – 83mm MiniMill twin screw extruder

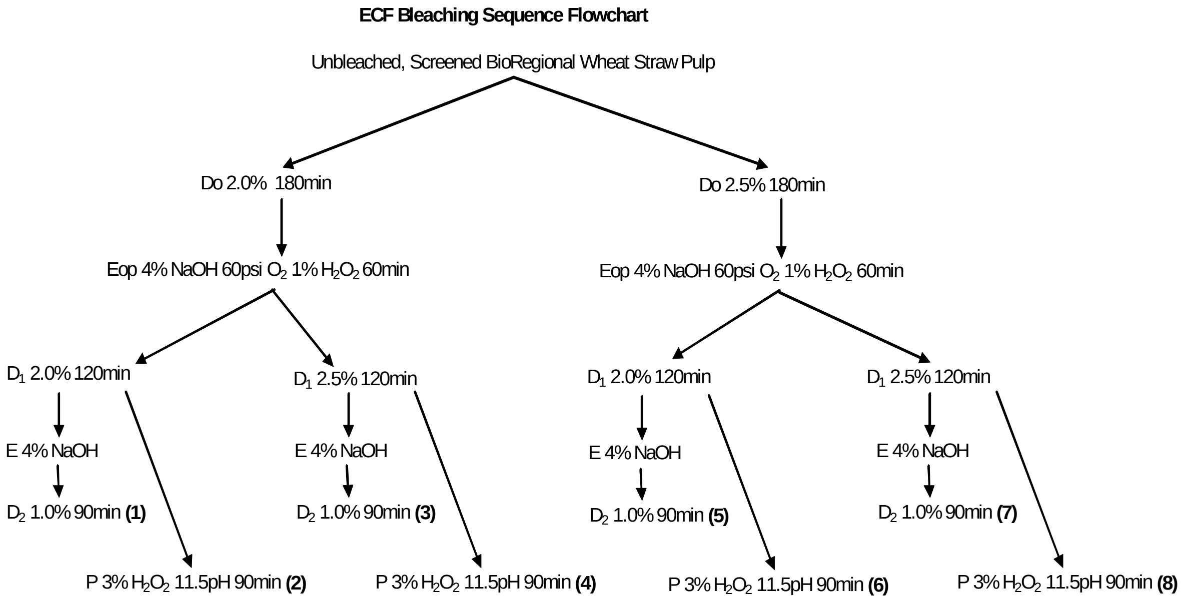
2.2.1 Pulp bleaching The consumer demands a bright white sheet of paper and chlorine gas has typically been used by the paper industry to bleach pulp. However, the use of chlorine gas is not preferable for environmental and health and safety reasons. Totally chlorine free (TCF) and elemental chlorine free (ECF) bleaching methods have therefore been developed for use in the wood pulp industry, primarily in Scandinavia. Bleaching agents used in TCF bleaching of wood fibres are oxygen (O2), hydrogen peroxide (H2O2), peracetic acid (PAA) and ozone (O3). However, although some research and demonstration projects have been carried out on non-wood pulps, only one, a relatively large mill in Shandong China (Wang Ping, Liao Yonghong 2001), has reported any success and the development of TCF bleaching of straw and non-wood pulp is in its infancy.

As part of the Manchester demonstration mill project, the University of Washington, USA carried out tests using the pulp produced to determine the optimum method of bleaching straw which could be economically viable at the relatively small MiniMill scale using the TCF or ECF method. The ECF method is somewhat easier to achieve and has been demonstrated at a lab scale in our previous trial work. The Washington study indicated that a four stage ECF bleaching process would be optimum. Once the researchers have optimized the pulping process larger quantities of straw pulp of around 500-1000 kgs will be washed and bleached using hired facilities and the resulting pulp will be made into paper on a small paper machine.

