

FINAL REPORT

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Recipient Organization: Georgia Institute of Technology

Principal Investigator: Dr. Yulin Deng
School of Chemical & Biomolecular Engineering
Institute of Paper Science and Technology
Georgia Institute of Technology, 500 Tenth Street, N.W., Atlanta,
GA 30332-0620
Tel: 404 894 5759, Email: yulin.deng@chbe.gatech.edu

Co-Investigator: Dr. Arthur J. Ragauskas
School of Chemistry & Biochemistry
Institute of Paper Science and Technology
Georgia Institute of Technology, 500 Tenth Street, N.W., Atlanta,
GA 30332-0620,
Tel: 404 894 1008, Email: art.ragauskas@ipst.gatech.edu

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EXECUTIVE SUMMARY

Sponsored by the DOE Industrial Energy Efficiency Grand Challenge program, our research team at the Georgia Institute of Technology conducted laboratory studies and confirmed the concept of making wood pulp using a dry pulping technology. This technology is a new process different from any prior pulping technology used in Kraft and CTMP pulping.

Three different kinds of dry pulping methods were investigated.

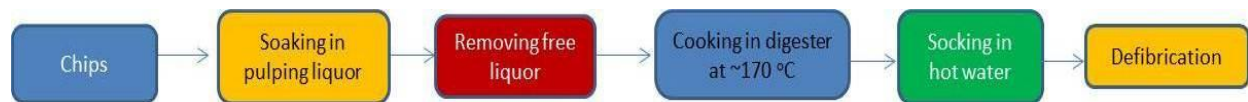
- a. Dry Pulping at Atmospheric Pressure: The first one is to dry and bake the pretreated woodchips in a conventional oven at atmospheric pressure without the use of a catalyst.
- b. Dry Pulping at Reduced Pressure: The second method is to dry the pretreated woodchips first in a vacuum oven in the presence of anthraquinone (AQ) as a pulping catalyst, followed by baking at elevated temperature.
- c. Liquid Free Chemical Pulping, LFCP. The third method is to first remove the free water of pretreated woodchips, followed by dry pulping using a conventional Kraft pulping digester with AQ and triton as additives.

Method one: Experimental results indicated that Dry Pulping at Atmospheric Pressure could produce pulp with higher brightness and lower bulk than conventional Kraft pulp. However, tensile strength of the acquired pulp is much lower than traditional Kraft pulp, and their Kappa number and energy consumption are higher than conventional Kraft pulp. By fully analyzing the results, we concluded that wood fibers might be damaged during the drying process at elevated temperature. The main reason for wood fiber damage is that a long drying time was used during evaporation of water from the woodchips. This resulted in an un-uniform reaction condition on the woodchips: the outside layer of the woodchips was over reacted while inside the woodchips did not reacted at all. To solve this problem, dry pulping at reduced pressure was investigated.

Method two: To achieve uniform reaction throughout the entire reaction system, the water inside the pretreated woodchips was evaporated first under vacuum condition at low temperature. Then, the dry woodchips were baked at high temperature (120-130 °C) at atmospheric pressure. The qualities of the pulp made with this method were improved compared to that made with method one. The pulp shows higher brightness and lower bulk than Kraft pulping. The tensile strength is significantly higher than the pulp made from the first method. Although the pulp is stronger than that of TMP pulp, it is still lower than conventional Kraft fiber.

Method Three: The third dry method was done in a Kraft pulping digester at elevated pressure but without free liquid in the digester. With this method, pulp that has almost the same qualities as conventional Kraft pulp could be produced. The screen yield, Kappa number, fiber brightness, pulp strength and pulp bulk are almost identical to the conventional Kraft pulp. The key advantages of this dry pulping method include ca. 55 % of cooking energy saved during the pulping process, as high as 50 wt% of NaOH saving as well as 3 wt% of Na₂S saving comparing to Kraft one.

Although the best process conditions have not been established, the following flow chart illustrates the major steps of our liquid free pulping technology.



By analyzing fiber properties, yields, chemical and energy consumptions, we concluded that the dry pulping method based on Liquid Free Chemical Pulping, LFCP, could be very attractive for the pulp and paper industry. More fundamental studies and scale up trials are needed to fully commercialize the technology. We expect to conduct pilot trials between 12 to 24 months of period if the DOE or industry can provide continual research funding. Based on the technology we demonstrated in this report, several pilot trial facilities in the United States will be available after small modifications. For example, the Herty Foundation in Savannah, Georgia is one of these potential locations. DOE funding for continuous study and final lead to commercialization of the technique is important.

1. ORIGINAL STATEMENT OF THE PROJECT OBJECTIVES AND ACTUAL ACCOMPLISHMENTS

1.1 Original project objectives:

The ultimate goal of the program is to develop a novel pulping technology that can replace the current Kraft pulping technique with significant less energy consumption, process cost and environmental pollution. The research includes the following objectives:

- Perform dry pulping using hardwood chips with different NaOH and Na₂S dosages and temperatures at ambient pressure without water as the medium. The pulping process will be carried out in N₂ and air.
- Evaluate the pulp properties (yield, Kappa number, fiber length, strengths, handsheet properties).
- Determine the energy consumption and chemical cost of the new technology.

1.2. Original tasks to be performed:

- Task 1: Potential Benefits Assessment

Under this task, the project team will estimate the potential energy benefits (% reduction in energy intensity, the year in which the savings will begin, total projected savings in Tbtu/year in year 2020), economic benefits (\$/year), environmental benefits (reduction in CO₂ emissions, Mlb/yr, other) and market benefits (US economy) that can be realized in year 2020, assuming successful development and commercialization of the technology being developed. Towards the end of the project, the potential benefits will be recalculated to reflect the impact of the results of the project. The final report will include the final assessment and a discussion of the differences between the initial and final assessment.

- Task 2 Optimize pre-soaking solution composition

Various composition and concentration of chemicals in the soaking solution for woodchip treatment will be tested. Different from regular Kraft pulping in which the chemical concentration change depends only on the amount added to the digester during the pulping process, the concentration of chemicals in dry pulping process will strongly depend on the content of water in the woodchips. To optimize the pre-soaking condition, the following subtasks will be conducted:

- Task 3 Optimize the atmosphere of dry-pulping

Dry pulping will be carried out in different atmospheres. Oxygen tends to react with sulfide, lignin, cellulose, and hemicellulose, which may have either positive or negative impact on the total performance. Therefore, the dry pulping under both air and nitrogen conditions will be tested.

- Task 4 Optimize the dry-pulping temperature

The reaction mechanism of Kraft pulping will be complicated. Alkaline will promote the formation of phenol salt and the release of ROH, which can happen at relatively lower temperatures. At the same time, alkaline also promotes degeneration of cellulose, i.e., causing peeling and breakage of cellulose fiber. Therefore, the effect of the baking temperature on the pulping efficiency and fiber quality will be studied.

- Task 5 Investigate the fiber quality

The composition of fibers (lignin, hemicelluloses and cellulose) and crystallinity of fibers will be analyzed using TAPPI (Technical Association of Pulp and Paper Institute) standard methods.

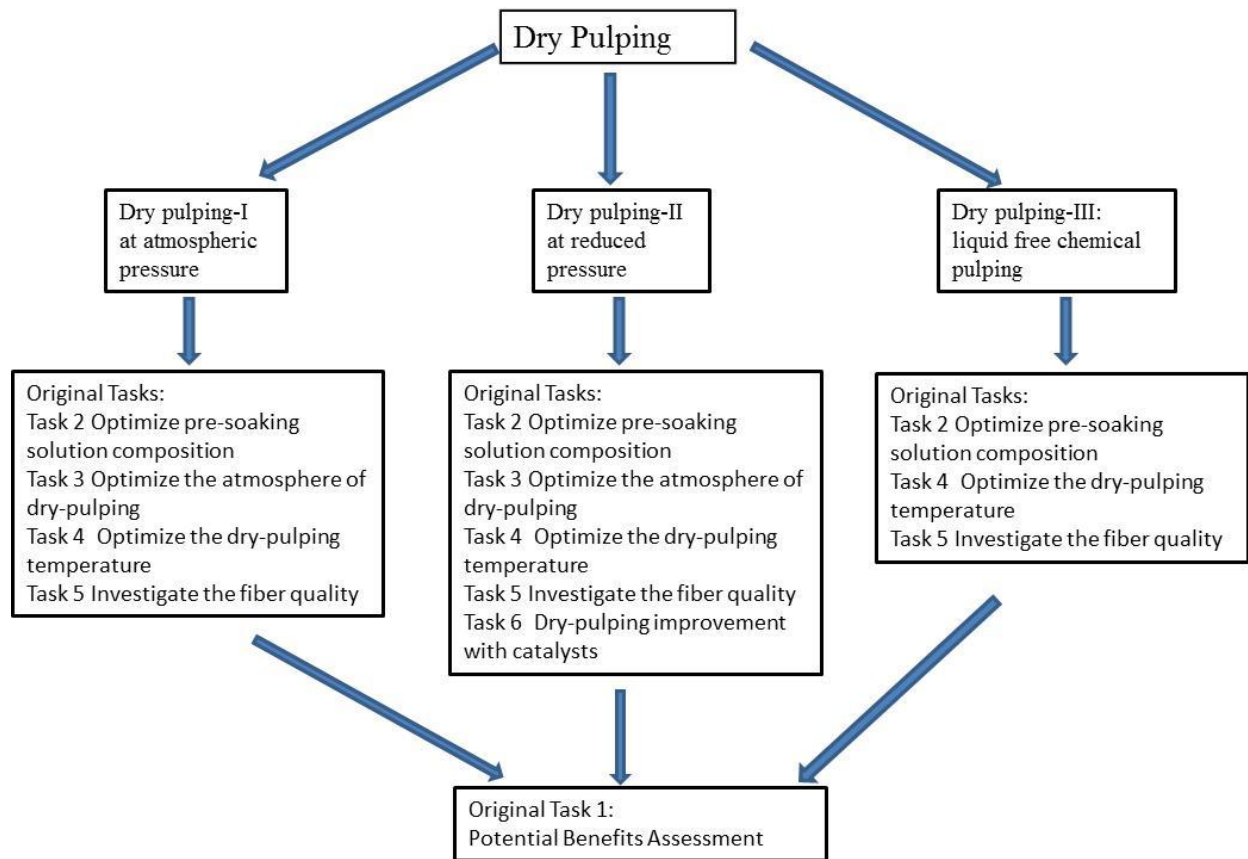
- Task 6 Dry-pulping improvement with catalysts

It was reported in conventional pulping process that some additives can improve Kraft pulping. These additives include quinone, anthraquinone, polysulfide, and surfactant. To enhance the dry pulping efficiency and reaction rate, selected catalysts (non-toxic with low cost) will be tested.

1.3. Final Assessment and discussion on the differences between the initial and final objectives and tasks

All three initial objectives and six tasks given in our original proposal (see above) have been accomplished. There is also a small difference between initial and the final tasks. In the original proposal, we proposed to fully dry the pretreated woodchips and bake them in an oven. This approach has been fully investigated. However, we found that fully drying the woodchips resulted in higher energy consumption than traditional Kraft method, and the pulp strength was lower than Kraft pulp. Therefore, instead of completely drying the woodchips, we removed free water in the pulping system but did not completely remove the water inside the chips. Results shows that the fibers obtained from modified method has a similar strength as that of traditional Kraft pulp, but about 30% heating energy can be saved.

In order to better organize the report, we divided our report in three drying methods, as shown below. All original tasks that were given in our proposal have been accomplished, which are delivered in a way as shown in the following chart.



2. RESEARCH BACKGROUND

2-1 Kraft pulping

2-1-1. Basic procedure: Pulping is a key operation process of papermaking. Pulping processes can be purely mechanical, in which the wood is ground into fibers by disk refiners or grindstones, and purely chemical, in which the fibers are separated by chemically degrading and dissolving the lignin that binds cellulose together in the tree. High yield mechanical pulping processes are electricity intensive, and there has been relatively little progress in decreasing electricity demand in mechanical pulping so far. Kraft process, developed by Carl F. Dahl in 1879, is one of the most common chemical pulping techniques. Pulp produced by the Kraft process is stronger than that made by other pulping processes. Acidic sulfite processes degrade cellulose more than the Kraft process, which leads to weaker fibers. Kraft pulping removes most of the lignin present originally in the wood; whereas, mechanical pulping processes leave most of the lignin in the fibers. Kraft pulp is darker than other wood pulps, but it can be bleached to a very white pulp. The Kraft process can use a wider range of fiber sources than most other pulping processes. All types of wood, including very resinous types like southern pine [1], and non-wood species like bamboo and kenaf can be used in the Kraft process.

In Kraft pulping a solution of sodium hydroxide and sodium sulfide are used to dissolve the lignin where woodchips are fed into digesters and cooked at 140 °C -180 °C under high pressure. Most of digesters operate in a batch manner except for a few of them, such as the Kamyr digester which works in a continuous process. The process entails treatment of woodchips with liquor containing sodium hydroxide and sodium sulfide that break the lignin network and the bonds between lignin and cellulose. woodchips are impregnated with the cooking liquors with ~17 % NaOH and ~7 wt% Na₂S and a ratio of solution/chips of 4-4.5. For example, Shawn and colleagues investigated pulping conditions and properties of Canada Aspen [2] where oven dried woodchips with a 4.5:1 ratio of liquor to wood was pulped at 170 °C with a solution of 25% sulfidity (defined as $\left(\frac{Na_2S}{Na_2S + NaOH}\right)100\%$) and 13% effective alkali (defined as $(NaOH + \frac{1}{2}Na_2S)g/L$). Under these conditions lignin and some hemicellulose are degraded to give fragments that are soluble in the strong basic liquid. The wood pulp (about 50% by weight based on the dry woodchips) is collected and washed. The pulping chemistry is complicated. One of the roles of Na₂S is to function as a nucleophilic agent as shown in Fig 1. The scission reaction of ether bonds by the nucleophilic sulfide (S²⁻) or bisulfide (HS⁻) ions will result in the depolymerization of lignin network.

