

The Chemical Engineer—

His Role in the Future Design of Pulp Processing Equipment

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The pulp and paper industry is one of the oldest manufacturing processes known to man and, like the metallurgical and textile industries, developed, of necessity, as a highly skilled art long before technology had advanced to the point where it could play an important role in that development. The first significant technological contribution came in the field of mechanical engineering with the invention of the Fourdrinier paper machine early in the nineteenth century. Late in the nineteenth century and early in the twentieth century the role of the chemist was primarily in the control laboratory, monitoring the processes developed by mechanical engineers. Since chemical engineering did not emerge as a profession until after World War I, its impact on the industry has only begun to make itself felt recently.

The chemical engineer cannot make his maximum contribution to the paper industry until the industry itself recognizes that the conversion of wood and other cellulosic materials into purified cellulose fiber involves a series of chemical engineering operations. The physical and chemical variables involved in pulping and bleaching not only control the rate of delignification; they also control the rate of degradation and solution of cellulose and hemicellulose. It is essential that the engineer evaluate each of the variables having an effect on quality and yield in the particular stage of processing in question. Furthermore, the equipment used to carry out the vari-

ous stages of processing must be so designed that each of the variables can be accurately controlled at pre-determined optimum levels.

At the present time most of the equipment available to the pulp mill for pulping, washing, bleaching, etc., was designed long before there was any real understanding of the variables controlling the operations. There have been very fine mechanical improvements in equipment, such as the conversion of the digester from batch to continuous operation, the introduction of high intensity blending units ahead of the chlorination towers, etc., but, fundamentally, there has been little thought given to quantitative process design.

Let us take, for example, kraft pulping, a process with which the writer is most familiar. The kraft batch digester was originally designed simply as a pressure vessel to withstand 100-125 psi, to hold the maximum weight of wood chips, and to provide a cone bottom, blow valve and blow line to remove the processed material as rapidly and completely as possible. Production considerations required that the maximum weight of wood chips be packed into the digester. Chemical recovery considerations required that the minimum liquor ratio (usually 3.5 to 4.5 lb. of liquor and wood moisture per lb. of dry chips) be used. Earlier use of liquor circulation pumps and indirect liquor heaters was abandoned in favor of direct steaming into the bottom of the digester. Steam generating capacity of the mill's boiler plant dictated the speed with which the digester contents could be brought to maximum cooking temperature.

Fortunately for the industry, this kraft batch digester constitutes an almost "foolproof" system capable of producing salable pulp. It is true that temperature and chemical concentration differences in the digester occur, caused by

steam and hot liquor channelling through the random voids in the densely packed chip mass, which bring about variations in yield and quality in a single digester charge and between digester charges. However, these differences in quality and yield are blended into a uniform salable pulp mixture by the intense mixing in subsequent processing.

Usual mill practice requires 1.0 to 1.5 hr. to bring the digester to its maximum steam pressure of 100-110 psig (170-173°C). However, delignification begins considerably before this maximum pressure is reached, probably at about 155-160°C. It has been shown that, by the time maximum temperature has been reached, total yield is about 60 per cent and about 60 per cent of the original lignin in the wood has been dissolved. Furthermore, 0.20-0.25 g of Na₂O are consumed per g. of wood dissolved. Therefore, by the time maximum temperature has been reached, the concentration of Na₂O in the cooking liquor, initially at about 50 gpl., has been reduced to about 18 gpl. It becomes apparent that at no time during the cook is there a combination of high temperature and high chemical concentration which might bring about serious damage to the pulp. This does not imply that the batch process produces pulps of maximum yield and quality; it simply indicates that, in spite of carelessness in maintenance of chip quality, liquor concentration, temperature and time schedules, a salable pulp can always be produced.

