289.4 PDF PAP 0088 P02492 (5)

FOR PRESENTATION AT THE "INTERNATIONAL SYMPOSIUM ON POLLUTION PREVENTION IN THE MANUFACTURE OF PULP & PAPER", AUG. 18-20, 1992 AT WASHINGTON, D.C.

ALTERNATIVE & EMERGING PULPING TECHNOLOGIES: NON-KRAFT PROCESSES

by

Bruce I. Fleming, Boise Cascade R&D, Portland, OR 97217

Kraft pulping, invented over 100 years ago, gradually achieved dominance as a result of continued refinements. In the last 40 years, scores of processes have been proposed to replace kraft pulping, but few have received even a single mill trial. It is a big step from a laboratory demonstration to commercial reality, and most of the competing processes have failed to do sufficiently well in pilot trials to convince investors to go ahead at full scale.

This does not mean that the kraft process will always be dominant, but it indicates the extreme effort and cost that is involved in commercializing any alternative to this established and versatile pulping technique. Kraft, of course, is itself a moving target. New refinements, like extended delignification, made it tougher to beat.

This brief review covers the main competitors to the kraft process for the production of chemical pulp, namely the sulfite processes, soda-anthraquinone (AQ) pulping and the solvent pulping processes. The processes selected for discussion are commercially proven, or at least have had extensive pilot plant trials.

1. SULFITE PROCESSES

The sulfite processes provide pulps which have inferior strength properties to those of kraft pulp but nonetheless are enjoying some success in the European marketplace at present because, unlike kraft pulp, they respond well to bleaching with hydrogen peroxide. 80% ISO brightness, totally chlorine free (TCF) softwood sulfite pulps are easily obtainable and 86% brightness aspen pulps can be produced by BCTMP mills.

1.1 Low Yield and Sulfite Pulping

No modifications to the pulping process have been required for the production of TCF pulps in sulfite mills - it was sufficient only to switch the bleach plant to peroxide bleaching. Often a single peroxide stage is sufficient to produce the required brightness. There is a significant market for this kind of pulp in Europe; it is currently supplying all the primary fiber used by the German tissue industry (Anon., 1992). However, the TCF pulp market was not strong enough to keep alive one Canadian mill (Fraser Co., Atholville, N.B.) which was capable of producing 120,000 t/year of peroxide-bleached sulfite pulp until it closed in 1991. Many papermakers cannot accept the lower strength of sulfite pulp - particularly those making lightweight coated and SC grades. For them, sulfite pulp is not an alternative.

1.2 BCTMP

Bleached chemi-thermomechanical pulp (BCTMP) is cheaper to produce than low-yield sulfite and, in the case of Millar-Western's Alkaline Peroxide Pulping (APP) process, pulp is obtained at a high brightness right out of the chip refiner. Other BCTMP installations use post-bleaching of CTMP with hydrogen peroxide.

Since BCTMP generally sells at ~15% below the price of comparable kraft pulp, papermakers are interested in trying it as a kraft substitute and BCTMP is moving into coated woodfree grades and printing & writing papers in Europe (Anon., 1992). Apart from the strength deficit of softwood BCTMP compared to softwood kraft pulp, the main disadvantage of this pulp is that it contains lignin. The lignin causes brightness reversion when BCTMP-containing paper is exposed to light. This reversion is inhibited, but not totally eliminated, in coated grades.

1.3 Closed Cycle Pulping

The Millar-Western Company recently began operations at its new closed cycle BCMTP mill at Meadow Lake, Saskatchewan (Evans, 1992). Within 3 months, the mill reached 95% of its target production -- a phenomenally successful start-up. If the mill continues to perform in this way to the end of the year, the feasibility of closed cycle operation for CTMP mills can be considered proven.

The profitability of closed cycle operations is something else; no cost figures are available for the Meadow Lake mill but these are expected to be somewhat higher than conventional BCTMP using the same wood furnish because of the extensive water treatment plant. Water use has been kept very low at Meadow Lake, but 13 m^3 of water still has to be evaporated for every ton of pulp produced. This compares with about 10 m^3/t which is evaporated from the black liquor in an average kraft mill. The difference is that a kraft mill has plenty of steam from the recovery boiler to drive the evaporation, whereas closed-cycle BCTMP mills must use electric power to operate the evaporators (or crystallizers).