After pulping, the combined liquid was known as black liquor, which contains a large quantity of excessive chemicals and has to be recovered. Multiple evaporation steps of 60% or even 80% solids, and burning in a recovery boiler, is generally used to recover the inorganic chemicals for reuse in the pulping process. The combustion is carried out in such a manner that sodium sulfate is reduced to sodium sulfide by the organic carbon in the mixture due to a mechanism of Thermo Chemical Sulfato Reduction. The molten salts ("smelt") from the recovery boiler are dissolved in process water known as weak wash. This process water is

composed of all liquors used to wash lime mud and green liquor precipitates. The solution of sodium carbonate and sodium sulfide is known as "green liquor". This liquid is mixed with calcium hydroxide to regenerate the white liquor used in the pulping process through an equilibrium reaction where Na_2S does not participate. Calcium carbonate precipitates from the white liquor and is recovered and heated in a lime kiln where it is converted to calcium oxide (lime). The calcium oxide (lime) is reacted with water to regenerate the calcium hydroxide. The combination of the above reactions forms a closed cycle with respect to sodium, sulfur and calcium and is the main concept of recausticizing process where sodium carbonate is reacted to regenerate sodium hydroxide.

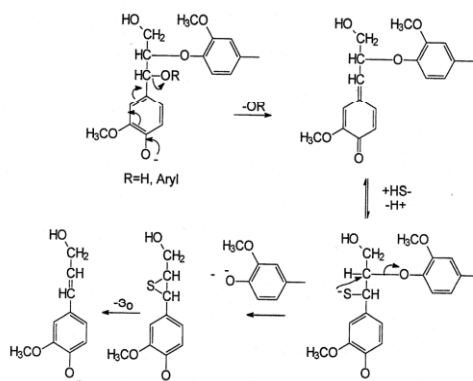


Fig. 1 Main reactions in Kraft pulping

2-1-2. Energy cost: The process of Kraft pulping has high energy costs. Steam and electricity consumption of the modern pulp mill was discussed by Nilsson et al. [3,4]. They summarized energy consumption in a Kraft mill as shown in Table 1. The further described steps are as follows. The woodchips were conveyed and transferred by belt from the chip piles to the pre-steaming vessel. Digester is a vessel, in which a pressure cooking will be carried out. The energy consumption of digestion directly depends on the ratio of woodchips to solution, the temperature and the cooking time. High-efficiency washers, such as pressure filters, are employed for brownstock washing. Oxygen delignification is used to further delignify the pulp prior to bleaching. Approximately 60 percent delignification is achieved in two stages. A modern mill is able to achieve fully bleached pulp from a four-stage elemental chlorine free (ECF) bleach plant. In a typical operation, weak black liquor is produced at 15 percent solids, which is then evaporated to 78 percent solids using a seven-effect multiple-effect evaporation system with an integrated superconcentrator. The mill would use a high solids recovery boiler that achieves a 75 percent heat-to-steam efficiency. The mill generates 0.150 billion BTU/tonne of air-dried pulp in the recovery boiler to satisfy the heat requirements of the process and electricity generation needs. The kiln utilizes flash drying and product coolers to minimize energy consumption. Natural gas is used to provide 0.0114 billion BTU heat energy for making one tonne of air dried pulp. The steam and electricity consumption mainly depends on two factors. The first is the amount of consumed solution in the digester and concentration. The higher the amount and the concentration, the higher the energy consumed in “washing and screening,” “black liquor evaporators,” “kiln and recausticizing,” and “waste-water treatment.” The second factor is

Kappa value or remaining lignin content in the fiber. The lower the Kappa value of the fiber, the lower the energy and steam consumption in “oxygen delignification” and “bleaching,” however, the lower the fiber yield will be.

Table 1. Modern Kraft market pulp mill-steam and electricity consumption

	Steam (Billion BTU/Air dried tonne)	Electricity (kWh/ air dried tonne)
Chip conveying	0.0	20
Digester	0.107	40
Washing and screening	0	30
Oxygen delignification	0.032	75
Bleaching	0.146	100
Pulp machine	0.146	141
Black liquor evaporators	0.196	30
Power plant	0.146	60
Kiln and recausticizing	0	50
Hot water suppl	0	32
Waste-water treatment	0	30
Miscellaneous	0	30
Total Consumption	0.772	638

2-1-3. Chemical consumption in Kraft pulping: The chemical consumption in Kraft pulping is significant [5]. In digestion sodium hydroxide and sodium sulfide are consumed and some additives, such as pulp defoamers, deposit control agents and digester aids are also used. The digester aids are Anthraquinone (AQ), select surfactants and specially blended products, which can increase actual yield. For bleaching grades of pulps, some bleaching chemicals are used. After pulping, the generated black ordered liquid is called weak black liquor. In weak black liquor, almost 50% chemicals are kept unreacted, and dissolved lignin. The chemicals in weak black liquor will be recovered. The recover processes include (1) concentrating the weak black liquor to form strong and heavy black liquor, (2) incineration of the liquor, (3) Dissolving smelt to form green liquor, (3) Causticizing green liquor with lime to form white liquor, (4) Burning of lime mud to recover lime. [6,7].

2-1-4. Corrosion[8]: Paper production consists of a series of processes and can be roughly divided according to the five major manufacturing steps: (1) pulp production, (2) pulp processing and chemical recovery, (3) pulp bleaching, (4) stock preparation, and (5) paper manufacturing. Each manufacturing step has its own corrosion problems related to the size and quality of the wood fibers, the amount of and temperature of the process water, the concentration of the treatment chemicals, and the materials used for machinery construction. Examples of corrosion affecting production are: (1) corrosion products polluting the paper, and (2) corrosion of rolls scarring the sheets of paper. Corrosion of components may also result in fractures or leaks in the machines, causing production loss and safety hazards. The digestion solution in Kraft pulping is a strong base corrosive liquid. The digester is a pressure device working at a temperature between 140°C - 180°C where serious erosion will happen. The total annual corrosion costs for the pulp, paper, and paperboard industry is determined at a fraction of the

maintenance cost, at approximately \$1.97 billion to \$9.88 billion (average \$5.928 billion per year). These estimates are between 1.2 % and 6.0 % of the total sales for the entire U.S. pulp and paper industry. The estimated cost of corrosion in 1998 for different kinds of pulp ranged from US\$4.67 per metric ton (US\$4.24 per short ton) for mechanical pulp, to US\$16.36 per metric ton (US\$14.84 per short ton) for fully bleached Kraft pulp. The cost of corrosion prevention and production safety markedly depends on working pressure and temperature of digester as well as the amount and concentration of digestion solution.

2-1-5. Pollution control of Kraft pulping [9]: Impact on air quality is the best known concern of the pulp and paper industry, while it is not often the most dangerous for human health. Odors, smoke, vapours and dust are emissions that people recognize immediately as characteristic of a pulp mill. The blowing process, where the finished cooked woodchips are blown by reducing the pressure to atmospheric pressure, is used to disperse fiber in Kraft pulping after the pressure cooking of pulp. This process will release a lot of steam and volatiles with a terrible odor because of sulfur containing chemicals. Table 2 shows the characteristics of different compounds, with their approximate odor threshold which is the main factor of this pollution because these thresholds are very low. If odors are the easiest gaseous emissions to identify, some others are less visible or odorous but much more dangerous.

Table 2 : Characteristics of Kraft mill reduced sulphur gas

CHARACTERISTICS OF KRAFT MILL REDUCED SULPHUR GAS			
Compound	Type of odour	Approximate odour threshold	Formula
Hydrogen Sulphide	Rotten eggs	1 ppb	H ₂ S
Methyl Mercaptan	Rotten cabbage	1 ppb	CH ₃ SH
Dimethyl Sulphide	Vegetable sulphide	10 ppb	CH ₃ SCH ₃
Dimethyl disulphide	Vegetable sulphide	10 ppb	CH ₃ SSCH ₃

Table 3 (Source: World Bank) shows the emissions of sulfur containing chemicals in different mills. Table 4 (Source: World Bank) gives the emission of SO_x and NO_x from Kraft pulp mill combustion sources without control. The amount of sulfur containing chemical released in the blowing process directly depends on the amount of digestion solution, the pressure and temperature. Solid pollution control is another main aspect of environment protection cost. The worst impact on soil related to industrial operations stems mostly from solid waste landfills.

Table 3: Typical Total Reduced Sulphur (TRS) emissions from older and modern mills

	Discharge rate	TRS emissions	
		Older mill	Modern mill
	Normal (m ³ /ADT)	kg/t	kg/t
Digester area	-	0.80	0
Washing and screening	2 500	0.30	0.10
Evaporators	10	2.00	0.05
Recovery boiler	10 000	5.00	0.05
Dissolving tank	600	0.20	0.02
Lime kiln	1 100	0.20	0.07
Miscellaneous	-	0.80	0.06
TOTAL		9.30	0.35

Table 4. Typical emissions rates of SO_x and NO_x from kraft pulp mill combustion sources (before control devices)

	Emission rate (kg/t of air dried pulp)		
	SO ₂	SO ₃	NO _x (as NO ₂)
Recovery furnace			
No auxiliary fuel	0–40	0–4	0.7–5
+ Auxiliary fuel	0–50	0–6	1–10
Lime kiln exhaust	0–2	-	-
Smelt dissolving tank	0–0.2	-	10–30
Power boiler*			
2% Sulphur FO	6–20		
2% Sulphur coal	7–30		

Table 5 shows some averages of solid waste generation in pulp and paper mills. This table shows the amount of solid waste from various processes but it does not give a detailed composition, even though it is the main factor. Some components of the additives used in the process (i.e., acids or alkali), of the equipment (i.e., PCBs in electrical equipment), or of the raw materials used (i.e., fuel oil) can pollute the soil at the plant site and/or at the dumpsites. This soil pollution can contaminate the underground water. All of these pollution control costs depend on chemical consumption in pulping.

Table 5: Solid wastes in pulp and paper mills

Type of wastes	Kraft pulp 200 000 t/yr. mill integr. (Europe) (1 000t/yr.)	Sulphite mill 220 000 t/yr. non integr. (Europe) (kg/t)
Bark, wood residues	56,8	(1)
Screening rejects	(2)	98(3)
Sludge, dregs	19	150(5)
Incineration residues	20	60
Others	2,5	(4)
TOTAL	100(approx.)	(4)

Source: UNIDO

(1) : Incinerated.

(2) : Included in sludge.

(3) : In waste water sludge.

(4) : data not available.

(5) : Sludge from biological treatment 15% concentration. Incinerated.

2-1-6. Most recent research in Kraft pulping: Many researches in literature have focused on the improvements of additives to improve the Kraft pulping, understanding the chemistry during the Kraft pulping and optimization of pulping conditions [10,11,12,13,14,15,16,17,18]. A number of methods have been proposed to increase chemical reaction selectivity. Using AQ [19] and polysulfide [20] to improve the pulping efficiency and reduce the odor are also investigated. Duggirala [21] investigated the effect of surfactants on cooking liquor penetration and diffusion and found that the use of surfactants resulted in a more uniform cook with lower Kappa numbers, lower screen rejects, lower pulp resin content, and improved black liquor

residual active alkali content. He also found [22] that the addition of 0.1% surfactant (on over dry wood) resulted in a significant reduction of the kappa number with no penalty on pulp yield. The resultant pulp yield at a constant kappa number increased 0.5-0.8% over the conventional kraft cook. Organic solvents are inherently better lignin solvents than water and can promote more efficient delignification. The addition of methanol to a high-sulfidity kraft cook on Scandinavian softwood chips was studied under different process conditions by Norman and his colleagues [23]. Delignification and the degradation of carbohydrates were accelerated. It was also found that methanol addition had no discernible effect on pulp strength or on pulp bleachability but the pulping efficiency could be improved. Bujanovic and his coworker [24] reported that borate increases yield, decreases rejects, improves the selectivity of lignin removal, and increases pulp viscosity at the same kappa number. Magnotta and colleagues [25] interrupted kraft pulping at a high kappa value and extended oxygen delignification. They found that this method could increase the overall yield, since oxygen delignification is more selective than the residual phase of kraft pulping. The influence of pulping conditions on strength of pulp was widely investigated [26,27]. Allison [28] found that increasing the extent of kraft delignification from 31 to 22 Kappa number reduced the pulp viscosity as well as handsheet strength of unbleached and bleached pulp. Increasing the extent of oxygen delignification from 35 to 58% Kappa number reduction also decreased pulp viscosity but had little effect on pulp strength. Olm and Tormund [29] investigated the importance of terminating the cook in the bulk delignification phase. They found that a long cooking time at a relatively low hydroxide ion concentration (residual alkali 0.15 mol/L), as when the cook is terminated in the residual phase, leads not only to poorer brightness of unbleached pulp and bleachability, but also to a loss of strength properties. The fact that the displacement kraft cooks are finished in the bulk delignification phase may be the major advantage; and, may explain the high strength potential and good bleachability of the pulps obtained in industrial displacement Kraft pulping.

Catalysts have been reported to be able to promote the pulping process [30]. Watson and colleagues [31,32] studied the cleavage of the beta-aryl ether bonds of the lignin model compounds under the presence of catalyst. Yawalata and Paszner [33,34] investigated a new salt-catalyzed alcohol organosolv pulping and found that the catalysts control the acidity of the cooking liquor, which is the key factor for pulping selectivity and fiber separation. Dimmel and colleagues found that Dimethylantraquinone (or DiMAO) and its precursor, octahydro-DiMAQ (or ODiMAQ) are twice as active as anthraquinone in soda, Kraft, and polysulfide pulping systems. [35] Some researches focus on decreasing cost and improving chemical recovery [36,37,38].

Some new techniques are continuously disclosed. Temler disclosed a technique [39], named as “high-yield semi-chemical carbonate pulping process” where hard woodchips were pulped at a temperature 180-192°C. A sodium carbonate solution of a concentration 65 to 120 g/L as Na₂O at a liquor to wood ratio of 1.2-2.5 was used. Yawalata and Paszner [40] disclosed a solvent pulping method using aqueous solution of a lower aliphatic alcohol in a plurality of batch extraction vessels at a temperature between 160 to 220°C. A multi-stage extraction was used. The extraction liquor from one extraction stage in one vessel is used in another extraction stage in another vessel. Explosive pulping, thermomechanical pulping [41], polysulfide pulping [42], vapor phase pulping [43], and boron-containing alkaline pulping [44] have also been investigated. Some additives and enzymes have been widely investigated to improve the pulping

process [45,46,47]. Li and Tschirner [48] found that 0.1%-0.2% phosphonates in cooking resulted in considerable reduction in kappa number (4-8 points), while pulp yield was increased substantially.