An early misconception of the physical and chemical mechanisms involved in pulping, whether with alkaline, acid or nearly neutral liquors, led to the extended cooking cycles used in batch pulping and in many of the continuous digester systems. It had been thought that extended periods at slowly rising temperatures must be provided in order that the cooking liquors

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could completely penetrate the wood chips before temperatures reached a sufficiently high value for delignification to proceed at an appreciable rate. During the past fifteen years experimental data have been published showing that this theory of complete penetration of liquor into the chips followed by delignification is not correct. In fact, if complete penetration of the cooking chemicals had occurred during the temperature rise period, particularly in the kraft process, very serious damage to cellulose quality and yield would have resulted. Under such circumstances, the cooking liquor at its high initial concentration would have penetrated into the fiber lumens and been in direct contact with cellulose at the time when temperature reached its maximum value. It would have been necessary for the pulping chemical to diffuse through the cell wall in order to attack the lignin in the middle lamella. Such a mechanism would have resulted in much lower yield and quality of pulp than are actually realized.

The true mechanism of pulping involves a moving, or penetrating, reaction interface of delignification. This interface begins its movement from the chip surface toward the chip center as soon as temperature is sufficiently high for delignification to begin. As temperature increases further, speed of movement of this interface toward the chip center increases. At any specified moment during the cooking cycle, the leading edge of this reacting interface is in contact with wood in its original form. Behind the interface, toward the original chip surface, is a reaction zone in which the cellulose fibers are at different degrees of delignification, varying from a minimum lignin content at the surface to a maximum at the interface itself. Within this zone of reaction, fresh chemical is diffusing from the main body of liquor, through the zone to the interface. Reaction products are diffusing outward from the reaction interface to the liquor outside the chip. Concentration drop in either fresh chemical or reaction products is not simply a matter of concentration gradient to supply driving force for the diffusion. There are concentration decreases in active alkali and concentration increases in reaction products across the zone due to the reactions taking place throughout the zone. It is quite possible, if chip cross-section is

sufficiently great, that fibres on the chip surface will be completely delignified and subject to degradation and dissolution from contact with the fresh chemical while fibers at the chip center have not yet been contacted by the reacting interface.

These considerations indicate the extreme importance of providing maximum wood surface and minimum cross-section through which the reacting interface must travel to delignify the fibers at the center of the chip. It becomes apparent that the ideal wood chip might be one half to three quarters of an inch long and only three or four fibers in cross-section. Of course, it is impossible to produce such a chip from the whole log. However, such a condition is approached in the case of bagasse which has been well depithed before pulping. Here we have very long, slim vascular fiber bundles which can be converted into high quality cellulose under very mild cooking conditions at constant temperature in ten minutes or less.

The ingenuity of the chemical and mechanical engineer might well be applied toward this goal of maximum chip surface and minimum cross-section without incurring excessive mechanical damage to the fibers in the process. A first step in this direction, chip shredding, has already been thoroughly described in the technical literature. This chip shredding is really an extension of the chip carding which takes place in the chipper. The shredding operation takes advantage of shear planes along the grain of the chip caused by the wedge shaped knives of the chipper. It is possible to reduce chip cross-section to the range of 6, 7 to 1.6 mm without significant breakage across the grain. However, any further reduction in cross-section of the green chips will result in excessive mechanical damage to fibers. Shredded chips are slightly less voluminous than conventional mill chips and the usual liquor-wood ratios of 3.5:1 to 4.5:1 can be used satisfactorily.

Much greater reduction in chip cross-section can be accomplished if one takes advantage of the fact that lignin becomes soft and the chips become very flexible at high temperatures. If mill size or, preferably, shredded chips are cooked at a constant steam pressure of 120-160 psi for about 10 min. in slightly alkaline solution of Na_2CO_3 or Na_2SO_3 to about

80 percent yield, they can then be fiberized into long, slim fiber bundles resembling depithed bagasse and transferred to a second digester for completion of the cook. The two stages of cooking and the intermediate fiberization should be carried out at constant steam pressure. The same chemical may be used in both cooking stages or two different but compatible chemicals may be used in each stage.

This fiberizing technique can be carried out with no mechanical damage to the fibers and at very low expenditure of energy. It opens up new possibilities as to yield, quality and uniformity of pulp fibers but also involves entirely new principles of equipment design.