1.3.1 How far off is a closed cycle kraft mill?

To answer this question, we must first recognize that we are dealing with two different problems:

(i) Closing an existing kraft mill.
(ii) Building a greenfield closed-cycle kraft mill.

The key factor for closed cycle operations is water consumption which must be brought to an absolute minimum if the economics and logistics of running with a closed loop are to be acceptable. There is little chance that any of the older pulp mills would be closed - water consumption is too high (Table 1). Even many of the pulp mills of modern design, like the Riocell mill in Brazil, still have effluent flows amounting to nearly 4 times the evaporator load at Meadow Lake.

So it appears that with one exception, *only greenfield kraft mills would be serious candidates for closed cycle operations.* The Ngodwana mill in South Africa was specially built for low water use (Coetzee et al., 1985), and represents an example of the type of kraft mill that could be closed; but it is unique. Besides water volume, of course, there are other steps to be taken before a closed-cycle kraft mill could be operated - namely:

- MINIMIZE CHLORIDE IONS IN LIQUOR LOOP
- PITCH CONTROL
- NON-PROCESS ELEMENT CONTROL

[Note: Meadow Lake has a purge of non-process elements because it is not presently recovering its pulping chemicals; an option which is not feasible for a kraft mill.]

2. HARDWOOD PULPS

2.1 Soda-Anthraquinone

This pulping process, although an *alternative* to kraft pulping, is not exactly emerging. It has emerged and has stalled. First proposed in 1977 (Holton, 1977), soda-AQ pulping is a proven alternative to kraft and now operates in roughly a dozen pulp mills around the world. The process is sulfur-free and works best with short-fibered hardwoods and annual plants.

Practically all the existing soda-AQ mills result from modification of earlier soda cooking operations. This brings benefits to a soda mill in terms of pulp strength, cooking rate and yield, all of which compensate for the cost of AQ. To my knowledge, there are no current soda-AQ operations which originally were kraft mills. Conversion of a kraft mill to soda-AQ offers no rate or yield improvements and, for long-fibered furnishes (softwood and eucalyptus), soda-AQ pulps are definitely weaker than kraft pulps.

In contrast, for short-fibered hardwoods, soda-AQ pulping offers a proven sulfur-free alternative to kraft pulping which produces an acceptable product. Conversion of an existing kraft mill to soda-AQ would entail capital and operating expenditures to expand the output of the lime kiln and recausticizing units by 20%. On the positive side, smoother recovery boiler operations can be anticipated in the fully-oxidizing soda furnace, leading to higher throughput.

Only a site-specific analysis can determine whether, after the cost of AQ has been deducted, the improved recovery operations would provide a decent return on the investment. Judging from the fact that no kraft mills have made this switch, we can guess that the return on investment does not look high enough.

For a greenfield mill, the size of the recausticizing unit is not an issue, but even so, the greenfield hardwood mills built in recent years have turned out to be kraft mills. Evidently the economics of greenfield soda-AQ mills are not impressive either.

2.2 Alcell® Pulping

In this technique, hardwood chips are exposed to an acidic (pH 3) alcohol-water mixture at 195°C (400 psig) which degrades and dissolves lignin and produces hardwood pulps at about 30 kappa. A considerable percentage of the residual lignin can be removed by an alkaline extraction and for that purpose oxygen delignification is particularly effective. Alcell® pulp strength is similar to that of kraft hardwood pulps from the same species (Petty, 1989), and some characteristics, such as opacity, are often superior.

True solvent processes, like Alcell®, do not use recovery boilers since there are no inorganic materials to recycle. After the solvent has been flashed off, lignin precipitates from the aqueous component of the pulping liquor leaving a carbohydrate solution.

The carbohydrate solution should be rather easy to dispose of as a cattle feed supplement, but the lignin is an important component in the economics and represents both a challenge and an opportunity for the true solvent processes. The absence of a recovery boiler (a big saving in capital cost) means that the true solvent techniques are heavy net energy consumers: the lignin "by-product" therefore needs to be credited with sufficient value to cover these energy costs, and this means using lignin for something other than hog-fuel. Here lies the challenge - to find new uses for lignin as a binder, resin extender, etc.