Figure 5 ECF Bleaching Sequences tested by University of Washington

Unbleached	28.1	Samples
$D_{(2.0\%)}E_{op}D_{(2.0\%)}$	83.9	1,2
$D_{(2.0\%)}E_{op}D_{(2.5\%)}$	84.2	3,4
$D_{(2.5\%)}E_{op}D_{(2.0\%)}$	85.5	5,6
$D_{(2.5\%)}E_{op}D_{(2.5\%)}$	85.8	7,8
$D_{(2.0\%)}E_{op}D_{(2.0\%)}ED$	87.7	1
$D_{(2.0\%)}E_{op}D_{(2.0\%)}P$	83.4	2
$D_{(2.0\%)}E_{op}D_{(2.5\%)}ED$	88.5	3
$D_{(2.0\%)}E_{op}D_{(2.5\%)}P$	84.5	4
$D_{(2.5\%)}E_{op}D_{(2.0\%)}ED$	87.5	5
$D_{(2.5\%)}E_{op}D_{(2.0\%)}P$	85.7	6
$D_{(2.5\%)}E_{op}D_{(2.5\%)}ED$	89.0	7
$D_{(2.5\%)}E_{op}D_{(2.5\%)}P$	87.1	8

Figure 6 Various ECF bleaching sequences tested by the University of Washington



The University of Washington found that an 85 ISO brightness was attainable with good strength in a three stage ECF bleaching sequence. It was not possible to reach a 90 brightness with four stages, but it was close to this with five stages, this could be optimized. An 87 Brightness was reached with four stages. However, peroxide in the final stage reduces strength with minimal brightness increase and so should be avoided.

Ongoing research will look at a chemical addition at the pulping stage and preprocessing of straw to improve pulping and bleaching response. An Oxygen first stage for O-D-E-D sequence will also be explored.

3. Silica

Wheat straw contains silica (sodium silicate) which in high temperature processes can lead, over time, to “glassy” deposits inside the equipment which interfere with the effectiveness of the process and lead to down time for cleaning which has to be carried out using hazardous acid cleaning agents. This is a significant problem in non-wood pulp mills. In the MiniMill it is intended to address this technical problem in two ways and determine the best method of dealing with silica. Firstly, the pulping unit allows pulping to take place at higher concentrations leading to a more concentrated black liquor effluent. It is anticipated that this will remove the need for an evaporation step required at all other pulp mills, as it is at the evaporation stage that most silica scaling occurs. In addition, the speed of the reaction in the black liquor fluidised bed reactor may mean that silica is not deposited. Certainly no deposits have been noted in previous trials. Secondly a method whereby calcium hydroxide is added at the pulping stage to precipitate the sodium silicate onto the cellulose fibres as insoluble calcium silicate will be developed in this project. The method was published some years ago by a Dr Rinman but has not been taken up. The company tested the process on a bench scale at Robert Gordon University, UK, see box 1 below, and it was found to be remarkably effective.

Box 1 - results of tests of silica precipitation method as tested by Robert Gordon University, UK

Pulping Liquor Analysis

10% weight on fibre of NaOH

Solids content of liquor	4.91 %	
Ash content of liquor		1.43% (wet) or 29% BD
Silica content of liquor		0.15g/100ml or 3.1 % BD

8% weight on fibre. Of NaOH + 4% weight on fibre of. CaOH

Solids content of liquor	4.6%	
Ash content of liquor		1.2% (wet) or 27% BD
Silica content of liquor		Too small to detect

Hand Sheet Analysis NaOH Cook
5.02g BD
1.8% Ash

Hand Sheet Analysis NaOH/CaOH Cook
5.6g BD
6.7% Ash

***Note: `wet'** is based on the starting material; **`BD'** is based on the solids content*

The calcium silicate on the pulp is partially removed in the wash water as the pulp moves through further processing stages. Any calcium silicate remaining in the pulp acts as a “filler” material similar to the chalk and clay that are routinely added in high proportions (25-40%) to printing and writing paper in the paper making process.