The fiberizer, an attritioned mill, must be designed so that the casing can withstand steam pressures in the range of 100-200 psi. Rotor and stator should be equipped with toothed rather than bar plates and fibrillation should be carried out at high density, in the range of 15-25 percent consistency. Under such circumstances, very high plate clearances can be used, 0.16 in. or more depending on feed rate. This insures that the mechanical treatment will consist of a rubbing action between softened chips to reduce them to fiber bundles, thus avoiding fiber cutting.

This advantage of enormously increased reaction surface and decreased cross-section carries with it the penalty of great increased bulk of the solid phase. Liquor-wood ratios of 12:1 to 14:1 must be used, in contrast to the 3.5:1 to 4.5:1 used for conventional chips. However, if a properly designed screw press is installed at the second-stage digester outlet, the cooked pulp can be compressed to 35-40 percent consistency and the required portion of the expelled black liquor, at digester temperature, can be returned to the digester inlet and mixed with the fiberized product from the attrition mill. Makeup chemical can be added at high concentration at this same point of mixing. Excess black liquor, over that required for the feed-back to the digester entrance, should be sent to the black liquor evaporators. A simple material balance will show that, in spite of the very high internal liquor ratio used, the volume of black liquor to the evaporators is less than when conventional liquor ratios are used with batch digesters and blow pits.

All of these considerations indicate that the pulp digester of the future, instead of being simply a pressure vessel to hold densely packed chips in contact with cooking liquor at poorly controlled temperature for sufficient time to achieve a varying degree of delignification at a cost of considerable degradation and solution of cellulose fibers, will become a carefully designed chemical reactor. Varying degrees of fluidity in the chip-liquor mixture can be attained by taking advantage of the fact that the wood chips or partially cooked chips can be drained very easily, thus replacing cold liquor with hot liquor, or replacing one type of liquor with another at constant pressure. Such liquor interchange can be accomplished with thoroughly softened or fiberized chips, where drainage is poor, through the use of screw presses. It thus becomes possible to use any desired high liquor-wood ratio in any unit of the digester system without sacrificing the low liquor-wood ratio necessary for efficient chemical recovery.

Accurate reactor design requires exact knowledge as to the effects of temperature, concentration, wood surface and time on rate of delignification and on rate of degradation of cellulose and hemicellulose. All of these variables except wood surface can be evaluated in experimental equipment. The wood surface variable can be handled by making surface so large, through fibrillation of softened chips, that this variable becomes, substantially, a constant in the kinetic equation for reaction rate. Once the reaction variables have been evaluated it becomes possible to carry out the pulping reactions at constant, carefully controlled temperature at controllable initial and final chemical concentrations, with the result that uniform pulps of high yield and quality can be realized in very short processing times. The increased volumes required by increased internal liquor-wood ratios can be more than compensated for in the greatly reduced reaction time. The net result will be considerably smaller units than those used in conventional digesters.

Efficient design of these new digester systems, or chemical reactors, can only be accomplished by close cooperation between the chemical engineer, with detailed knowledge of the effect of the variables on reaction rate, and the mechanical engineer skilled

in the physical design of the reactor components. It is through such cooperation between these engineering groups that modern pulping equipment, capable of accurate, automatic control, can be made available to the pulping industry. The design of digester systems for kenaf, bagasse and other annuals will probably differ widely from those using wood chips.

The chemical processes available for the delignification of cellulose materials should be reviewed, in the light of research data and processing techniques made available during the past several years. An example of the adaptation of new information to pulping can be found in the Sivola and other two stage bisulfite and acid bisulfite processes. In the first stage of cooking, hemicelluloses are stabilized by slightly alkaline liquors such as sodium sulfite or carbonate. Liquid SO_2 is added in the second stage, creating a cooking liquor at starting pH anywhere from about 5.0 down to 2.0. Magnesia base may be used instead of sodium, with the one exception that a slightly acid condition must be used in the first stage.

With these acid processes, a wide variety of pulps may be produced, ranging from high purity dissolving pulps, through book and bond grades, all the way to fiberized pulps for liner and bag grades. Yields as high as 65 to 70 percent may be realized in the coarser grades of pulp. However, in all of these acid processes, the tearing strength of the resultant pulps is inferior to that attained by the kraft process.