Since true solvent lignins are free of sulfur and sodium, they are well-suited to developing the special market niches which are required to establish the first North American solvent mills.

The absence of a recovery boiler means also that Alcell® units should be economically viable at a scale of about 300TPD and 550TPD units are said to offer the same return on investment as a world scale (1200TPD) kraft mill. The small scale should make Alcell® pulping attractive in situations of limited wood resources or capital availability. Another possibility is the addition of solvent pulping units alongside existing kraft mills, perhaps providing a hardwood furnish component so that a softwood pulp mill can become integrated with papermaking operations. In this case the existing kraft recovery furnace could possibly be used to recover the effluent from the oxygen stage in the solvent pulp bleachery.

[Note: The BOD output from a Alcell® bleachery could be relatively high unless the O-stage filtrate is recovered - this is a consequence of the high kappa number of Alcell® brownstock compared to kraft.]

Alcell® has practically completed its trials in a batch pilot plant running at about 15TPD. Larger scale trials are now contemplated in order to demonstrate improved recovery efficiencies for the methanol solvent (Maddern, 1991).

As happens with most new technologies, Alcell® is likely to begin commercial production into a niche market - producing special grades of lignin and a bleached hardwood pulp which might at first be captive. Whether Alcell® will become a serious competitor to hardwood kraft mills depends on (i) controlling solvent losses and making process refinements, (ii) expanding the markets for lignin, (iii) refinements still occurring in kraft pulping.

3. SOFTWOOD PULPS: ALKALINE SOLVENT PROCESSES

It should be no surprise that the two main alternatives to kraft in this category are emerging in Germany. No kraft mills were ever built in W. Germany because of concern over odor problems. Germany has an abundance of softwood and while German sulfite mills have thrived on pulping the spruce, much of the pine wood was exported. Some of this fiber was later re-imported from Scandinavia or Austria in the form of bleached kraft pulp. As a result, there has been for many years a sizeable effort in Germany to develop a process for converting the native softwoods to pulp of kraft quality without using reduced sulfur compounds.

Two solvent pulping processes have been extensively researched at pilot scale and one will soon be in commercial operation. Both use alkaline conditions, which so far seem to be essential to produce high strength softwood pulps.

3.1 Organocell

The Organocell process, soon to begin commercial operations (430TPD of fully-bleached fluff pulp) at Kelheim, uses a soda-AQ-methanol cook to obtain a pulp with a strength somewhat below that of kraft, but eminently suitable for fluff pulp. The Organocell mill resembles a kraft mill in many respects, except that (i) the continuous digester vessel has thick walls to withstand the extra pressure from the methanol vapor, (ii) the recovery furnace will be run in a fully oxidizing condition with very little smelt, but a heavy carryover of the sodium carbonate ash (it therefore needs an oversized electrostatic precipitator), (iii) there is a methanol recovery unit, (iv) the bleach plant is planned to be chlorine-free with the sequence OZP (medium consistency ozone).

The capital cost of greenfield Organocell mills will be about the same as that of a conventional kraft mill because although there is a need for high pressure equipment, flame-proof electrical gear and methanol recovery units, compensation is obtained in the form of a smaller, cheaper (fully-oxidizing) recovery furnace (Murrinen et al., 1989).

Organocell operating costs will exceed those of kraft because of the need for nitrogen padding, AQ addition (adds about $17/ton pulp) and increased lime usage. There will also be power and steam costs to operate the methanol recovery, but no "make-up" methanol is anticipated. That is because methanol is generated during alkaline pulping and it is expected that this source will balance the solvent losses.

3.2 ASAM

Alkaline sulfite anthraquinone methanol pulping is the only emerging pulping process which can produce softwood pulps that consistently exceed kraft pulp strength (Zimmerman et al., 1991). Pulp viscosities are remarkably high, as a result of the low alkalinity at which the cooks are carried out (Kordsachia, 1988; Zimmerman et al., 1991). The pulps also have good bleachability (Zimmerman et al., 1991) and can be cooked to low kappa numbers (Patt et al., 1990).