4. Black Liquor Energy and Chemical Recovery System

A key component of the MiniMill is the processing of the black liquor effluent to recover pulping chemicals and energy.

Black liquor is the generic term for the waste produced during the chemical or mechanical pulping of raw materials for paper production. Typical pulp feedstocks include hard and softwoods, straw and other agricultural crops. The black liquor produced contains inorganic material used as the cooking chemical, and both inorganic and organic material leached from the fibre raw material during cooking. The chemical composition, solids content and other properties (e.g. viscosity and density) of black liquor vary with the pulping process and feedstock used. Table 3 gives typical values of the proximate and ultimate (elemental composition) analysis for straw and Kraft black liquors. The key differences between the two types of liquor are the higher levels of sulphur and sodium and lower levels of nitrogen, chloride, silica and potassium in the Kraft liquor when compared with the straw.

Table 3. Typical properties of black liquor

	Straw	Kraft
Ultimate Analysis (%-mass)		
C	37.0 – 45.0	34.0 - 39.0
H	4.0 - 4.5	3.0 - 5.0
N	0.8 – 1.3	0.04 - 0.2
S	0.5 – 0.9	3.0 - 7.0
Cl	3.0 – 4.0	0.2 - 2.0
K	3.5 – 4.5	0.1 - 2.0
Na	7.5 - 9.0	17.0 - 25.0
Si	0.1 – 1.0	-
O*	30.0 – 40.0	33.0 - 38.0
Proximate Analysis (dry basis, % mass)		
Ash	20.0 - 30.0	30.0 - 50.0
Volatile matter	59.0 - 66.0	35.0 - 55.0
Fixed carbon	12.0 - 14.0	6.1 - 10.0
GCV (MJ/kg, dry basis)	13.5 - 15.0	11.0 - 15.0

* by difference

All modern pulp mills include a black liquor recovery process that is designed to:

i) Treat the black liquor to recover pulping chemicals,
ii) Use the organic non-cellulose material (up to 50% of the original material before cooking) to generate energy for the pulp mill, and,
iii) Recycle process water.

The efficient recovery of chemicals and energy from black liquor is a critical factor in the economics of pulp manufacture. The type of recovery system used depends upon:

i) The feed material used, i.e. wood or non-wood feedstocks,
ii) The pulping process, e.g. Kraft, alkali, potassium or steam explosion,
iii) The mill location and relevant environmental regulations, and,
iv) The quantity of liquor to be treated, i.e. plant size.

The black liquor effluent treatment developed by the company is the key new technology. Typically in large pulp mills, black liquor is evaporated and conveyed to a separate processing stage for recovery of the digestion chemicals and energy content. The most common process for the treatment of the black liquor is high temperature combustion in an apparatus known as a Tomlinson (or Kraft) recovery boiler. The disadvantages of the Tomlinson process include the requirement to use large and complicated furnaces making them uneconomic at small throughputs (<60,000 TPA), the corrosive nature of the recovered smelt product and the risk of explosions between the smelt and water.

In the MiniMill design, a new process making use of advanced fluidised bed technology has been designed and tested. The organic constituents in the liquor are gasified at relatively low temperatures to produce a low to medium calorific value gas for use as fuel in the mill (e.g. to produce steam). The pulping chemicals, e.g. sodium and/or potassium, report to the ash where they are recovered for re-use in the pulping process. The design of the fluidisation process avoids the agglomeration problems associated with previous attempts to use fluidised beds for black liquor treatment. The MiniMill reactor provides for fast throughput, precise temperature control and good mixing.

