

Enzymatic Pretreatment during 15th to 18th Century Papermaking in Europe

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Enzymatic pretreatment of cellulose is generally considered to be a new area of research, but in fact it was a standard step in European pre-industrial papermaking between 1300 and 1800. Specialized handmade papers are routinely prepared in our Center for use in the care and conservation of rare books and manuscripts. Our attempts to replicate some of the early papers have led us to an investigation of retting (or fermentation) of hemp and cotton fiber as a pre-beating step. Results of twenty-two production runs show that increased fermentation time gives increased Canadian Standard Freeness and improved formation quality while permitting a decrease in beating time.

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Pretreatment of wood chips and other raw materials has seen a good deal of interest in modern machine papermaking as the costs of energy, chemicals, and wastewater treatment have gone up. More importantly perhaps, interest in renewable energy sources is driving academic research in the pretreatment of cellulosic materials to facilitate conversion to sugars, which can then be used to produce ethanol, butanol, or other biofuels and other monomeric chemicals. Enzymatic techniques are one of the approaches under investigation. (See, for example, Taherzadeh and Karimi 2007, "Enzyme-based hydrolysis processes for ethanol from lignocellulosic materials: A review," *BioResources* 2(4), 707-738). In addition, researchers are considering the enzymatic pretreatment of cellulose fibers for use before mechanical preparation of nanocellulose. (For instance, see Pääkkö *et al.* 2007, "Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels," *Biomacromolecules* 8, 1934-1941). In all these cases, issues of space and time in processing scenarios persist, but the idea of getting various strains of microbes, and the enzymes they produce, to help with delignification and other aspects of fiber preparation seems like a new idea.

What many do not realize is that the enzymatic pretreatment of fiber was in routine use in papermaking for centuries in Europe before the invention of the paper machine, and very likely before then in the Islamic world and in Asian papermaking.

Pre-industrial papermaking in Europe between 1300 and 1800 used linen, hempen, and sometimes cotton textile rags as a raw material for making quality writing and printing papers. For such fibers, delignification was not really the goal. Instead, the process of "fermentation" or "retting" was used in part as a cleansing process; to rid the rags of bits of food, bodily fluids, and other non-cellulosic residue. Thereafter, the process, if taken to the right point, reduced beating time and improved drainage rate (or freeness) and formation quality with limited reduction in yield.

My own recent research has focused on recreating some of these historical processes, in an attempt to produce handmade papers that are more similar in appearance and feel to historical papers than commonly available handmade papers. These modern handmade sheets are used in the conservation and repair of rare books and works of art on paper, and thus the new paper needs to be as similar as possible to the old paper.

While non-destructive analysis of historical papers has revealed that the longer lasting historical sheets had higher levels of calcium and gelatin in them, making modern handmade paper with similar ingredients doesn't yield sheets with the desired aesthetic properties.¹ So if it is not the ingredients in the sheet, what is it? My suspicion is it is connected with the production routines used to make the paper. In particular, a three-person team could make 2,000 or more sheets in a day. In that atmosphere, skilled workers left the paper with various marks and imperfections in the midst of a well-executed, uniform, high quality piece of paper. So how would one produce those same qualities today? Our latest efforts have focused on literally trying to make 2,000 sheets in one 10-hour workday using only the old hand processes.²

We haven't been able to do it, at least not yet. The main issue is freeness. No matter how skilled the artisans, they could only work as fast as the pulp would drain. Interestingly, many centuries later modern day papermakers are still dealing with exactly the same challenge, which is to get the water out of the freshly formed sheet as soon as possible in order to make a certain amount of paper in the shortest possible time.

We work with new textile quality hemp and cotton fiber. Tough and strong, it resists beating and tends to make a slow draining sheet, even in heated water. The old rags used during the history of the craft on the other hand, responded quickly to beating and yielded a fast draining pulp and a well-formed sheet.

We need to get the same quality of prepared pulp from new fiber because reliable sources of old linen and hempen rag free of synthetic fibers are unavailable. So we cut the textile quality fiber, which we receive in sliver form, into 1.5 to 2 mm lengths. This helps, but we still don't get really even formation at the vat with laid and chain lines showing clearly. In one experiment, a 50-50 mixture of hemp and cotton fiber, (cooked unpressurized in a 0.4% calcium magnesium hydroxide solution for 3 hours) required 160 minutes of beating in our Hollander beater and gave us a corrected Canadian Standard Freeness of 240 mL. (Fig. 1). A specially selected old, well-worn and tender linen tablecloth was fully beaten in only 20 minutes, gave a CSF of 400 mL, and showed superior formation quality (Fig. 2).