The disadvantages mostly lie in the cost of liquor preparation and chemical recovery. Besides the usual extra costs associated with solvent pulping (pressure vessels, flame-proof items, nitrogen padding, solvent rectification column), ASAM also needs a full sulfite recovery system plus a Tomlinson recovery boiler, lime kiln and recaust unit (Fuchs et al., 1991). In fact, ASAM needs 3 separate recovery loops (Fig. 1) to recover methanol, caustic and sodium sulfite. Even though the lime kiln and recaust unit can be much smaller than for kraft, the additional items are expected to raise the capital cost of an ASAM plant 10-20% above that of kraft (Maddern, 1991). Operating costs at first sight also appear to be higher: the AQ alone adds about $17/ton of pulp. The inorganic chemical charge is also higher and so is the digester operating temperature: both of which increase the operating costs compared to kraft. However, much of the increase is compensated by the higher bleached yield of ASAM pulp (45.5% vs. 43.5%). These yields are calculated from data in Zimmerman et al., (1991) after allowing for recooking of rejects.

In summary, while ASAM makes excellent pulp, the process is definitely the most complex of all the emerging technologies and the capital cost is therefore likely to be high. Operating costs are likely to be somewhat above kraft unless TCF pulps are being produced, in which case ASAM's low kappas and good bleachability become very significant.

CONCLUSIONS

The kraft process has gradually risen to its present dominance as a result of continual refinements in the last 100 years. There have always been competing processes which looked good at laboratory scale but few managed to remain promising after extended pilot trials. Of the six competing processes discussed here, none seems destined to replace kraft as the major source of virgin chemical pulp for papermakers.

Soda-AQ pulping will stay restricted largely to non-wood pulping and a handful of hardwood mills. Once non-chlorine bleaching of kraft pulp is made cheaper, acid sulfite pulping will lose its only current advantage over kraft. BCTMP will continue to nibble at the kraft pulp market, but in many paper grades it cannot be used as a substitute. The Alcell® process will find a niche in locations where its small economic size is important; development beyond that point will depend more on finding outlets for the lignin rather than cellulose. The hybrid solvent processes Organocell and ASAM are very significant in Germany where kraft mills are not welcome and emission regulations are strict. Neither technique seems capable of directly challenging kraft - nonetheless the start-ups of these processes in Germany will be followed with keen interest in N. America.

References

Anon., PPI This Week, 25-29 May, 1992 Vol 7, 21.

Coetzee, B., Davies, C. J., Mera, F. E. and Swift, L. K., Tappi J., 68(4):92-97(1985).

Evans, T., Presentation at CPPA Pacific & Western Branch Meeting, Jasper, Alberta, May 1992.

Fuchs, K., Rimpi, P. and Brown, C., TAPPI Pulping Conf., Orlando, FL, 1991, p. 259.

Holton, H. H., US Pat. 4,036,681. July 1977.

Holton, H. H., Pulp Paper Can., 78(10):T218(1977).

Kordsachia, O. and Patt, R., Holzforschung, 42(3):203(1988).

Maddern, K. N., Int. Conf. on Bld. Kraft Mills, Melbourne, Australia, 4-7 Feb, 1991, p. 81.

Murrinen, E., Sohlo, J., Vanhanen, T. and Kivela, E., 1989 TAPPI Wood & Pulping Chemistry Symposium, p. 223.

Patt R., Schubert, H.-L., Kordsachia, O., Oltmann, E., and Ridder, W., "The ASAM Process - Competitor to Kraft Pulping?", 7th Sunds Defibrator Tech. Seminar, Pori, Finland, Sept. 1990.

Petty, G., Paper Technol., 30(2):10(1989).

Zimmerman, M., Patt, R., Kordsachia, O., TAPPI Pulping Conference, Orlando, FL, 1991, p. 115.

TABLE I

EFFLUENT VOLUMES DISCHARGED BY PULP MILLS			
		m^3/ADMT	USgal/ADT
BCTMP MILLS	Whitecourt, Alberta	22	5,300
	Meadow Lake, Saskatchewan	12-14*	2,900-3,400
KRAFT PULP MILLS	Older Mills	80-300	19,000-72,000
	Alberta Pacific, Alberta	~58	~14,400
	Riocell, Brazil	47	11,280
	Ngodwana Kraft Mill, Republic of South Africa	8-10**	1,920-2,400

* This effluent is discharged to a holding pond and is completely recycled.