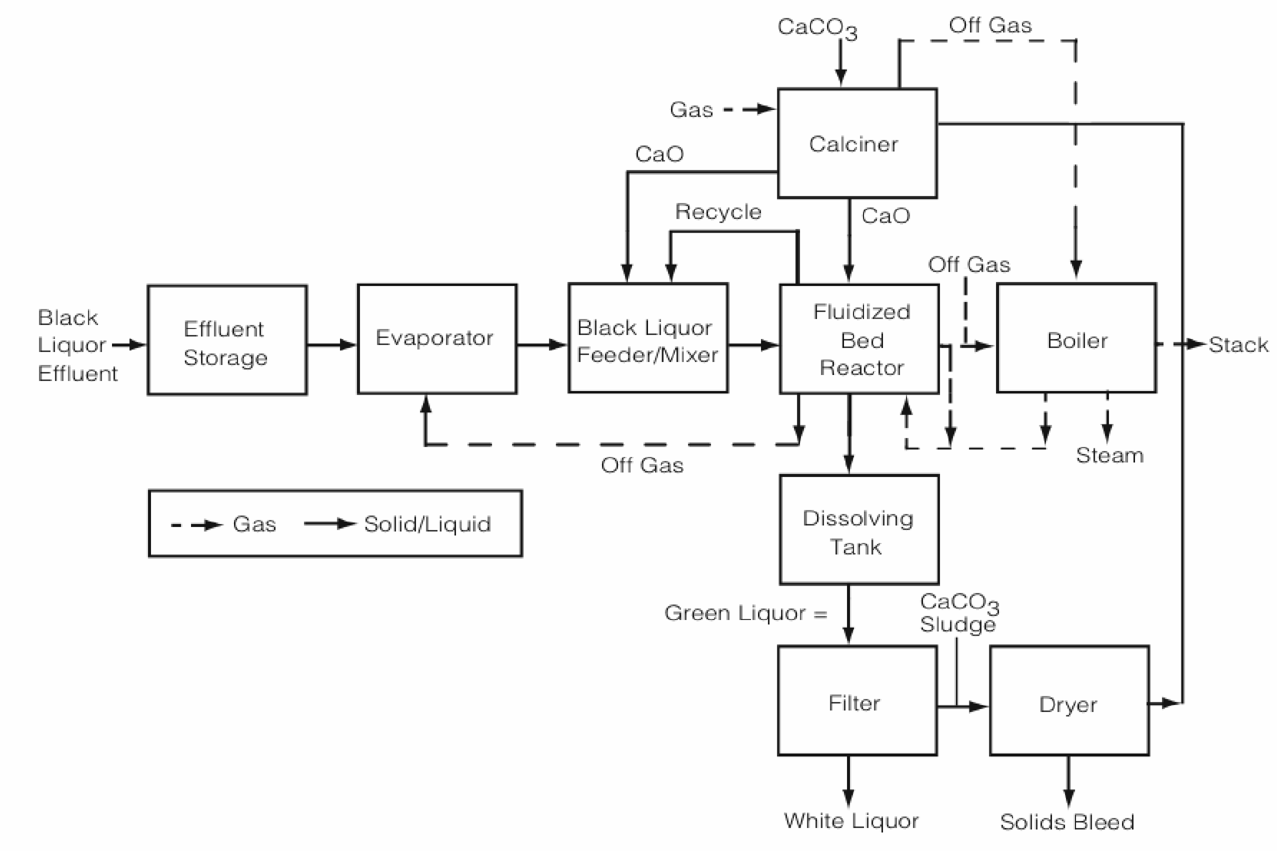
A schematic of the MiniMill black liquor process is given in Figure 8 and a rendered image of a complete unit is given in Figure 9.

The process has been tested in a number of laboratory trials at Cambridge University UK and Sydney University, Australia and in the Netherlands and at a pilot semi-industrial scale at a paper mill site in the UK during 2003. The process treats both dilute (10% solids) and concentrated (45% solids) black liquor and sodium hydroxide and organics are recovered.

The large pilot scale rig is being operated in Manchester at the time of writing in 2006 (figure 7). The aim of the trials is to build upon previous trial work, to operate under low oxygen conditions, to more accurately measure the composition of the fuel gas produced and to obtain data for the sizing of a larger demonstration unit to be installed in 2007. Both wheat straw and abaca black liquor are being tested in the system. It is intended that results of these trials will be available for presentation at the conference.