2-2. Mechanical pulping and progress: The mechanical production of pulp can be divided into two categories: ground wood pulp production and the thermo-mechanical process (TMP), the latter in some cases with chemical support (CTMP). In ground wood pulp production, the logs of wood are pressed on grinding stones by means of mechanical presses. The wood is split into fibers with the help of water. As a result of which the wood fibers are released but still contain a large variety of contaminants. Ground wood pulp has a high yield of approximately 95% and has a high level of opacity but its strength is relatively low, due to its lignin content [49].

2-2-1. TMP: Manufactured grindstone with embedded silicon carbide or aluminum oxide can be used to grind small wood logs called "bolts" to make stone ground wood pulp (SGW). The wood generally is steamed prior to grinding. Most modern mills use chips rather than logs and ridged metal discs instead of grindstones. If the chips are just ground up with the plates, the pulp is called refiner mechanical pulp (RMP) and if the chips are steamed while being refined the pulp is called thermomechanical pulp (TMP). Steam treatment significantly reduces the total energy needed to make the pulp and decreases the damage (cutting) to fibers [50].

An overview of TMP production is given below [51, 52]: Pulp is made by heating the chips with steam and mechanically separating the fibers in a pressurized refiner. Chips are fed to a presteamer and are steamed with process steam. The chips are screwed to a pressurized refiner which separates the fiber via mechanical means (e.g. between rotating disc plates). The pulp is often refined in two stages, see Fig. 2. For the grinding process the logs are cut in ~ 1 m length. These logs are pressed by chains or presses onto a rotating stone. Depending on the roughness of the stone surface different pulp qualities can be achieved. A sharp stone (rough surface) provides rough fibers at high yield. A smoothed stone provided long fibers, but with low yield and high energy demand. With the grinding process the wood fibers are severely damaged and contain different contaminants. Additional efforts need to be taken in the stock preparation to get an acceptable pulp quality.

Manufacture of TMP is high energy cost process in which the energy cost is as high as 2276 kWh/ODMT. Ground wood pulp has relatively high yield (up to 95%), high opacity, but low strength values. Because of remaining lignin in the fibers this pulp is not light resistant over time. Mechanical pulps are used for products that require less strength, such as newsprint and paperboards [49].

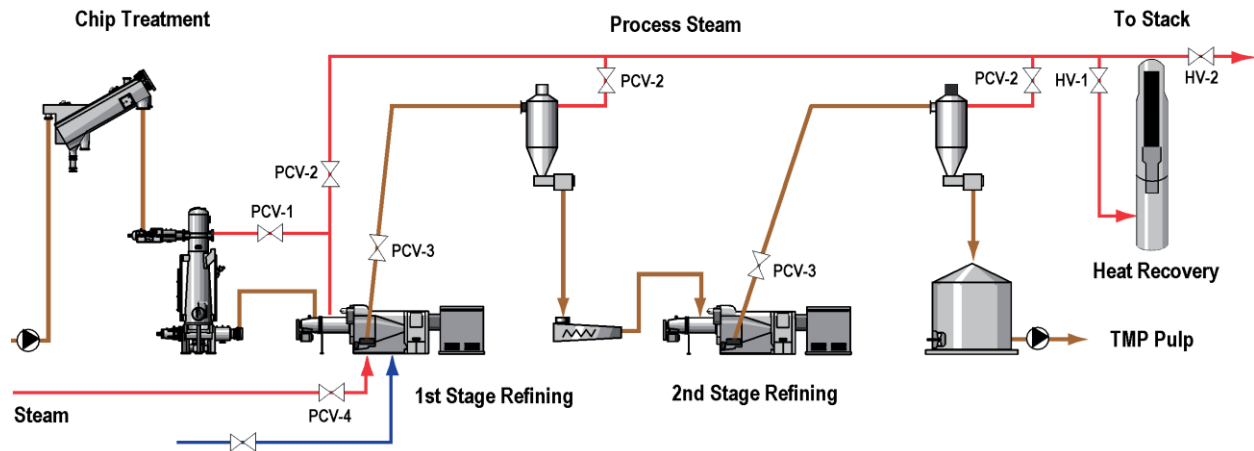


Fig. 2 Overview of two stage TMP

Currently, main researches on TMP focus on energy saving [53-55]. Chang et al. highly treated wood by alkaline peroxide resulting in gains in pulp properties that would allow reduced energy in-put in second-stage refining. As a result the total electrical cost can be evidently reduced [55]. Wang Zhaorong and coworker [56] found that cellulases pretreatment of the woodchips prior to refining could reach refining energy saving of to 7.05% compared to untreated chips in TMP processes. Walter, Karin and colleagues [57] found that acid hydrogen peroxide and some organic additive, used in refining can lower electrical consumption by 20-35%. Some researchers focus on lowering the energy consumption by improving geometry of plate [58] or studying influence of static mechanical compression on the characteristics of TMP of white birch chips [59]. Keeping fiber quality generally is a precondition in those researches of energy saving. For example, Gorski, Dmitri and coworker [60] combined selective wood disintegration by mechanical pretreatment and refining at elevated intensity with chemical treatment after defibration, such as hydrogen peroxide, alone and in combination with alkali. They found that this kind of ATMP (Advanced Thermomechanical Pulp) can markedly increase electrical energy efficiency at no cost of fiber quality decrease.

Bian, Yuzhou and colleagues [61] investigated the effect of alkaline peroxide pretreatment on TMP rejects. They found that a 2.2% total alkali charge was not sufficient to achieve noticeable energy reduction or physical property improvement. However, at a total alkali charge of 5.2%, alkaline peroxide pretreatment reduced the specific refining energy by 20% to a given freeness, and increased pulp density and tensile strength, which most likely as a result of increased fiber flexibility and conformability.

2-2-2. CTMP (Chemithermomechanical pulp): CTMP, which spends more chemical, is a developing direction of TMP. In CTMP, woodchips are pretreated with sodium hydroxide, sodium carbonate, and sodium sulfide and other chemicals prior to refining. The conditions of the chemical treatment are much less vigorous than in a chemical pulping process since the goal is to make the fibres easier to refine, not to remove lignin as in a Kraft pulping [62].

Most of CTMP properties are closed to TMP. However, pulp density and fiber strength of CTMP are evidently higher than TMP. Fiber Sheffield Roughness of CTMP is much lower. Pulp color of CTMP is deeper. The energy cost of CTMP is higher than TMP. These differences can be found in reference [63]. Corresponding pulp properties comparison is given in Table 6 and Table 7.

Table 6. Properties of thermomechanical and chemical pulps of sound and blue stained lodgepole pine standardized to a freeness of 100 mL CSF

Process	Wood Type	Specific Refining Energy (MJ/kg)	R - 48 Fraction (%)	Fines (P-200) (%)	Length Weighted Fibre Length (mm)	Apparent Sheet Density (kg/m ³)	Tensile Index (N·m/g)	Tear Index (mN·m ² /g)	Sheffield Roughness (SU)	Scattering Coefficient (cm ² /g)	ISO Opacity (%)	Brightness (%)
TMP	Sound	11.3	52.7	25.4	1.29	338	31	6.4	216	622	96.9	54.7
TMP	Blue-Stained	11.6	54.3	25.8	1.45	340	33	7.0	221	591	96.7	55.2
CTMP	Sound	13.4	54.9	23.0	1.37	379	40	6.9	160	522	95.4	53.9
CTMP	Blue-Stained	12.3	50.9	23.0	1.29	386	39	6.8	148	513	95.6	54.8

Figure 7. Properties of thermomechanical and chemithermomechanical pulps of sound and blue stained lodgepole pine standardized to a specific energy of 10.0 MJ/kg

Process	Wood Type	Screened CSF (mL)	Length Weighted Fibre Length (mm)	Apparent Sheet Density (kg/m ³)	Tensile Index (N·m/g)	Tear Index (mN·m ² /g)	Sheffield Roughness (SU)	Scattering Coefficient (cm ² /g)
TMP	Sound	153	1.41	301	28	7.0	269	590
TMP	Blue-Stained	171	1.63	300	29	8.3	263	554
CTMP	Sound	198	1.48	327	33	8.0	248	494
CTMP	Blue-Stained	173	1.36	341	32	7.2	217	479

Energy saving is still a main research direction for the production of CTMP [64-70]. Li Dong et al. found that microwave pretreatment of poplar pulpwood chips can markedly decrease energy cost [67]. Grossmann H and Salmen L indicated that oxidative treatments in the production of CTMP production can evidently save energy and improve fiber property. They thought it is possible that the most promising approach being used in refining strategies for chemical pulps can give energy savings up to 30% [68]. Gilbert CD, Long PX and Hsieh J [69] design a computer monitor as well as control system in which torque was used as an effective control parameter for CTMP production, as a result evident energy saving was found. Another research indicated that by decreasing the impregnating liquor pH of sulfite liquor to approximately 4.5 and conducting the first-stage refining at a relatively low specific energy and

high refining intensity (by operating the refiner at 1800 rpm), an energy saving up to 33% could be achieved with no adverse effect on the pulp quality [70].

Some attention was paid to fiber quality. Jansson K et al. indicated that the pulp quality was improved by treating press filtrate after alkaline peroxide bleaching of mechanical pulps [71]. Argyropoulos Ds and Heitner C [72] impregnated black spruce chips with sodium sulphite solutions at pH 4.2, 5.9, and 8.6 then the chips were refined in a pilot plant two-stage TMP system. They found that reducing the pH of the chip impregnation liquor from 8.6 to 4.2 decreased the refining energy required to obtain a given freeness. At a given specific energy, the CTMP made from chips sulphonated at pH 4.2 had the highest strength and best optical properties. Ozone was used on the production of the TMP and CTMP [73] in primary and secondary refining stages. Petit-Conil M and colleagues found that ozone treatment improved the high-yield pulp quality for softwoods (spruce) and for hardwoods (poplar). This enhancement of the pulp strengths was associated with no brightness loss and with energy savings.

Comparing to Kraft pulp, CTMP has some specific advantages, such as lower environmental impact, greater flexibility of properties through process adjustments, and light scattering coefficient. However, the fiber strength of TMP and CTMP are much poorer than chemical pulp. Both CTMP and TMP generally were used in the production of newsprint and board production. The ratio of CTMP in board production strongly depends on electrical power costs because that the production of CTMP still is high energy costing process. New researches both on energy saving and fiber quality improvement didn't promise to give marked improvement [74].

3. THE MERIT OF THE PROPOSED PROJECT

3-1. The scientific and technical merit of the proposed technology

In summary, improving pulping efficiency and pulp quality, reducing the energy consumption and pollution are continually attracting research attention. The literature search indicated that although many new pulping improvement methods have been explored, no revolutionary idea that can replace Kraft Pulping has been developed. Although Kraft pulping has many advantages compared with other pulping techniques and it can produce the strongest fibers, there are still some technical disadvantages. For example: A) the chemical consumption of Kraft pulping is still very high, which produces huge amounts of black liquor; B) the pressure process limits continual flow pulping, which limits production efficiency; C) erosion resistance and high pressurized equipment increases the cost; D) hot black liquor releases odor, etc. Therefore, reducing the amount of chemical consumption and generated black and white liquors could remarkably reduce the total cost and energy consumption of Kraft pulping. It has been well known that Kraft pulp is still dominating pulp production today. However, it has been generally agreed that the principle and main process of Kraft pulping have been almost the same since the invention of the Kraft pulping technique in 1879.

In this project, we conducted an entirely different pulping technique. Although this was

a high risk research program, preliminary results show that the new technique may revolutionarily change the current Kraft process and pulp quality. The energy consumption in the digester cooking could be reduced by more than 55%, and the chemicals used could be reduced by about 50%. As a result, black liquor treatment energy would be significantly lower.

3-2. Innovation, originality, and feasibility of the proposed technology

The ultimate goal of this research is to develop a new pulping process to replace the current Kraft pulping technique. The new pulping technique was based on the concept of depolymerization of woodchips without free liquor medium. It has been well known that chemical in digester is excessive. Much chemical in black liquor are remaining unreacted. The energy cost of digestion mainly comes from heating both liquor and the woodchips. In the case that the woodchips are fully pre-soaked with the pulping liquor, a digestion without free liquor would markedly decrease energy cost and save chemical consumption.

Other approaches were also explored. For example, the ideal of woodchips depolymerization at atmospheric and reduced pressure without a liquor medium. This approach aimed at decreasing chemical consumption because the concentration of the chemical in the chips could be markedly increased due to the evaporation of water in the chips. For example, if 99% of the absorbed water is evaporated the chemical concentration in chips will increase by 99 times.

4. RESEARCH APPROACHES

The goal of this program is to develop a new pulping technology that can replace the current Kraft pulping with significantly less energy consumption, process cost and environmental pollution. The concept is to make wood pulp using a dry pulping technique. To achieve this goal, we studied three different approaches (see below). The initial objectives and tasks are given in Chapter One. These tasks include effects of temperature, pulping time, chemical dosage, pre-treatment and catalysts on the pulp quality. Both hardwood and softwood were investigated. The influence of chips size and shape were studied using both regular chips and pin chips. Practically, we studied three dry pulping methods, and the economic and energy saving is also studied. The major dry pulping approaches are

- **Dry pulping at atmospheric pressure:** Experimental approach included performing dry pulping using hardwood and softwood chips with different NaOH and Na₂S dosages at atmospheric pressure but elevated temperature, investigation of different pulping procedures, and evaluating the pulp properties (yield, Kappa number, fiber length, strengths, handsheet properties).

- **Dry pulping at reduced pressure:** Experimental research include performing dry pulping at reduced pressure using both hardwood and soft woodchips with different conditions, which include chemical dosage, temperature and time as well as different pre-treatment methods. Anthraquinone was investigated as a catalyst. The evaluation of the pulp properties also includes screen yield, Kappa number, fiber length, strengths.

- **Dry pulping at elevated pressure (liquid free chemical pulping, LFCP).** Practically, the woodchips was first soaked in pulping liquor. After that, the soaking liquor was filtered till no free liquor existed. The liquid free chips were then undergone the pulping at about 120 psi

and 170 °C. The pulping was conducted using an Aurora digester. The research included method and procedure designing and experimental investigation. Pulp properties, such as screen yield, Kappa number and pulp strength were tested. Traditional Kraft pulping at corresponding conditions was performed for comparison with the dry pulping. Besides AQ, surfactant (Triton-100) was also investigated as an additive.