** This effluent is used for irrigation of grasslands.

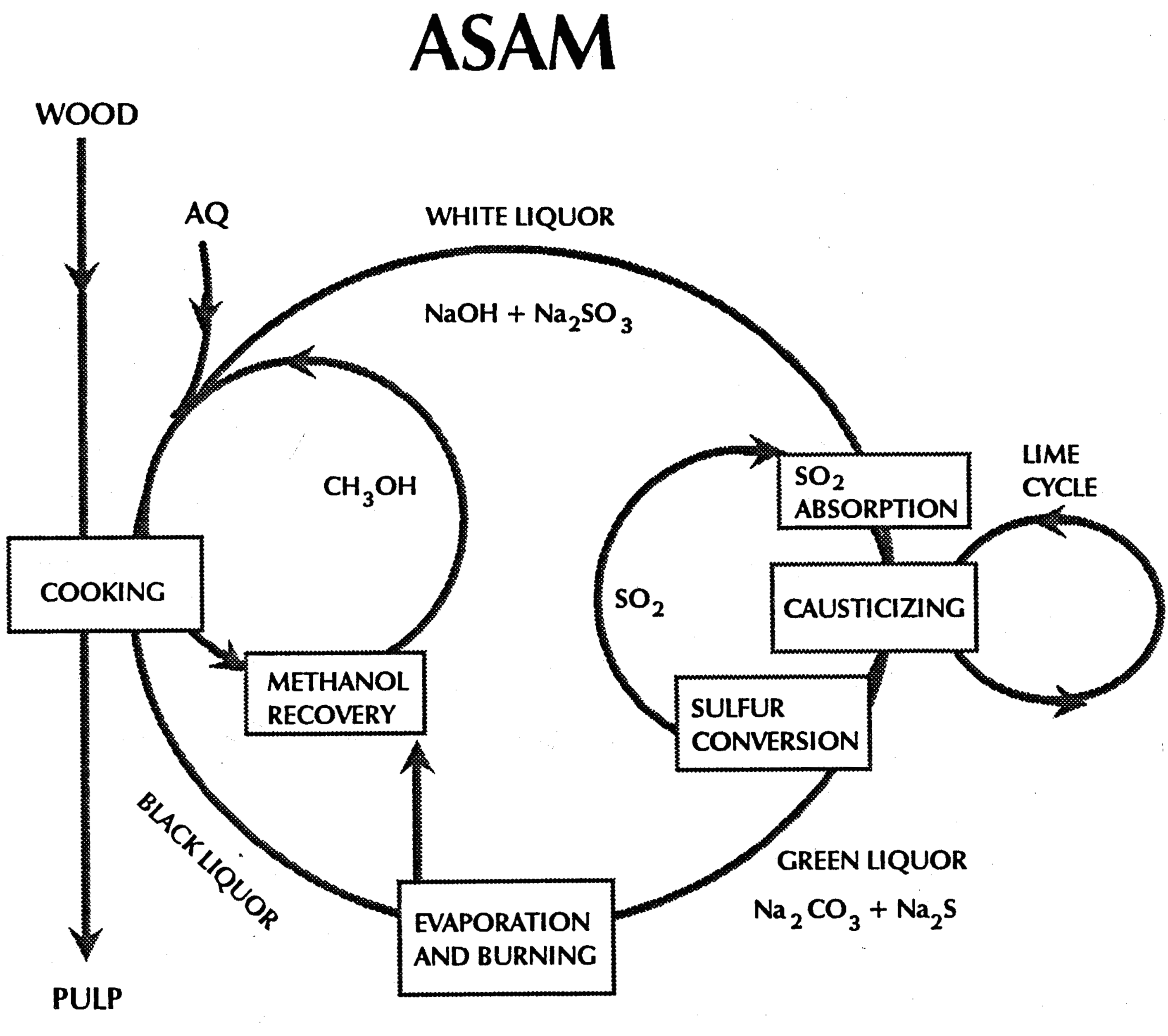

Fig. 1 Chemical Recovery Cycles for an ASAM Pulp Mill