When single or two stage acid processes are applied to the Southern pines, high yields of 65 to 70 percent can be realized but all strength characteristics of pulps are inferior to kraft. These Southern pines, with their coarse, stiff fibers are particularly adapted to the higher strength pulps used in liner board and industrial bags. The kraft process has always been used for these grades. However, at yields above 50-52 percent, burst and tensile strength of the kraft pulps diminishes rapidly, while tear strength increases. Yield can be increased to 56-57 percent through H_2S additions in a preliminary treatment or by additions of polysulfides to the liquor. These high yield pulps are high in strength but the additional sulfides in the system create recovery problems

and increase the air pollution problem.

Recent work by the author indicates that southern pine pulps as strong as fully cooked kraft but in yields of 62-63 percent might be realized by cooking with Na_2SO_3 solutions. These cooks are on the slightly alkaline side, with an initial pH of 8.5-9.0 and a final pH of 7.8-8.1. However, delignification rates are quite sluggish, requiring temperatures in the range of 180-190°C in single stage cooking. Preliminary work indicates that two stage pulping with fiberizing between stages might be carried out at constant temperature in the range of 175-180°C at total cooking times of only 40-60 min. The combination of decreased temperature and greatly reduced contact time between cellulose and liquor should result in high strength pulps of high yield. It should be possible to use any desired combination of sodium sulfite and carbonate in either of the two stages.

The very sharp increases in wood cost that can be anticipated in the next few years make it imperative that all available pulping chemicals be re-examined for their possibilities in producing higher yield pulps of good quality. Combinations of the sulfites and mixtures of sulfite and carbonate should be explored. Even the old hydrotropic pulping process, using sodium xylene sulfonate, should be reviewed. It might be used in combination with fiberizing techniques, with possible additions of Na_2SO_3 or Na_2CO_3 to prevent acidity in the latter stages of the cook. Any of these processes would have the additional advantage of eliminating the air pollution problems involved whenever the sulfide ion is used in the cooking liquor.

Pulp washing, the next step in pulp processing, should also be examined critically by the chemical engineer. At the turn of the century and shortly thereafter, the old diffuser washers, requiring retention tanks of very large volume and complex shifting of counter-current wash liquor flow, were popular. Later, these diffuser washers were replaced by vacuum drum washers. Here, equipment designed for non-compressible metallurgical materials, was applied without major design changes, to the washing of cellulose fibers, a highly compressible material. It must be remembered that par-

tially or completely delignified fibers are flexible tubes, closed at both ends. The hollow center, or lumens, of these fibers are quite voluminous. One pound of dry fiber will hold, within its walls, about four pounds of liquid. As the cooked fiber leaves the digester, this liquid is black liquor of the same concentration of solids as the black liquor surrounding the fibers. On the first stage of vacuum washers, the fiber-black liquor suspension is changed from a suspension of less than one per cent consistency in the vat to a cake discharge consistency of 13-14 per cent. None of the black liquor inside the fibers can be removed until a consistency of at least 20 per cent has been reached. The only way this internal black liquor can be removed is by diffusion through the cell wall into the more dilute wash water surrounding the fibers. This diffusion requires a definite time interval to approach equilibrium, a much longer time than that provided on the washer drum or in the pulp mixer between washer stages. As a result of the characteristics of these vacuum washers, unnecessarily large amounts of black liquor leave the washing system in the pulp and, in subsequent screening operations, are eventually lost to the sewer. These losses, after three stages of washing, may amount to 60 lb. or more of equivalent salt cake loss per ton of pulp.