5. EXPERIMENTAL RESULTS AND DISCUSSIONS

5-1. Task one---Dry pulping in atmospheric pressure

Basic conditions of dry pulping at ambient pressure were explored using hard wood. The main procedure is given in Fig. 3. The woodchips were firstly soaked in NaOH and Na₂S solution. The soaked woodchips were then removed from soaking solution followed by a simple baking process in oven under air or nitrogen. The chemicals inside the woodchips were concentrated during the baking by evaporating the water. Although the initial concentration of pulping chemicals in the woodchips was low, the final concentration of the chemicals in the woodchips could be much higher than conventional pulping liquor after water evaporation. This high concentration of chemicals in the woodchip could speed up the degradation of lignin. As a result, the lignin in the woodchips was cracked at atmospheric pressure and 120-130 °C. The treated woodchips were then soaked in hot water for 5 hours (the woodchips swelled) followed by disintegration. Wood fibers were released during the disintegration. The results are given in Table 8. Some interesting phenomena were found. When the pulping chemical concentration was too low, the chips cannot be completely converted to fibers after pulping. If the solution concentration was too high, the chemical reaction at elevated temperature was too fast, resulting in woodchip surface burning. A microwave heating experiment was also conducted. However, the reaction was too fast to be controlled. It was noted that microwave heated both the surface and internal part of the chips. Table 8 indicates that the dry pulping method can break woodchips into individual fibers.

Table 8. Influence of EA

Sample	HWDS-5	HWDS-6	HWDS-7	HWDS-8	HWDS-9	HWDS-10	HWD-4
Na ₂ S (wt%)#	5.50	6.04	6.63	7.05	7.46	7.72	8.48
NaOH (wt%)#	12.89	14.15	15.53	16.52	17.47	18.09	19.86
EA (%)	11.59	12.73	13.97	14.86	15.71	16.27	17.86
Sulfidity (%)	25.6	25.6	25.6	25.6	25.6	25.6	25.6
Yield (%)	*	45.8	37.1	33.6	21.6	22.8	burn
Kappa	--	32	27.2	27.6	21.5	25	--
Fiber length (mm)	--	0.59	0.56	0.50	0.48	0.46	--

#: solution concentration; *: too much bundles and residue

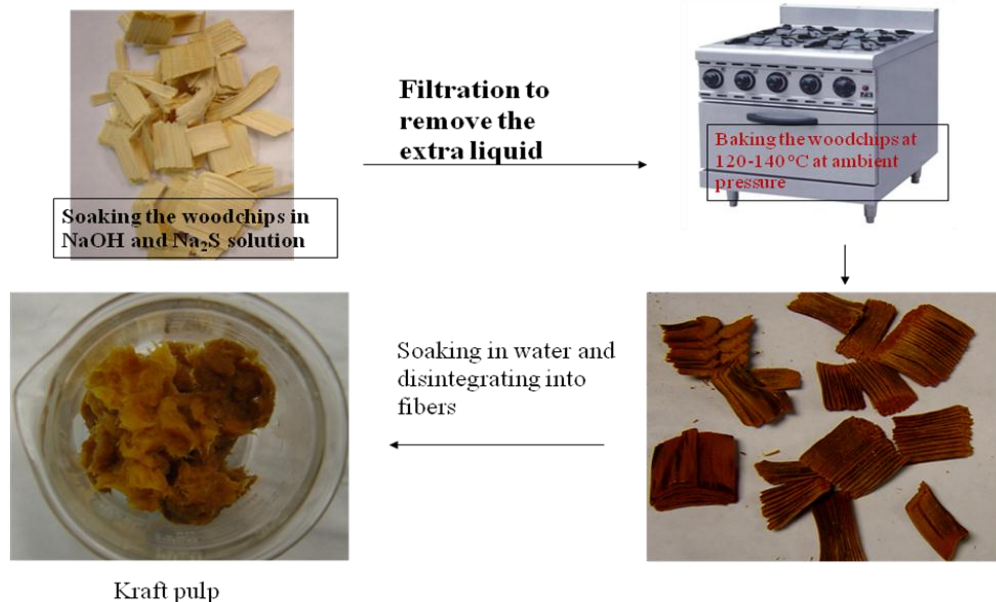


Fig. 3 Basic procedure of dry pulping at atmospheric pressure

Different from traditional Kraft pulping (TKP), in dry pulping the chemical concentration could be much lower initially but markedly concentrated during the drying process by water evaluation. In order to remove excessive pulping solution inside the woodchips to reduce the evaporation energy, compressing the presoaked woodchips with mechanical pressure followed by centrifuge separation was employed. The mechanical pressure could crack some cellulose wall and squeeze out the water in the woodchips. A diagram showing the major steps of dry pulping is given in Fig. 4. For each dry pulping method, more detailed steps will be described in separated sections. After soaking in pulping solution and centrifugation, the chips were pressed with a pressure of $52.35\text{lb}/\text{cm}^2$. The mechanical pressuring can squeeze the water out the woodchips but also crack the woodchip which improved heat transfer within the woodchips during the drying and backing. Experiment indicated that the mechanical pressuring at the same pressure is more difficult to destroy the dense structure of untreated woodchips. These pressed chips were soaked in the solution again. Because of the damage of the dense structure of woodchips by mechanical pressing treatment, the pretreatment liquid could easily penetrate into the woodchips in this stage, resulting in a uniform distribution of chemical inside the woodchips. The chips were then centrifuged to remove excessive liquor.

The influence of sodium hydroxide and sodium sulfide concentration were investigated again using modified procedure. The results are given in Tables 9 and 10. Although there is no clear trend was found, by comparing the results without pressing (Table 8), it shows that the mechanical pressing after baking can improve the woodchip defibration.

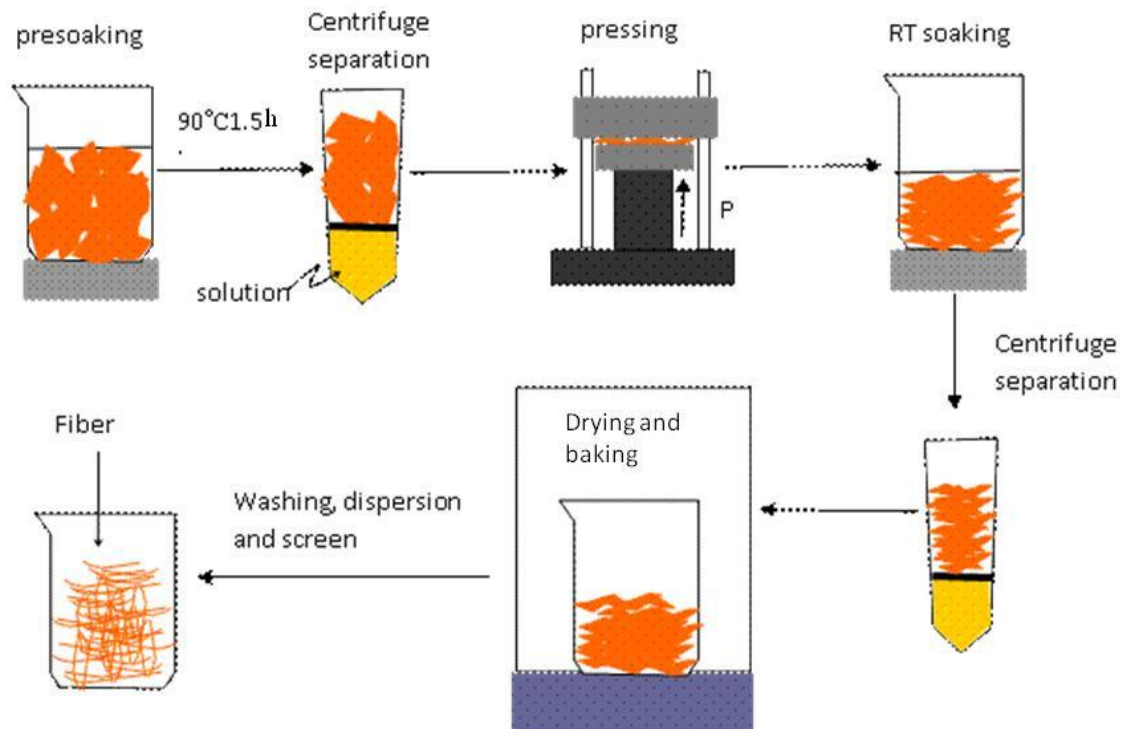


Fig. 4 Sketching illustration of modified dry pulping procedure.

Table 9. Influence of sodium sulfite concentration (presoaked woodchips were pressed $52.35\text{lb}/\text{cm}^2$)

Sample	HWDS-11	HWDS-13	HWDS-6	HWDS-14	HWDS-12
Na ₂ S (wt%)#	0	3.285	6.570	9.855	13.14
NaOH (wt%)#	26.18	19.64	13.09	6.545	0
EA (%)	20.09	16.09	12.08	8.06	4.06
Sulfidity (%)	0	11.87	28.78	54.80	100
Yield (%)	19.4	25.2	46.0	58.2	60.3
Kappa	24.9	51.2	91.0	105.6	113.4

#: Solution concentration

Table 10. Influence of chemical composition (presoaked woodchips were pressed $52.35\text{lb}/\text{cm}^2$)

Sample	HWDS-15	HWDS-16	HWDS-17	HWDS-18
Na ₂ S (wt%)#	15.91	14.32	9.55	11.14
NaOH (wt%)#	0	0	6.545	3.274
EA (%)	4.916	4.425	7.975	5.955
Sulfidity (%)	100	100	54.02	73.26
Yield (%)	55.25	62.2	52.71	57.22
Kappa	---	---	---	---

#: Solution concentration

In order to evaluate fiber properties of dry pulping, handsheets were prepared and evaluated. Traditional Kraft pulping was performed using the same hardwood chips. Handsheet with the same base weight was prepared from the fiber with similar Kappa number. Tappi

handsheets at a basis weight of 160-180g/m² were prepared. The handsheets were conditioned at Tappi conditioning room (23 °C, 50% relative humidity), and evaluated to obtain tensile, tear strengths and brightness. The tensile strength was performed on Thwing Albert tensile test machine according to T494. The test was performed on 8 specimens (25mm x 100mm). The tensile and tear strengths were determined using the average values and expressed in index values. Tear test was performed according to Tappi T 414 on an Elmendorf tear tester. Optical properties for handsheets were also obtained on a Color Touch2 (Technidyne Corp.). A fiber and handsheet pictures of both dry pulping and Kraft pulping are given in Fig. 5. The properties of both dry pulping paper and Kraft pulping paper are given in Table 11. Higher pulp brightness of dry pulping pulps at the same or even higher Kappa number comparing with traditional Kraft pulp was noted. As shown in Fig. 5, a marked color difference between two pulps (unbleached Kraft pulp and unbleached dry-pulping pulp) can be readily observed. The density of the handsheets shows marked difference between two pulping methods. Unfortunately the handsheet strengths, including tensile, burst and stiffness from dry pulping fiber are lower than Kraft pulping. The results indicated that although the dry pulping based on above described method can give higher yield fibers than Kraft pulping, the strengths of the handsheets are low. Clearly, lignin was not effectively removed (evidenced by high yield of >60%). It was also found that some wood fibers were damaged during dry pulping using the above dry pulping conditions (evidenced more short fiber fractions from image observation).

Table 11. Comparison of paper properties between dry pulping and Kraft pulping

Paper	Freeness (mL, CSF)	Brightness (% , ISO)	Bulk (g/cm ³)	Tensile index (Nm/g)	Burst index (kPam ² /g)	Tear index (mNm ² /g)	STFI index (Nm/g)
Kraft pulping	455	21.2 ± 0.174	0.809 ± 0.0088	91.8 ± 1.29	6.0 ± 0.05	8.1 ± 0.41	38.3 ± 0.73
Dry pulping	431	32.0 ± 0.09	0.553 ± 0.0041	33.3 ± 0.41	1.4 ± 0.04	3.7 ± 0.17	24.7 ± 0.33

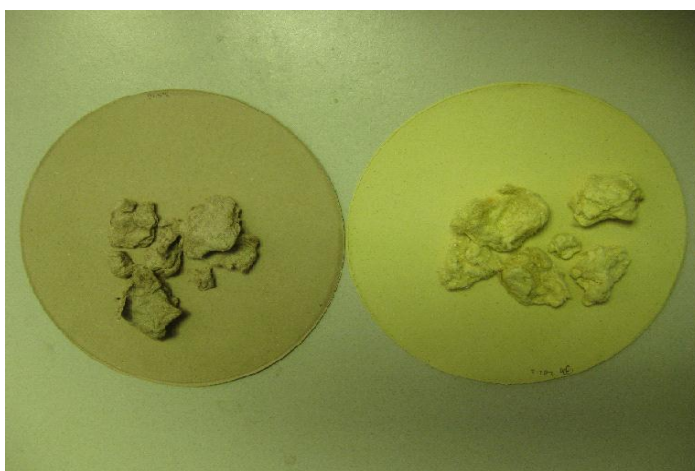


Fig. 5 Image of pulps and handsheets from Kraft (left) and dry pulping (right) at similar Kappa number

Conclusion of task-1: Dry pulping at atmospheric pressure could successfully disperse hardwood chips into individual fibers. Both brightness of the fiber and pulping yield were higher

than Kraft one. However, the strengths of the handsheets made from these fibers were evidently lower than that of Kraft fibers. This is tentatively attributed to that during the baking process of at atmospheric pressure, the heat transfer is not uniform in the woodchips. The outside layer of the pretreated woodchips dried much faster than inside woodchips. The temperature of outside layer of woodchips rose quickly after drying, but the inside woodchips was still wet. As a result, the outside chips baked at high temperature much longer than inside the woodchips. The gradient of temperature and water content from outside layer to inside the chips resulted in ununiform reaction: the surface of the chip was over cooked, but inside the chip did not fully reacted.

5-2. Task two---Dry pulping at reduced pressure

Although the above results demonstrated that dry pulping at atmospheric pressure could successfully disperse the pretreated woodchips into fiber and give higher yield and fiber brightness as well as lower bulk than Kraft pulping, however, the fiber strengths are lower than Kraft pulping. This maybe because the heat transfer and pulping reaction are not uniform from surface to inside the chips as described above. To solve the problem, a method that could lower the drying temperature and shortening the pulping time is needed to improve the properties of generated fibers. The second dry-pulping method explored in this study focuses on dry-pulping at reduced pressure. It is expected that at reduced pressure, the pre-treatment liquor inside the woodchips can evaporate and woodchips can be completely dried at relatively lower temperature before they are baked at high temperature, which could protect the woodchips and fibers from being over cooked or damaged.