Figure 7 - Pilot scale black liquor chemical and energy recovery process being tested in Manchester, UK in 2006

Figure 8 - schematic of the MiniMill black liquor process



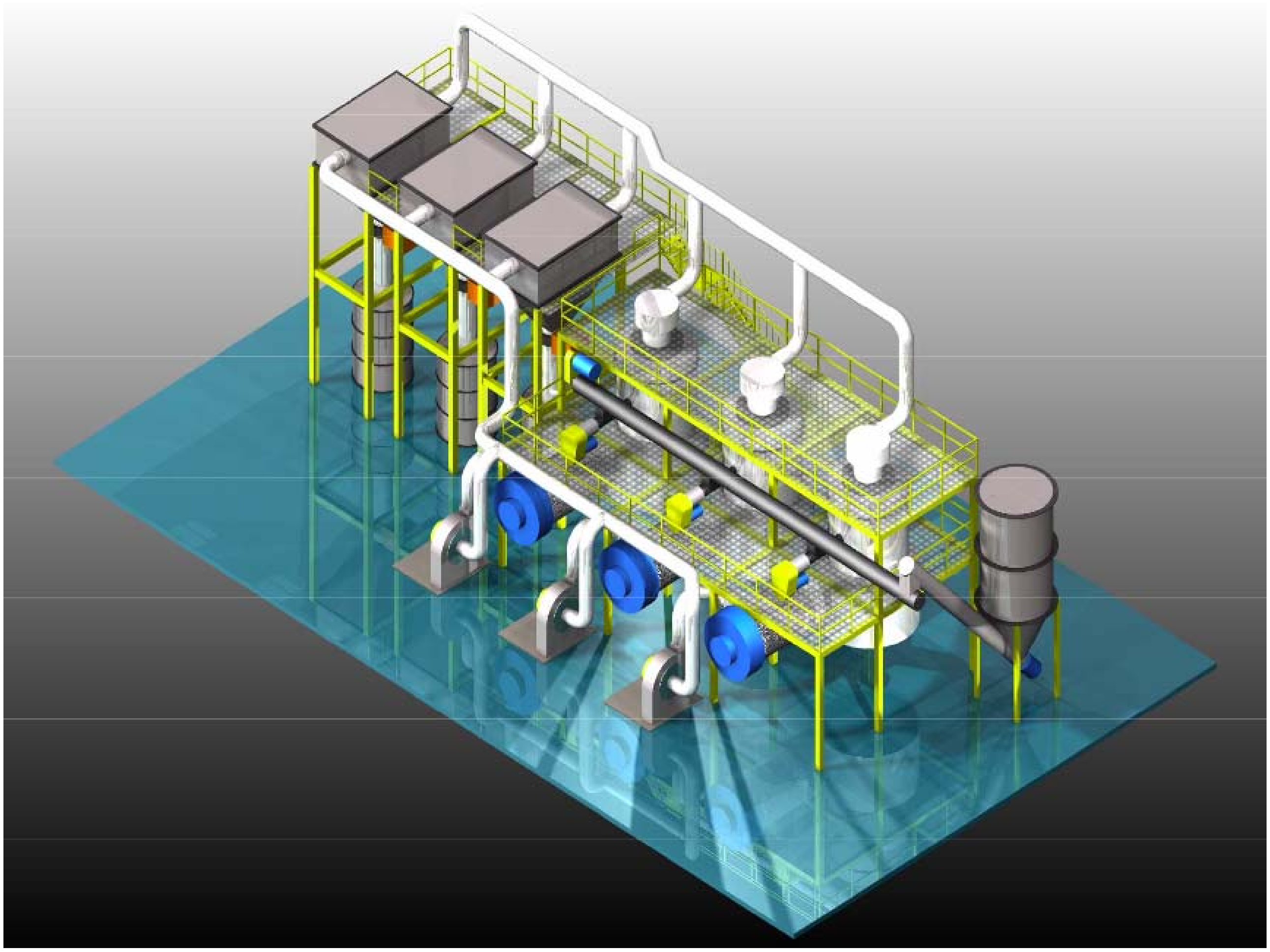


Figure 9 - rendered image of a complete MiniMill black liquor process unit

A chemical equilibrium and energy balance has been carried out by an expert in this field from AF-IPK in Sweden as illustrated in Table 4 below.