At the present time there is a trend back to diffuser washing through the use of cross-flow washing in the bottom sections of continuous digesters and in specially designed, continuous diffuser washers. However, the writer feels that the most efficient washing equipment lies in properly designed screw presses which can take advantage of the compressible nature of cellulose fibers. The first stage of a screw press can be fed at consistencies of 3-5 per cent in contrast to the 1.0 per cent or less required by vacuum washers. Pulp fibers can be discharged from the press at about 40 per cent consistency. (Discharge consistencies much higher than 40 per cent are attainable but increased power expenditure at these higher consistencies are not justified by the slight improvement in washing efficiency.) At 40 per cent consistency, the liquor inside the fibers has been reduced from 4.0 lb. of liquor per lb. of fiber to 1.5 lb. This involves a flattening

out of the fibers with a 62 per cent reduction of lumen volume. If, at the discharge end of the press, the compressed fibers are mixed with dilute wash water, with the exclusion of air, the fibers will expand to their original volume diluting liquid will be drawn into the lumens and the equivalent of almost instantaneous diffusion takes place. Three stages of screw presses in series, with counter-current washing, can result in only 15 lb. equivalent salt cake loss per ton with no higher dilution ratios than now used in vacuum washers. Total retention time in the three stages is about three minutes. If four stages of screw presses are used, salt cake losses can be brought to a very low value and the stream pollution caused by inefficient pulp washing can be brought to a very low level.

Screw presses have been used for many years in the pulping industry. However, they have been designed by mechanical engineers, with little thought being given to the compressible nature of the fibers. These characteristics of compressibility and resiliency of cellulose fibers can be used to great advantage in press design. Another characteristic of fibers, somewhat similar to pulp freeness, has been ignored in press design. As pulp fibers are compressed into a cake, a definite time interval is required for the expelled liquid to flow from the interior of the cake to the drainage screen where it is removed from the system. This drainage time is characteristic of the fiber being handled, having a minimum value of coarse pine fibers, increasing for northern conifer, sulfite pulps, and reaching a maximum for groundwood pulps. This drainage time governs the retention time that must be allowed for the cake to reach the desired terminal consistency and dictates the length of the compressing section of the unit. These retention times of the various fibers can be accurately evaluated in the laboratory without the use of a screw press. Such information is essential to efficient press design.

It can thus be seen that the chemical engineer can put his knowledge of unit operations and diffusional processes to work in producing the most efficient pulp washer. Here, again, the chemical and mechanical engineer must work together to produce the best possible combination of process and mechanical design.

Pulp bleaching with various oxidizing agents and intervening caustic extraction stages should be re-examined from a chemical engineering standpoint. New processing tools, unknown when conventional bleaching stages were developed, are now available and permit exploration of entirely new processing techniques which can drastically shorten the bleaching cycles, permit accurate automatic control and greatly reduce the loss of chemicals to the sewer.

About fifteen years ago, it was demonstrated on both a pilot plant and commercial scale that the attrition mill could be used to blend small amounts of bleach solution (peroxide) very uniformly into high density pulp. The unbleached pulp, pressed to 40 per cent consistency, was fed to an attrition mill, equipped with toothed plates, whose rotor and stator were oriented in the horizontal plane. This permitted feeding the comparatively dry pulp by belt conveyor into the top of the mill. The first few rows of teeth on rotor and stator carded the dense pulp into very fluffy fibers. Bleach solution was metered into the mill at three points on a circle about half the distance between the inner and outer circumference of the plates. In the case of peroxide bleaching, only about 0.2 lb. of bleach were added per lb. of dry pulp, bringing the mixed consistency to 33 per cent. This technique permitted the bleaching of groundwood pulp in 45 min. instead of the usual 4.0 hr. required when 10 per cent consistency was used.

The same procedure was used in single stage bleaching of well cooked kraft pulp to produce semibleached pulp. Here it was found that heat of reaction controlled consistency. It was found necessary to dilute the bleach solution so that terminal consistency was 18-20 per cent in order to provide sufficient heat capacity so that terminal temperature did not exceed 38°C. Even at this reduced consistency, bleaching time was 7.0 min., as compared to 60 min. at the conventional 10 per cent consistency.

This combination of the attrition mill and the screw press can be exploited in all stages of bleaching. In chlorination, terminal consistency will have to be in the 8.0-10.0 per cent range because of the low solubility of chlorine in water. However,

chlorination can be carried out in the range of 1.0-2.0 min., and the chlorination tower can now be replaced by a variable speed screw conveyor. An ORP cell located at the discharge end of the conveyor can automatically control conveyor speed to provide the desired chlorine consumption. The chlorinated pulp is then passed through the screw press, compressing the pulp to 40 per cent consistency. The expressed liquor can be stripped of its chlorine content by steam stripping, the chlorine being reabsorbed in water for reuse.