5-2-1. Influence of AQ on pulping yield and pulp strength: It is well known that anthraquinone (AQ) and derivatives are excellent catalysts for Kraft pulping. The beneficial of anthraquinone and its derivatives have drawn much attention in Kraft pulping research over the last two decades [75], although other additives, such as polysulfide [76], sodium borohydride [77] and phosphonates [78-81] were investigated, and the latter was thought to be able increase yield and brightness of pulp, only AQ has been widely commercially utilized. A catalytic redox reaction mechanism [82] has been adopted to explain the influence of AQ in Kraft pulping (see Fig. 6).

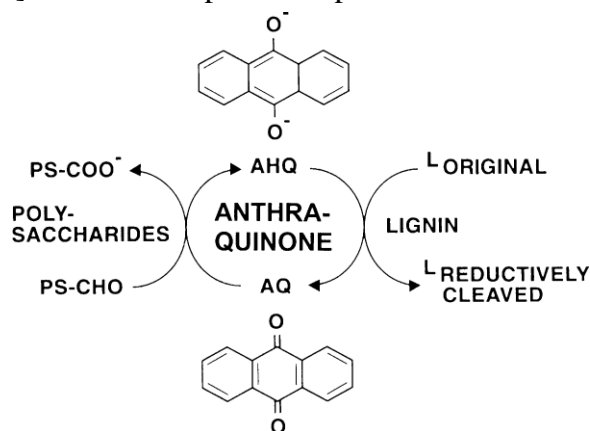


Fig. 6 Redox cycle between AQ and AHQ

A lot of researches indicated that AQ can improve both yield and pulp strength of Kraft pulp. Traditional Kraft pulping is a solution reaction in which the AQ is used. In this work, the

AQ was mixed with pre-soaking liquor in and loaded into the woodchips during the pre-soaking. The effect of AQ on the pulping efficiency with dry pulping at atmospheric pressure (See section 4.1) was first conducted.

The influences of AQ and sodium hydroxide concentration on pulp properties and yield are given in Table 12. The pulping was performed in a vacuum oven at 140 °C for 6 h (including drying and baking). Samples HDSW-41 and HDSW-44 were prepared in the same batch. It can be found that the decrease of sodium hydroxide concentration did not result in an increase on pulping yield. The addition of AQ indeed resulted in a marked increase of pulping yield (58% for HDSW-41 and 63.38% for HDSW-44). The addition of AQ was found to slightly improved pulp strength properties.

Table 12. Effect of NaOH concentration and anthraquinone

Sample	HDSW-21	HDSW-41	HDSW-44
NaOH (wt%)	2.95	1.68	1.68
AQ(wt%)	0	0	0.059
Yield (%)	57.4	58.0	63.9
Brightness (% , ISO)	32.0	29.6	29.8
Bulk (g/cm ³)	0.56	0.57	0.57
Tensile index (Nm/g)	33.3	26.0	29.9
Burst index (kPam ² /g)	1.4	1.0	1.3
Tear index (mNm ² /g)	3.7	3.2	3.3
STFI index (Nm/g)	24.7	21.6	24.1

#: Solution concentration

5-2-2. Dry pulping at reduced pressure: The results shown in Table 12 indicate that by decreasing NaOH concentration and adding AQ the handsheet strength made with the dry-pulping fibers could only be slightly improved. Nonetheless, from these studies it became apparent that the baking temperature and time are two important factors for improving fiber quality. Even in vacuum baking condition, though the water evaporation speed could be accelerated, the 140 °C is still too high, which as described above still cause the surface of chips being over dried and cooked, inside the chips is still wet and not thoroughly dried and cooked, as a result, the fibers on the surface of chips were damaged seriously. So, continuing to reduce the baking temperature and time should be further tested.

In order to conduct a low temperature and short time reaction, the baking was performed at 120 °C under vacuum. In this manner, the water in the presoaked woodchips can be quickly removed at relatively low temperature. The results of this modified procedure are summarized in Table 13. Several conclusions were made from these data, including:

- A) The high temperature and long reaction time (see samples HDVA-1 to 4) resulted in lower pulp yield, and using a low temperature and short reaction time (see samples HDSW-48, 49, 50) resulted in higher pulp yields.
- B) An increased yield was also observed when AQ was added. The yield of the pulp made at 95 °C could be higher than 70%.

- C) Comparing to the results in Table 11 and 12, the strength properties of the handsheets made from the dry pulping pulp were much improved. Although the strength properties are still lower than the commercial Kraft pulp (hardwood pulp) at this point, the results in Table 13 did suggest that low temperature and short baking time are two key factors to enhance pulp properties. However, further studies indicated that if the baking temperature is lower than 110 °C the woodchips could not be effectively pulped to individual fibers.
- D) Brightness of the dry-pulping pulp was much higher than traditional Kraft pulp. This is interesting, but the reason has not been understood. It seems that dry pulping pulp is more like CTMP pulp.

Table 13. Effect of sodium hydroxide concentration, AQ, dry pulping method and conditions on paper properties of hardwood chip

Sample	HDV A -1	HDVA- 2	HDV A -3	HDVA- 4	HDSW -47	HDSW -48	HDSW -49	HDSW -50
Chamber Temperature (°C)	130	130	130	130	130	105	130	95
Reaction time after it reached 130 °C (min)	60	60	30	30	0	14.5 hrs	0	0
Total time (min)	120	120	90	90	60	15 hrs	110	210
AQ(wt%)	0	0.072	0.07 3	0.137	0.036	0.080	0.025	0.030
Yield (%)	59.0	62.1	61.6	59.3	67.3	68.2	68.0	70.1
Brightness (% , ISO)						34.1	29.6	31.0
Bulk (g/cm ³)						0.655	0.657	0.668
Tensile index (Nm/g)						42.5	46.2	41.9
Burst index (kPam ² /g)	----					2.0	2.3	2.2
Tear index (mNm ² /g)						6.4	6.1	6.2
STFI index (Nm/g)						25.1	25.4	25.3

5-2-3. Optimization of dry pulping of hardwood chips at reduced pressure: In the above study, we demonstrated that fiber strength could be slightly improved by drying the pretreated woodchips at relative low temperature in vacuum, however, all the strength properties, such as tensile strength, tear index, bust index and stiffness index were still lower than that of Kraft pulping with the conditions we used. At the same time, the Kappa number of the dry-pulping fiber is much higher than that of Kraft pulping. This result suggests that the poor strength probably comes from high lignin content in the dry pulping fiber. Therefore, following work aimed at improving fiber strength by decreasing lignin content of the pulp. In order to achieve this goal, three methods were explored.

First, different temperatures in pre-soaking, drying, and baking were investigated. The results are given in Table 14. The difference between sample HDSW-51 and HDSW-53 is that the NaOH concentration of the former is higher. No marked difference of their fiber properties was found. A slightly higher yield, strength and brightness were obtained for sample HDSW-56. These results indicated that the influence of temperature is more marked than concentration.

The influence of both temperature and concentration were investigated in a wide concentration range. Moreover, the presoaking temperature was increased from 90 °C to 98 °C. Comparing sample HDSW-55 and -56, we found that a higher pulping temperature under vacuum gave evident high fiber strength at relative a lower chemical concentration. However, comparing the samples HDSW-57 and -58, we found that the influence of temperature is not so marked for high chemical concentration. It can be found by comparing sample HDSW-55 with HDSW-57 that pulping with lower temperature but higher chemical concentration could evidently increase pulping yield but gave almost the same paper strength. By comparing the samples of HDSW-56 and -58 we found that the fibers with similar strength properties as Kraft pulp could not be achieved by only changing temperature and chemical concentration.

Table 14. Influence of pulping conditions at reduced pressure on paper properties

Sample	HDSW -51	HDSW -52	HDSW -53	HDSW -55	HDSW -56	HDSW -57	HDSW -58
NaOH (wt%)#	7.69	6.50	4.55	6.50	6.50	13.7	13.7
AQ (wt%)	0.127	0.110	0.110	0.110	0.110	0.110	0.110
Temperature program	A*	B**	A*	A*	B**	A*	B**
Soaking temperature	90 °C	90 °C	90 °C	98 °C	98 °C	98 °C	98 °C
Yield (%)	65.6	70.4	68.1	68.8	69.9	74.3	70.1
Brightness (% , ISO)	30.82	34.33	32.11	34.4	31.4	32.7	31.3
Bulk (g/cm ³)	1.405	1.453	1.502	1.453	1.406	1.382	1.393
Tensile index (Nm/g)	42.0	46.5	44.7	45.1	51.6	44.8	45.5
Burst index (kPam ² /g)	2.3	2.5	2.2	2.4	2.9	2.4	2.5
Tear index (mNm ² /g)	5.4	5.7	5.5	5.8	6.1	5.7	6.0
STFI index (Nm/g)	23.3	24.0	23.7	24.5	25.2	24.9	25.1

#: based on dry wood chips; *A: The chamber temperature was kept at 70 °C and the chips were dried under vacuum till the bed temperature was increased to the same one as the chamber. Then the chips bed temperature was increased to 110 °C and kept for 20 minutes. **B: The chamber temperature was heated and kept at 130 °C, and then chips were baked under vacuum till a temperature of 122 °C. Handsheets were prepared at a basis weight of 160-180g/m².

5-2-4. Dry pulping of softwood chips at reduced pressure

5-2-4-1. Effect of chemical charges on dry pulping of softwood chips: We have discussed the dry pulping of hardwood chips at reduced pressure in section 4-2-3, while in this section, the same dry pulping procedure was applied to softwood chips. The softwood chips were subjected to pre-soaking at various chemical charges. After mechanically pressing, the woodchips were soaked in original solution again and then were baked in vacuum oven at 80 °C or 130 °C followed

by overnight post-soaking in water, the woodchips were disintegrated in Warning blender on low speed for 2 min. The obtained pulp was then screened on a laboratory Valley screen. The pulp was placed into sealed plastic bags, allowed to equilibrate for several days and tested for moisture content followed by determination of screened yield and kappa number. The results of five samples are summarized in Table 15.

Table 15. Softwood dry pulping results

Sample	SW-1	SW-2	SW-3	SW-4	SW-5
NaOH (wt%)#	10.93	10.93	19.05	19.05	13.51
Na ₂ S (wt%)#	10.93	10.93	7.94	7.94	18.92
RT presoaking (h)	45	45	45	45	5
Vacuum pulping (°C)	130	80	130	80	130
Kappa number	141.4	134.2	137.3	133.4	150.4
Yield (%)	72.8	65.1	74.1	71.3	78.2

#:Based on dry wood chips

It can be seen that at lower baking temperature, the pulps have slightly lower kappa number, but considerably higher rejects after screening. At two different presoaking chemical charges, both pulps did not show significant improvement. With increased alkali charge, the kappa numbers of pulps slightly decreased but the yields increased. We also found that softwood was more difficult to be fiberized than hardwood using dry-pulping technology. For softwood, high chemical concentrations and long pre-soaking time were required. After dry-pulping process, softwood chips still had incomplete fiber liberation and rigid fiber clusters. Furthermore, dry pulped softwood chips required long disintegration time to complete fibrillation.

5-2-4-2. Effect of AQ on the pulping of softwood chips: The dry pulping of softwood chip was also performed using higher chemical charge. Table 16 shows yield and Kappa numbers for the pulps prepared at 130°C baking temperature. Screened yields dropped with higher chemical charge. When compared to the results shown in Table 15, screened yield decreased by about 15-21% but Kappa numbers was only reduced by about 6-9 points. The addition of anthraquinone was also evaluated for softwood dry pulping. The results show that the addition of 0.08% AQ (based on solution) to presoaking liquor caused a decrease in Kappa number and an increase in screened yield. With the addition of 0.08% AQ, Kappa number was decreased by 6.4 points and screened yield increased by 2.4%. From Table 16, clearly the extremely high Kappa number suggests that a significant amount of lignin was not removed from woodchips.

Table 16. Softwood dry pulping results and the effect of AQ

Sample	SW-6	SW-7	SW-8	SW-9
NaOH (wt%)#	18.46	20.29	16.67	18.46
Na ₂ S (wt%)#	12.3	14.49	8.33	12.3
AQ (%)	0	0	0.083	0.077
Kappa number	132.2	135.6	137.2	125.9
Yield (%)	57.8	53.1	64.7	60.2

#:Based on dry wood chips

5-2-4-3. Effect of high chemical charge on the pulping: Additional dry pulping tests were conducted by increasing the chemical addition. The pulp yield and Kappa numbers from four different pulping conditions are summarized in Table 17. A Kappa number about 118 was reached and it seems that increasing chemical dosage does not reduce the Kappa number (comparing A with C). The pulp yields were in range of 55.1 - 65.9% with slightly decreasing the pulp rejects.

Table 17. Softwood dry pulping results and the influence of chemical composition

Sample	DONG-A	DONG-B	DONG-C	DONG-D
NaOH (wt%)#	30.8	30.8	34.48	33.33
Na ₂ S (wt%)#	12.55	12.55	17.24	16.67
Liquor/chips	5.28	5.28	9.67	10
Temperature (°C)	130	80	130	80
Kappa number	117.7	147.7	139.4	144.1
Yield (%)	55.1	56.1	57.2	65.9

#:Based on dry wood chips

Conclusively, softwood chips could be converted into the pulp fiber by dry-pulping. Because the dry pulping pulps were produced in yield of more than 60% with high lignin content, the dry pulping methods tested above were very similar to semichemical pulp. It was realized that the key issue to make high strength Kraft pulp is to reduce the lignin content in the final products.

5-2-5. Conclusion of dry pulping with AQ at reduced pressure: Dry pulping of hardwood using AQ as catalysts has a very high yield (up to 74%), which means a significant amount of lignin has not been removed. The tensile strength of the pulp come from reduced pressure with AQ could reach as high as 51.6 Nm/g, which is much higher than 33.3 Nm/g of dry pulping at atmospheric pressure. Using similar dry pulping conditions for softwood could give a screen yield as high as 78.2%. All of these yields are much higher than Kraft pulping, which means significant amount of lignin is still remained in the final pulps. Dry pulping at both atmospheric pressure and reduced pressure gave higher brightness fiber than Kraft pulping. However, the Kappa number of the pulp coming from dry pulping was much higher than Kraft pulping. The fiber strength was still lower than Kraft pulp. Based on all tests we did above, we concluded that a simply baking the pre-treated woodchips could not make good pulps with similar properties as that of Kraft pulp.