Table 4

			Unit: GJ/Adt
		Wheat straw	Hemp/ flax
Input (primary fuels)			
Black liquor (70 % fuel efficiency)		14.5	11.5
Natural gas		0.0	3.0
		14.5	14.5
Consumption			
Fibre line:	Digester, washing, screening	4.5	4.5
	Bleaching	1.0	1.0
	Pulp drying	0.5	0.5
	Bleach chem prep/handling	0.1	0.1
Recovery area:	BL Evaporation	4.5	4.5
	Hot water production, etc	1.0	1.0
	Steam for fluidising	2.0	2.0
	Misc.	0.4	0.4
		14.5	14.5
Source: AF-IPK			

The energy balance shows that the pulp mill should be thermal energy self-sufficient through this process and that at larger end of a small mill scale (100 tonnes of pulp per day), it may be economically viable to add a steam turbine to generate electrical energy as well. A fuel efficiency of 70% is anticipated, with a recovery of 85-90% of NaOH. This compares well with existing large pulp mill systems.

A second fluidised bed can be installed as a calciner to recover 90% of the lime used for re-use in the process: 10% of the lime mud will need to be discarded to avoid a build up of heavy metals in the process (even though only small amounts build up), as this can interfere with the subsequent bleaching process. For a 30,000 TPA mill there will be 1,400 tonnes per annum of such waste, which can be used in the construction industry. This is the only waste product from the MiniMill process.

Data gained from running the more extensive trials at the industrial scale in Manchester will be used to produce a more detailed mass and energy balance for the process. This will be used to develop more detailed process and instrumentation diagrams, and allow capital costs and variable costs such as chemical consumption and energy use to be calculated even more accurately. The MiniMill, though innovative, has been developed from technology used in other industries, so reducing the risk. The remaining equipment in the complete MiniMill will be standard “off the shelf” technology. Scaling up is not expected to create problems as it is more difficult to operate the twin screw and the fluidised bed on a small scale.

5. Life Cycle Assessment

Any industrial process consumes energy and raw materials and gives rise to emissions which can cause environmental impacts. To obtain a complete representative estimate of these impacts, it is necessary to consider all the supply chains providing energy and materials to or receiving them from the process. Life Cycle Assessment (LCA) is the established tool for carrying out this kind of analysis and Surrey University, UK are therefore undertaking an LCA of the MiniMill which will be completed in Autumn 2006. For low density materials, such as the biotic materials (straw) which are used in the MiniMill, it is also important to ensure that transport distances are not so large that they outweigh benefits of processing local agricultural crops and wastes. By analogy with biomass/energy schemes, this is likely to set upper limits on the scale of operation which should be contemplated, dependent on the density of “arisings” to be processed in the mini-mill. The LCA will aim to show under what circumstances and at what scale the straw mill is environmentally sustainable. The LCA will include a quantitative analysis of the environment impacts associated with processing materials in a MiniMill including direct burdens from the process and transport, indirect burdens from “background” operations providing energy and ancillary materials and avoided burdens displaced by recovered materials and energy.

Conclusion

The company has developed a new technology that is nevertheless based on tried and tested technologies used in other industries. The process intensification of the innovative MiniMill chemical and energy recovery system will bring significant capital cost and technical advantages which will provide an overpowering incentive for mills to switch from the 1930’s Tomlinson or Kraft recovery boilers to the MiniMill process. The companies technology will contribute to reducing the human ecological footprint through cleaner and more efficient use of local resources, whilst at the same time incorporating wider social benefits.

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