The caustic extraction stage following chlorination can be modernized in a similar manner. Until rather recently caustic extraction had been considered as a simple extraction of chlorinated lignin in dilute alkali. Actually, this extraction is a two-stage process. In the first stage the chlorinated lignin reacts with NaOH to form the sodium salt which is soluble in dilute alkali. It is in this stage that pH drops sharply from an initial value of 12 or higher to a final value of about 9.5. The second stage of extraction consists of the solution of the sodium salt in dilute alkali.

Taking advantage of these principles, the chlorinated pulp at 40 per cent consistency is passed through the attrition mill where it is mixed with caustic solution at a strength of about 3.8 per cent NaOH. Since only 0.2 lb. NaOH are required per lb. of dry pulp, terminal consistency will be 33 per cent. Retention time of this high density mixture in a variable speed screw conveyor can be controlled by pH electrodes at the conveyor discharge, setting conveyor speed to achieve a terminal pH of 9.5. The reacted pulp can then be diluted to any desired consistency between 3.0 and 10.0 per cent, to carry out rapid solution of the sodium salt of chlorinated lignin. Finally, the extracted pulp is screw pressed to 40 per cent consistency. Under these conditions, the complete caustic extraction process can be carried out in 10 min. or less, in contrast to the 60-90 min. now used at 10 per cent consistency. It will probably be advisable to carry out complete removal of lignin from the pulp in two chlorination stages, each followed by caustic extraction. This complete removal of lignin by chlorine is advisable so that subsequent stages using hypo, chlo-

rine dioxide or chlorine dioxide and peroxide can bring about maximum brightening effects.

In using chlorine dioxide or peroxide, tower retention will probably still be required because of the low bleaching rates of these chemicals. However, high density mixing of bleaching agent with pulp should be done in the attrition mill to keep retention time at a minimum. It is felt that further exploration of peroxide as a brightening agent as well as a stabilizing agent against color reversion will produce profitable results.

The chemical engineer must keep an open mind and use an imaginative approach in the improvement of existing pulping and pulp processing methods as well as in the development of new processes. He must not only improve the efficiency of utilization of wood; he must explore the use of the annuals as a source of cellulosic materials. These annuals, while usually yielding much higher tonnages of cellulose per acre than tree plantations, generally require some degree of pith removal. Also, since harvesting of these annuals can be carried out in only a small part of the year, efficient methods of storage must be developed so that the crop can be utilized throughout the whole year. These annuals will become increasingly important as urban and industrial development encroach on forest areas and as land taxes on forest acreage increase.

The engineer, in all of his research and development work, must keep in mind the social responsibilities involved in such work. He must continually strive to minimize or eliminate air and stream pollution in the area of his industrial operations. In addition, he must examine the characteristics of the products made available to the public through his company's operations. With the ever-increasing combination of pulp fibers and plastics in consumer products, a farsighted approach should be taken in the selection of materials used in these products. Pulp fibres should be of as high a quality as possible so that they may be of significant value for reuse. Plastic used with the fibers should be selected so that they are readily soluble in industrial solvents, making possible the eventual separation and recovery of both components when

the paper products finally reach the garbage disposal plant.

The possibilities of an imaginative, scientific approach to all of the pulp mills' processing problems seem limitless. How far the engineer can go in this field of development will depend largely on the attitude of mill management. A long range view on the part of management toward radical changes in processing will, initially, involve high costs for development and for new equipment resulting from such development. However, such changes should bring about improved efficiency in fiber utilization, reduced labour cost through automated, computer-controlled processing, and greatly improved public relations through reduced air, water and land pollution.

The recognition of the pulp mill as a chemical processing industry will bring about radical changes and involve more and more chemical engineers in such changes. It seems quite probable that, in the not too distant future, the pulp and paper industry will become a complex, heavy chemicals industry, where byproducts may approach paper products in their economic value.