5-3. Task three---Chemical consumption of dry pulping at atmospheric and reduced pressure

5-3-1. Black liquor analysis: In order to calculate the chemical and energy consumption, it is important to know the spent liquor chemical composition from the dry-pulping process. The characteristics of spent liquors from two different pulping conditions were analyzed and summarized in Table 18. A black liquor sample (HDSW-57) generated from dry-pulping process

was used for measuring residual alkali concentration and lignin content. The residual alkali concentration in black liquor was determined by titration. Lignin content was determined by gravimetric measurement after precipitation by acid dilution of black liquors. The liquors were first filtered through a Whatman #4 filter paper over a Buchner funnel. Approximately 0.5 grams of EDTA-2Na⁺ was added for 100 ml of the liquor. The liquors were neutralized with 2 M H₂SO₄ until a pH of approximately 6.0 was reached. The solutions were then stirred vigorously for one hour. The liquors were further acidified to a pH of 3.0 and frozen. After thawing the solutions, the precipitate was collected on a medium sintered glass funnel and was washed twice with cold water by suspending the precipitates in the water. The precipitates were oven dried and weighted. The results in Table 18 indicate that active alkali and sulfidity of the liquors are in the range of 60.9-81.3g/L and 81.7-86.3%, respectively. This indicates that the collected liquors still contain high alkali concentrations and sulfidity.

During the presoaking process, it is assumed that a small amount of the lignocellulosic materials was dissolved into the spent liquor. The dissolved organics consist primarily of lignin and degraded carbohydrates. After presoaking, both liquors contain 1.91 and 1.92(g/100ml) lignin.

Table 18. Characteristics of black liquors

Sample	EA (g/L)	AA (g/L)	NaOH (g/L)	Na ₂ S (g/L)	Sulfidity (%)	Lignin (g/100ml)
HDSW-57	46.2	81.3	11.1	70.2	86.3	1.92

Klason lignin of hardwood pulp samples: To evaluate the amount of lignin remaining in pulp after the dry pulping, Klason lignin content was measured. Klason lignin is the residue obtained after acid hydrolysis of the carbohydrate portion of pulp. The content was determined according to Tappi standard T222 om-88 "Acid insoluble lignin in wood and pulp". Pulp was treated with 72% sulfuric acid at 30°C for 1 hour, and then it was diluted to 3% sulfuric acid followed by refluxing for 1 hour at 121 C in an autoclave. The lignin was filtered in a tared medium crucible, washed, dried and weighed.

Table 19. Klason lignin content in handsheet

Sample	HDSW-55	HDSW-56	HDSW-57	HDSW-58
Klason lignin (%)	24.4	23.3	25.1	24.1

The data in Table 19 shows the Klason lignin content in pulp after dry pulping. The results indicate that a significant portion of the lignin was retained in the pulp produced by dry-pulping. After dry-pulping, the level of Klason lignin content in the pulps was 22.8 - 25.1%. The pulps obtained from dry pulping had very high lignin contents. All dry pulps had much higher Klason lignin content in comparison to the highest Kappa number pulp (kappa number 55.1) produced in conventional Kraft process. The high lignin content in fibers could be reflected in lower strength properties.

Conclusion: Pre-soaking process at elevated temperature consumed some pulping chemicals and released some lignin in the pre-soaking liquor. High lignin content in the final dry pulping pulp probably was the reason of poor fiber strength.

5-3-2. Dry pulping with steam treatment and chemical consumption of dry pulping at reduced pressure: In the above study, the woodchips was soaked in pulping liquor at 90 °C for several hours. Long time presoaking at relative high temperature would result in chemical consumption, which has been demonstrated by lignin titration analysis of black liquor. Moreover, long time presoaking is not beneficial for continuous large pulping production line. Therefore, an improved method that can decrease chemical consumption in presoaking and speed up the pretreatment process is needed.

Steam is widely used as heating resource in pulp mill. The cost of steam is much lower than electricity in an intergraded-pulp mill. One of the problems we had in our dry-pulping approach was the poor loading of the pulping chemicals inside the woodchips during the pre-soaking process. To improve the pre-soaking efficiency, we soaked the woodchips in hot water (~90 °C) for a few hours. In this part of the study, presoaking process was further improved. Practically, the dry woodchips were first treated by steam for 20 minutes. It was found that the steam treatment could remove a large amount of rosin and fatty resins from woodchips, which makes the following chemical loading much easier. Evident positive function was found from only 10 minutes steam pre-treatment of hardwood chips. Some results are given in Table 20. As the increase of chemical charge, the reject of the pulping was decreased. The reject in the sample SHP-20 was almost negligible. In these experiments, steam treatment followed by 20 minutes of chemical soaking at room temperature was used. The pretreated woodchips were put in a vacuum oven. The water was evaporated and temperature of the oven was increased. Once the temperature was raised to 130 °C, the baking stopped, and woodchips was re-dispersed in water for 4 hours followed defibrition process.

The results indicated that the woodchips could be pulped by chemical pre-soaking followed by backing in vacuum. For the pulps with similar reject (SHP-20 and Kraft Pulping in Table 20), the chemical consumption of dry pulping is lower than that of traditional Kraft pulping by almost 30%. The pulp strengths were evaluated by measuring handsheet properties. A tensile strength index of around ~60 Nm/g was obtained, which is higher than thermo-mechanical pulp, but still lower than Kraft pulp. The lower strength may be caused by residue lignin in the pulp. It was found that the typical yield of dry pulping is above 70%, which is higher than that of Kraft pulp, confirming the pulp contains more lignin and wood fines.

Table 20. Dry pulping with steam treatment followed by chemical soaking

sample	SHP-19	SHP-20	Kraft Pulping
NaOH (g) in presoaking solution	19.73	31.57	----
Na ₂ S (g) in presoaking solution	10.73	17.17	----
Water (g) in presoaking solution	161.5	143.3	----
NaOH (%) in solution after presoaking	10.28	16.45	----
Na ₂ S (%) in solution after presoaking	5.589	8.944	----
Solution (g) of presoaking solution	192	192	----
Solution weight after soaking (g)	159.5	156.1	----
Absorbed solution (g)	32.51	35.9	----
Chips weight (g) (55.53%)	80	80	----
O.D. Chips Weight (g)	50	50	----
Actually consumption of NaOH (g/100g O.D. chips)	6.683	11.83	16.58
Actually consumption of Na ₂ S (g/100g O.D. chips)*	2.18	3.853	5.41
Reject (wt %)	4.252	0.12	<0.1
Na ₂ S saving (%)	59.7	28.8	--
NaOH saving (%)	59.7	28.6	--

*: Assume purity of Na₂S is 60%

5-4. Task four---Dry pulping by liquor free chemical pulping (LFCP) approach

Energy calculation (will be given in Section 4.5) indicates that if the pretreated woodchips are fully dried, the energy consumption is higher than other pulping technologies. Therefore, the water inside the woodchips should not be completely removed. For this reason, we modified the dry pulping process in which all free liquor was removed but the water inside the woodchips was remained during the pulping process. The modified dry pulping method, called as liquid free chemical pulping (LFCP), is discussed in detail in this section. Based on both experimental results and calculation (See next section), it was concluded that LFCP method can saving about 55% of heating energy used in Kraft pulping.

5-4-1. LFCP principle: In traditional Kraft pulping, woodchips are soaked in pulping solution and the pulping is usually conducted at a ratio of liquor to woodchips of 4~4.5:1. After pulping all of the solution is treated as black liquor and sent to the chemical recovery device. Actually, in a typical Kraft pulping process, only about 50% of pulping chemicals are actually reacted and other 50% are remained as unreacted. The unreacted chemicals are presented as waste

chemicals in black liquor which increase the total chemical charge and the cost of chemical recovery.

Instead of totally drying the woodchips, the LFCP process is based on the Kraft pulping technique but with no free liquor in the digester. In this process, all reaction chemicals are previously loaded into the woodchips. Those chemicals in the presoaking liquid, on the other hand, will be removed from woodchips and reused. The pulping reactions occur only inside the woodchips with relatively high local concentrations, but the total amount of the chemical consumption is significantly lower than that of traditional Kraft pulping process because no free pulping liquor is in the digester. The reaction between the chemicals and lignin is localized and *in situ*, which means the chemical diffusion and exchange between woodchips and surrounding liquid are not necessary. Therefore, although the chemical concentration in the woodchips is higher than Kraft pulping, the actually total chemical consumption in LFCP process is lower than Kraft pulping because only the chemicals that pre-loaded into the woodchips will be carried out to the pulping process.

On the other hand, a significant energy saving will be achieved by LFCP approach because that only wet woodchips but not free liquor will be heated in the digester. A schematic draw of LFCP is given in Fig. 7. Detail calculation of energy saving is given in next section.

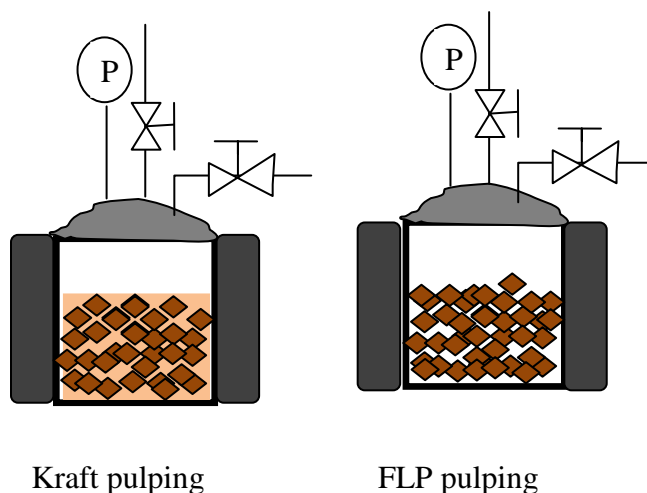


Fig. 7 Diagram of LFCP principle

Based on the previous dry pulping results, in this part of work, we examined the dry pulping (LFCP) first by Parr reactor under different conditions. Both pin chips and normal chips with the size of ~ 2.5 cm x 2.5 cm x 0.5 cm were treated by pulping liquor, and added into a stainless steel cup, which was covered with an aluminum plate with a hole to allow the thermocouple to insert into the chips. The stainless steel cup with chips was put into the one liter Parr reactor which was heated by snake shape tube. The Parr reactor was heated to 170 °C, and kept at 170 °C for two hours. The temperature and pressure of the chips can be monitored by thermocouple and pressure gauge. Then the Parr reactor was cooled to room temperature, and the chips were disintegrated and screened. The pulp fiber samples were analyzed to acquire the properties of Kappa number, fiber yield etc.

Table 21 summarizes the effect of the charge of NaOH, Na₂S in soaking solution, soaking time, and heating intermediate on the dry pulping (LFCP) results of softwood pin-chips by Parr reactor. The data of top two rows in Table 21 reflect the charge of NaOH, Na₂S in soaking solution. To improve the heat transfer, small amount of water (30 ml in total) was added between the Parr reactor wall and cup of the samples PIN 5 and PIN6 as heating intermediate. The conditions in Table 21 were not designed systematically; the main purpose was to examine effect of the heating intermediate in Parr reactor on the LFCP pulping results. The absorbed amounts of NaOH, Na₂S by woodchips after presoaking were measured by titration of presoaking solutions before and after soaking.

Comparison between the data of PIN 1 and 2 in Table 21 indicates that longer soaking time will decrease the reject and lower Kappa number of the pulp. This is because the long soaking time allows more chemical absorbed and the chemical distribution could be more uniform in the chips. In Table 21, the chemical concentration and treatment conditions of PIN 3 were close to PIN 5, and those of PIN 4 were close to PIN 6. However, the fiber yield of PIN 5 and PIN 6 were much higher than others due to the utilization of 30 mL of water as heating intermediate. The results suggest that although large amount of water in the reactor will result in high energy consumption, small amount of water working as heating intermediate is helpful in that the saturated vapor from the water could improve the heat transfer and the stability of the temperature profile.

Table 21. The effect of chemical charge and soaking time on the dry pulping of softwood pin-chip*

Sample	PIN 1	PIN 2	PIN 3	PIN 4	PIN 5	PIN 6
NaOH (wt %)	13.66	13.66	10.92	8.18	11.73	9.03
Na ₂ S (wt %)	6.86	6.86	6.87	6.87	7.41	7.61
AQ (g)	0.11	0.11	0.11	0.11	0.11	0.11
Triton-100 (g)	0.11	0.11	0.11	0.11	0.11	0.11
Soaking liquor/chips	6.38	6.38	6.38	6.38	5.87	6.01
Soaking time (h)	12	20	12	20	12	20
Consumed NaOH (g/100g chip)	17.47	20.66	13.10	8.99	14.50	10.27
Consumed Na ₂ S (g/100g chip)	5.19	5.18	4.18	5.05	4.05	3.65
Water in the digester (g)	112.7	106.0	106.7	89.0	140.0	135.8
Ratio of Water to O.D chip (w/w)	1.30	1.22	1.23	1.03	1.66	1.56
Reject (wt %)	2.5	1.1	3.7	11.6	1.7	5.6
Kappa number	47.2	27.4	48.4	-	34.9	59.2
Pulp amount (O.D.g)	31.6	31.7	36.3	-	37.0	38.8

*: 180 g woodchips with o.d. wood content of 48.3%. i.e. 87g o.d. wood.

5-4-2. Exploration of basic condition of LFCP and the influence of chips shape on LFCP:

When transacting above LFCP process of softwood pin-chip by Parr reactor, it was found that the temperature of pulping was not uniform within the Parr reactor and not easy to control, so that the pin-chips are not uniformly pulped. In order to improve the heat transferring efficiency and pulping uniformity, all the pulping experiments followed were done by using Aurora digester. The Aurora digester is one of lab scale Kraft pulping instruments, see Fig. 8. When using Aurora digester, the Kraft pulping extent was controlled by H-factor, and the H-factor is a kinetic factor for measuring rate of delignification in Kraft pulping. It is a single variable model combining temperature (T) and time (t) and assuming that the delignification is one single reaction, the H-factor is expressed by following equation:

$$H = \int_0^t \exp(43.2 - 16115/T) dT$$

H-factor can be changed by both changing temperature and cooking time, usually the cooking temperature is set up to some point, then H-factor changes as cooking time changes.