But since we don't have access to the old rags in quantity, to gain more freeness and better formation quality, we have been experimenting with fermenting our 50-50 hemp cotton fiber blend for up to three months; 4.540 kilos (10 pounds) of the fiber mix is soaked in 60 L of chlorine-free hard water mixed with 60 grams of lime (calcium magnesium hydroxide) and 300 mL of fragrance- and brightener-free liquid laundry detergent (added to aid in wetting out the fiber).

¹ For a report on our recent research on historical papers see <http://paper.lib.uiowa.edu/index.php>
For an overview of historical methods see <http://paper.lib.uiowa.edu/european.php>

² See our two videos by searching "Chancery papermaking" at youtube.com.



Fig. 1. 50-50 hemp/cotton unfermented



Fig. 2. Old linen rag



Fig. 3. 120 day fermented 50-50 hemp cotton

The ferments are mixed up in 44 gallon Continental Huskee plastic waste containers. Once mixed with the solution, each ferment is covered with a disk of 2 mil sheet plastic, and any air bubbles are worked out to the edge to minimize mold growth at the surface. The ferments are stirred every week or two, but otherwise left to ferment on their own. We term this a “wild” ferment, as no cellulosic enzymes or microbe cultures are added to the ferments. The obvious (from the smell) activity is likely due to airborne microbes or strains left over from the original retting of the hemp fiber undertaken to separate the bast fiber from the stalk of the plant. The ferments are ended with a three hour unpressurized cook in a 0.4% lime solution, 6% fiber on solution.

The following plot (Fig. 4) shows the positive effect of increased fermentation time on CSF and beating time over the course of processing twenty-two 4.54 kg batches of fiber (each yielding about 300 sheets of paper). CSF increases and the required beating time decreases. Normally formation quality would decline with a decrease in beating time, but as a result of the fermentation step, it too improves (Fig. 3). Not shown here is the impact on mechanical properties. Sheets made from well-fermented pulp are almost certainly weaker, but that is secondary to the needed improvement in aesthetic properties. Two of the twenty-two batches were monitored for yield and showed minimal loss of finished paper weight over the starting weight of the raw fiber.

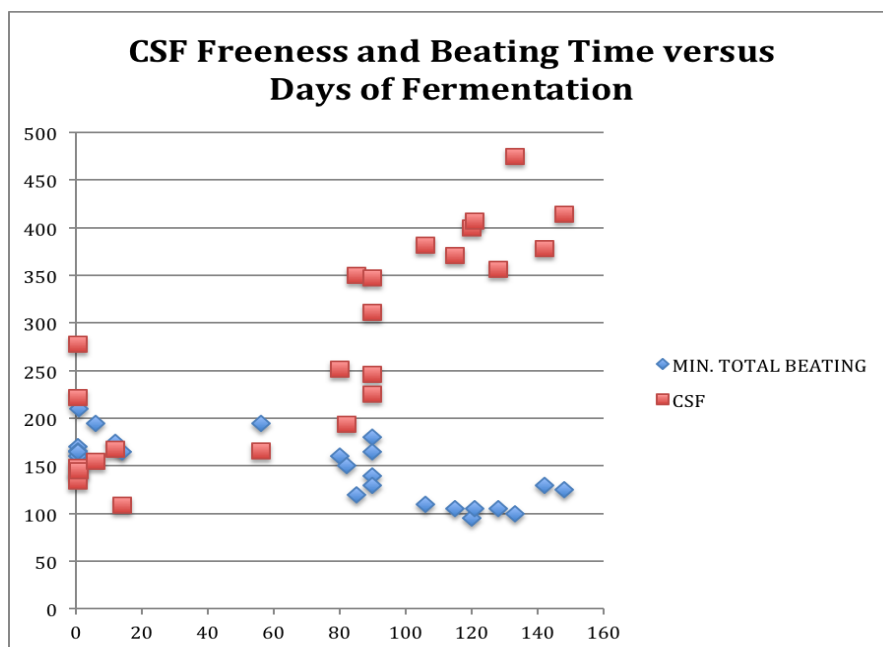


Fig. 4. Freeness and required beating time as a function of fermentation time

As research progresses in the field of enzymatic pretreatment of wood chips, agricultural waste and other forms of cellulose, a look at the history of the craft, and the impact of earlier techniques on the fiber and the permanence and durability of paper may be worthwhile, if not profitable.

For an example of contemporary research related to this editorial see Eriksson *et al.* 2009, “Freeness improvement of recycled fiber using enzymes with refining,” in: *Enzyme Applications in Fiber Processing*, ACS Symp. Ser., Vol 687, Ch. 4, pp. 41-54.).