Fig. 8 Aurora digester

LFCP of softwood pin-chips and normal chip (NSWC), $\sim 2.5\text{cm} \times 2.5\text{cm} \times 0.5\text{cm}$ were performed with Aurora digester and were compared to traditional Kraft pulping (TKP), the conditions and pulping results are summarized in Tables 22 and 23. For LFCP samples in Tables 22 and 23, the consumed Na_2S and NaOH were measured from the change of solution volume and concentration before and after pre-soaking based on titration analysis; different separation methods including filtration and centrifuge were used to remove and collect free solution after the presoaking. Filtration was used to separate free solution in samples PIN 7 (Table 23) and NSWC 1 (Table 22) while centrifugation was used in sample PIN 8 (Table 23), which removed more liquor than filtration.

In traditional Kraft pulping (TKP) the chemical charge was calculated by volume and the effective concentration of the pulping liquor and all of the chemicals were assumed to be completely consumed. All of these samples were pulped to an H-factor of 2014 in an Aurora digester. In these researches surfactant triton-100 was used as additive to promote pulping. The sample NSWC 1 in Table 22 was prepared using LFCP method, which gave almost zero reject. The weight ratio of liquor to woodchips for sample NSWC 1 is much smaller than that of Kraft pulping sample NSWC 2, which means the energy cost would be much lower than Kraft pulping. However, evident chemical saving could be found that NaOH consumption was decreased 18.4% and Na₂S consumption was decreased 4.21 %. Both pulping methods give almost the same Kappa number and pulping yield. After refining to the same freeness LFCP gave lower fiber strength than TKP but much higher than the pulp prepared from dry pulping at reduced pressure. These results suggest it is possible that both energy and chemical consumption could be saved by using LFCP technology.

Table 22. Comparison of effect of chemical charge and reject on pulping between LFCP and traditional Kraft pulping (TKP) of normal softwood chip (NSWC)*

Sample	NSWC 1 (LFCP)	NSWC 2 (TKP)
NaOH (wt %)	9.03	11.73
Na ₂ S (wt %)	7.61	7.41
AQ (g)	0.11	0.11
Triton-100 (g)	0.11	0.11
Soaking liquor/chips	6.38	-
Soaking time (h)	72	
Consumed NaOH (g/100g chip)	12.6	15.44
Consumed Na ₂ S (g/100g chip)	5.23	5.46
Water in the digester (g)	134.1	312.4
Ratio of water to O.D chip (w/w)	1.61	3.75
Reject (%)	0	0.03
NaOH Saving (%)	18.4	--
Na ₂ S Saving (%)	4.21	--
Kappa number	17.9	17.1
Pulp yield (%)	41.7	42.3
Freeness CSF (ml)	450	440
Tensile index (Nm/g)	65.2	80.1

*:180 g NSWC woodchips with o.d. wood content of 46.3%. i.e. 83.3 g o.d. wood.

There were two possible functions of pressing regular woodchips after steam treatment and pre-soaking as described above. Pressing destroys dense structure of chips and make

structure of chips looser, a loose structure is beneficial both to heat transfer and to mass transfer in pre-soaking. Softwood with pin shape chips was pulped using both Kraft and LFCP technology. The results are given in Table 23. The sample LFCP (PIN 7) has more reject than traditional Kraft pulping sample (PIN 9). Chemical consumption for LFCP (PIN 7) however, was higher than that of Kraft one. More results of pin chips dry pulping have been given in above Table 21 in a broad chemical consumption range and different conditions, though these data were acquired by using Parr reactor.

Based on the results in Tables 21 and 23, it seems that although the Kappa value and pulping yield of pin shape LFCP pulp (comparing reject) was very close to that of Kraft one, The chemical charge, however, didn't decrease evidently. These results demonstrate that decrease chips size is not helpful to dry pulping yield.

Table 23. Chemical charge and reject comparison between LFCP and traditional Kraft pulping (TKP) of pin-chip (PIN)

Sample	PIN 7 (LFCP)	PIN 8 (LFCP)	PIN 9 (TKP)
NaOH (wt %)	9.03	9.03	9.03
Na ₂ S (wt %)	7.61	7.61	7.61
AQ (g)	0.11	0.11	0.11
Triton-100 (g)	0.11	0.11	0.11
Soaking liquor/chips	6.01	6.01	-
Soaking time (h)	34	69	
Consumed NaOH (g/100g chip)	13.89	10.82	10.79
Consumed Na ₂ S (g/100g chip)	6.18	4.32	5.34
Water in the digester (g)	165.3	113.2	331.9
Ratio of Water to O.D chip (w/w)	1.90	1.30	3.81
Reject (%)	0.15	3.36	0.03

5-4-3. Optimization of LFCP technology: Above preliminary results show that Aurora digester was a better cooking reactor for LFCP which could improve the LFCP pulping process and pulp quality of softwood chips by improving heat transfer, decrease in Kappa number, rejects content and lowering chemical consumption. However, the pulp fiber acquired by LFCP method showed lower strength than that from TKP method, which was maybe caused by higher H-factor and higher chemical absorption in the chips which made the local concentration of chemical in chips too high, so the chips were over cooked and fibers damaged.

Based on above Aurora digester LFCP results, more efforts were paid on optimization of the conditions so that all of the pulp properties could be improved by Aurora digester. These

conditions include different composition of soaking solution and H-factor of the pulping reaction. The softwood chips (180 g with solid content of 46.3%, i.e. 83.3 g o.d. wood) with the size of ~ 2.5cm x 2.5cm x 0.5cm were soaked in white liquor (soaking solution) at room temperature for above 24 h, the white liquor contained 0.11g surfactant (Triton-100), 0.11g anthraquinone (AQ) and different contents of NaOH, and Na₂S for all tests. After soaking in presoaking solution, the mixture was filtered to get the chemical loaded and the liquid free chips the amount of chemicals loaded into chips could be obtained by titrating the soaking solution before and after soaking. This presoaking process is illustrated in Fig. 9. The color of the liquor only slightly became deeper than original solution, which means that no evident chemical was consumed in pre-soaking at room temperature. The liquid free chips were put into Aurora digester (see Fig. 7) and cooked at 170 °C to different H-factors. The pulped samples were cooled down to room temperature and disintegrated in a laboratory Waring blender at low speed for two minutes, followed by screening separation to acquire pulp fibers and reject data.



Fig. 9 Before and after presoaking process of chips in soaking liquor

The effect of soaking solution composition and H-factor on the pulp yield, reject, Kappa number, and handsheet strength made from generated fibers were examined. To evaluate the efficiency of LFCP cooking method, the traditional Kraft pulping (TKP) for the softwood (SW) chips by Aurora digester was also performed and compared to the LFCP method.

Table 24 summarizes the effect of different chemical loading and cooking H-factor on the traditional Kraft pulping (TKP) and LFCP sample of normal softwood chip. It could be seen that at all given conditions, the chips were pulped successfully by both LFCP and TKP methods, the rejects were zero and the Kappa number of LFCP pulp was even lower than TKP pulp (19.2-21.2 vs 21.4-24.8). As H-factor was increased, the strength of fibers acquired both from LFCP and TKP decreased. The strength of pulp fiber samples generated from LFCP method is still lower than the fibers generated from TKP method, though the samples by TKP method

consumed a little more chemical (Na₂S, 4.86-5.23 vs 6.13-6.30 g/100g chip). These results clearly demonstrated that the LFCP can produce better pulps with less energy consumption. However, further optimization of the condition is needed.

Table 24. Effect of chemical loading and H-factor on the traditional Kraft pulping (TKP) and liquid free chemical pulping (LFCP) of normal softwood chip. ^a

Samples	LFCP			TKP		
	1700	1500	1300	1700	1500	1300
H-factor	1700	1500	1300	1700	1500	1300
wt % NaOH ^b	8.62	8.62	8.62			
wt % Na ₂ S ^b	7.26	7.26	7.26			
Consumed NaOH (g/100g chip)	12.63	12.70	12.97	12.63	12.70	12.97
Consumed Na ₂ S (g/100g chip)	4.86	4.93	5.23	6.13	6.17	6.30
Water in the digester (g)	137.3	136.2	138.0	333.3	333.3	333.3
water / O.D chip (w/w)	1.65	1.64	1.66	4.00	4.00	4.00
Reject (%)	0.01	0	0	0.02	0	0
Kappa number	19.2	20.3	21.2	21.4	24.6	24.8
Pulp yield (%)	43.0	45.0	45.0	44.4	45.4	44.2
Freeness CSF (ml)	440	450	470	450	450	470
Tensile index (Nm/g)	67.4	74.5	76.1	90.9	97.1	95.3

^a 180 g woodchips with solid content of 46.3%, i.e. 83.3 g o.d. wood. ^b wt% of NaOH, Na₂S in soaking solution

Based on the results in Table 24, the chemical concentration in the soaking solution was decreased, and the effect of this decreasing in chemical concentration in soaking liquor and the absorbed chemicals in chips on the LFCP results are summarized in Table 25.

Table 25. Effect of the concentration of NaOH, Na₂S in soaking solution for SW chip ^a at the H-Factor of 1500

Samples	LFCP-1	LFCP-2	LFCP-3	TKP-1	TKP-2	TKP-3
wt % NaOH ^b	7.88	6.68	5.50			
wt % Na ₂ S ^b	6.64	5.62	4.64			
Consumed NaOH (g/100g chip)	12.22	10.08	8.65	12.22	10.08	8.65
Consumed Na ₂ S (g/100g chip)	4.79	4.01	3.38	5.80	4.82	4.08
Water in the digester (g)	137.8	137.2	137.9	333.3	333.3	333.3
water / O.D chip (w/w)	1.65	1.65	1.66	4.00	4.00	4.00
Reject (%)	0.02	0.01	0.05	0.02	0.01	0.01
Kappa number	24.8	33.6	58.9	26.8	44.1	73.7
Pulp yield (%)	45.7	47.5	52.9	43.5	46.8	53.4
Freeness CSF (ml)	460	450	430	480	440	460
Tensile index (Nm/g)	82.9	88.3	86.0	96.9	95.0	97.6

^a 180 g woodchips with solid content of 46.3%, i.e. 83.3 g o.d. wood. ^b wt% of NaOH, Na₂S in soaking solution

Comparing the data in Table 24 and Table 25, it can be seen that even if lesser chemical was loaded in SW chips for LFCP pulping at H-factor of 1500, the chips could still be successfully pulped with negligible rejects. The data in Table 25 also shows that as the chemical loading in the chips was decreased, the Kappa number and pulp yield are increased for the pulps acquired by both methods. However, at almost the same chemical charge condition, LFCP gave evidently lower Kappa number than TKP pulping. Although the strength of LFCP pulps obtained at above conditions was still lower than traditional Kraft pulping pulp, evidently the strength improvement of LFCP pulps was observed. These results suggest that if chemical loading was further decreased, the tensile strength of LFCP pulping fiber could be increased further.

To improve the fiber properties acquired by LFCP method, we managed to keep the NaOH concentration in the soaking solution as same as or close to those shown in Table 25, but we increased the concentration of Na₂S in the soaking solution, the effect of these changing on the LFCP of SW chips are shown in Table 26. It can be seen that the increase in Na₂S concentration in presoaking solution resulted in decrease of the Kappa number of the fibers compared to the data in Table 25. Moreover, the most striking result shown in Table 26 was that higher strength of handsheets was obtained by the increase in Na₂S concentration in soaking solution. The tensile strength of the handsheet from LFCP pulp reached to 89.7 ~100.4 Nm/g, which is comparable or even higher than that data acquired by traditional Kraft pulping (see Table 25). However, the NaOH consumed in LFCP process is much lower than in traditional Kraft pulp process. As a result, the NaOH charge and the total chemical charge were markedly decreased, and this decrease in NaOH charge was up to 53.3% as compared to NaOH consumption in traditional Kraft pulping.

Table 26. The effect of lowering the concentration of NaOH but keeping Na₂S unchanged in soaking solution on the pulping and fiber properties of SW chip ^a at the H-factor of 1500

Samples	LFCP-4	LFCP-5	LFCP-6
wt % NaOH ^b	7.76	6.55	5.31
wt % Na ₂ S ^b	7.27	7.35	7.42
Consumed NaOH (g/100g chip)	10.45	9.42	7.21
Consumed Na ₂ S (g/100g chip)	4.76	5.21	5.29
Water in the digester (g)	138.7	134.8	131.5
water / O.D chip (w/w)	1.67	1.62	1.58
Reject (%)	0	0	0
Kappa number	20.8	27.7	37.8
Pulp yield (%)	53.0	46.8	46.0
Freeness CSF (ml)	430	450	460
Tensile index (Nm/g)	100.4	95.5	89.7
NaOH Saving (%) ^c	32.3	39.0	53.3
Na ₂ S Saving (%) ^c	12.8	4.58	3.11

^a 180 g woodchips with solid content of 46.3%, i.e. 83.3 g o.d. wood. ^b wt% of NaOH, Na₂S in soaking solution. ^c related NaOH charge of 15.44 % and Na₂S charge of 5.46.

The effect of H-factor on the pulping and fiber properties of SW chip by LFCP method was also studied using Aurora digester. With the same chemical composition of presoaking solution as used for samples shown in above Table 25, the SW chips were LFCP pulped by Aurora digester to H-factor 1300; and the results are summarized in Table 27. The data in Table 27 shows that at given conditions the lower H-factor (1300) did not significantly affect the pulping and fiber properties, the Kappa number and handsheet tensile strength of the fibers generated at 1300 H-factor are close or comparable to these properties of the fiber produced at 1500 H-factor (Table 25). On the other hand, the relative slightly lowering of tensile strength shown in Table 27 indicates that at this low chemical consumption level, H-Factor cannot be further reduced.

Table 27. Effect of lowering H-factor (1300) on the pulping and fiber properties of SW chip ^a by LFCP compared to the data in Table 25 which was acquired at H-factor of 1500

Samples	LFCP-7	LFCP-8	LFCP-9
wt % NaOH ^b	7.88	6.68	5.50
wt % Na ₂ S ^b	6.64	5.62	4.64
Consumed NaOH (g/100g chip)	10.69	9.09	7.71
Consumed Na ₂ S (g/100g chip)	5.18	5.08	3.80
Water in the digester (g)	131.5	135.8	133.7
water / O.D chip (w/w)	1.57	1.63	1.61
Reject (%)	0	0.02	0
Kappa number	26.6	43.6	58.1
Pulp yield (%)	43.1	48.3	50.7
Freeness CSF (ml)	440	450	430
Tensile index (Nm/g)	84.4	84.1	89.0

^a 180 g woodchips with solid content of 46.3%, i.e. 83.3 g o.d. wood. ^b wt% of NaOH, Na₂S in soaking solution

Further decrease in NaOH loading in chips by lowering 10%, 20%, and 30% of NaOH in presoaking solution with a constant Na₂S concentration and fixing other conditions as used for sample LFCP-3 in above Table 25, resulted in poor pulping results, and the rejects were as high as 0.24, 3.41 and 23.41%, respectively. So the consumption of NaOH for samples in Table 25 seems to reach an optimum value.

Synthesizing above researches, the best results so far for the SW chips by LFCP method compared to the traditional Kraft pulping using Aurora digester are presented in Table 28 and Figs 10-13. Through Table 28 and Figs 10-13, it can be seen that, as the consumption of total chemicals (NaOH plus Na₂S) was decreased from 7.88-5.55 wt%, the fiber yield is actually not affected for LFCP, while the fiber yield increased by TKP method. This is tentatively attributed to the effective concentration of the chemicals in woodchips. For LFCP, the chemicals were preloaded directly and concentrated inside the woodchips, but most chemicals are presented in the solution in traditional Kraft pulping. Clearly, the former is more effective in terms of chemical reaction.

Table 28. The comparison of LFCP pulping to the TKP pulping results at given conditions by Aurora digester at H-factor of 1500

Samples	LFCP			TKP		
	4	5	6	1	2	3
Consumed NaOH (g/100g chip)*	10.45	9.42	7.31	12.22	10.08	8.65
Consumed Na ₂ S (g/100g chip)*	4.76	5.21	5.29	5.80	4.82	4.08
Consumed NaOH plus Na ₂ S	15.21	14.63	12.60	18.02	14.90	12.73
Kappa number	20.8	27.7	37.8	26.8	44.1	73.7
Pulp yield (%)	45.8	46.8	46.0	43.5	46.8	53.4
Tensile index (Nm/g)	100.4	95.5	89.7	96.9	95.0	97.6

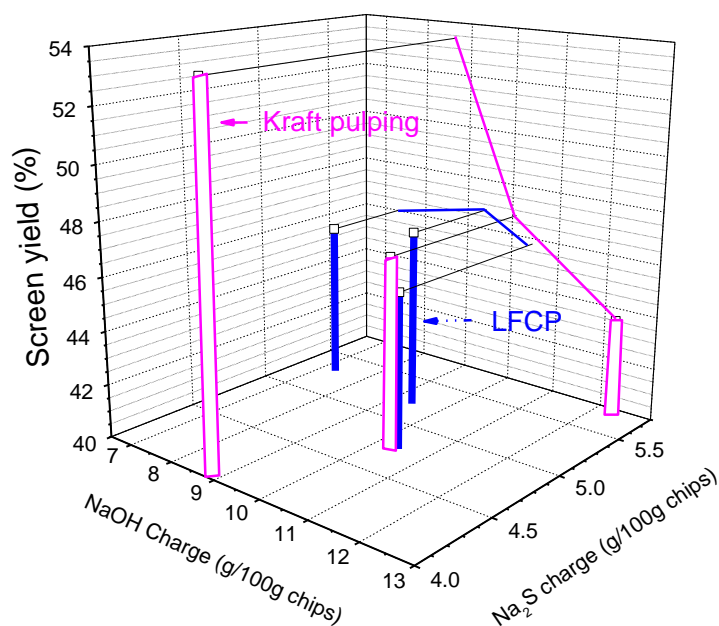


Fig. 10 The effect absorbed NaOH and Na₂S charge in SW chips on the pulp yield by LFCP and TKP with Aurora digester at H-factor 1500

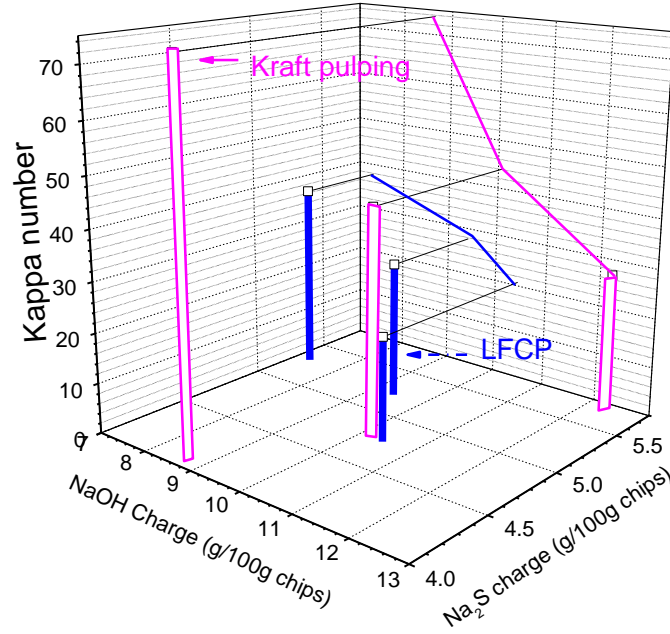


Fig. 11 The effect absorbed NaOH and Na₂S charge in SW chips on the Kappa number of the fibers generated by LFCP and TKP with Aurora digester at H-factor 1500

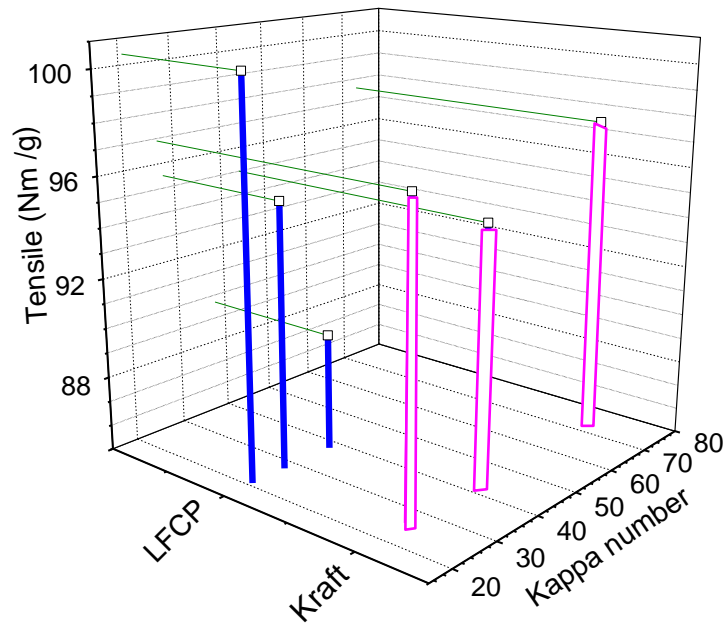


Fig. 12 The relationship between Kappa number and the tensile strength of fibers acquired from LFCP and TKP with Aurora digester at H-factor 1500

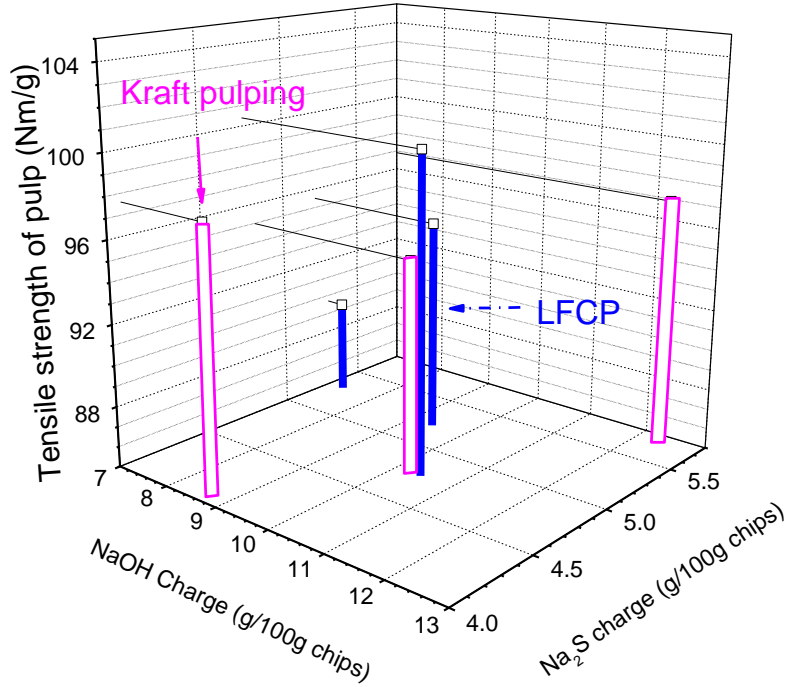
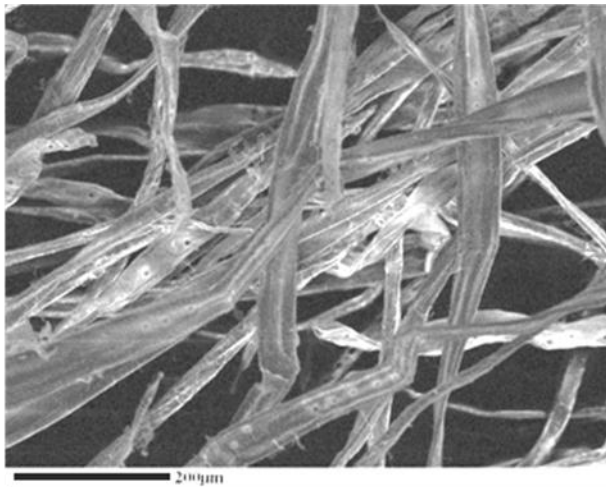
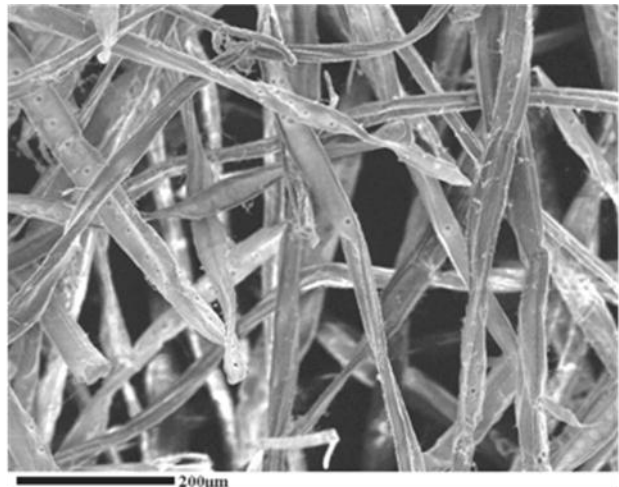


Fig. 13 The effect absorbed NaOH and Na₂S charge in SW chips on the tensile strength of the fibers generated by LFCP and TKP with Aurora digester at H-factor 1500

SEM images of fibers both from dry pulping at elevated pressure and from Kraft pulping (Table 28, LFCP 4 and TKP 1) are given in Fig. 14. No evident difference between these two fibers can be seen from the SEM pictures.



Fiber from dry pulping at elevated pressure



Fiber from Kraft pulping

Fig. 14 SEM images of pulps.

5-5 Energy consumption analysis of dry pulping

5-5-1. Comparison of energy consumption if woodchips are completely dry: It is well known that water evaporation is a huge energy consuming process. In our original proposal, the dry-pulping energy was estimated by the energy consumed by heating and evaporation during drying and baking processes. We did more study about the energy consumption, and compared the dry pulping energy with other pulping techniques. By comparing large amount of literature reported data, it was found that fully drying woodchips is not a good choice from energy saving point of view because the water evaporation from woodchips is much slower than free water evaporation. Detail calculation of energy consumption of different pulping technology was reported in previous publications [83-87]. The energy consumption of the dry pulping process was compared with other pulping techniques and results are given in Table 29.

Dry pulping energy cost of baking approach [87-90]: Calculation approach one: Energy cost to remove 1 lb water from woodchips is taken as 1550 BTU. 1 ton (1000kg) of O.D. pulp need 1.5385 ton of chips (water content 52 wt%), which means 1.667 t water need to be removed. Therefore, the energy cost is 1668 kWh for getting 1 t of O.D. pulp. Calculation approach two [89]: Specific energy consumption is taken as 900kWh/t water (page 5 table 1 of [89]). 1 ton (1000kg) of O.D. pulp need 1.5385 ton of chips, which means 1.667 t water need to be removed. Therefore, the energy cost is 1500 kWh for getting 1 t of O.D. fiber. An average 1584 kWh of the above two calculation results is taken. In Kraft pulping 569 kWh/ O.D. ton of pulp will be cost in digester. In our dry pulping of baking method, digestion was replaced by baking. Therefore, the total energy cost should be $2346-569+1584=3361$ kWh/ O.D. ton of pulp.

Table 29. Energy analysis of different pulping techniques

Pulping method	Kraft[83,84]*	CTMP[83,85]**	Dry pulping (baking) [87-90] ***	TMP[84]
Total energy consumption (kWh/O.D. ton of pulp)	2346	2328	3361	2450

*:Energy cost: 7500 lb of steam + 400kWh of power /ADT pulp; **: Power cost: 2095 kWh/ ADT of pulp; ***Yield =65%; solution content in the chips before baking=52%.

5-5-2 LFCP energy consumption analysis

The traditional Kraft pulping needs large amount of free liquor (4 to 4.5 times of woodchips), which consumes significant amount of heating energy. For a typical Kraft pulping, the ratio of liquor to woodchips (O.D.) is usually ~4.5. If the original wood contains 50wt% of moisture (it was confirmed in this study), the actual mass fraction of O.D. wood in the digester (water+chemicals+wood) is only 15.38 wt%. Specific heat capacity of white pine, oak and water is 2.5, 2.0 and 4.186 kJ/kg.K respectively [91]. Therefore, the energy consumption on heating woodchips is only 7.99% of the total energy in hardwood Kraft pulping and 9.79% in softwood Kraft pulping. In other words, more than 90% of heating energy is consumed by heating the free water in the digester.

If we assume no free liquor in the digester, the energy saving with LFCP method for softwood and hardwood is compared with Kraft pulping process in Table 30. Table 30 indicates that LFCP can save more than 65% of heating energy compared to Kraft pulping. However, it was experimentally found later that small amount of free liquor in the digester will be necessary for stabilizing the temperature in the reactor. Therefore, the actual energy saving is slightly lower than the numbers given in Table 30.

Table 30. Energy cost analysis of LFCP technology

Pulping method	Original woodchips (g)	O.D. weight (g)	Wood content in the chips (%)	Total liquor in the reactor (g)	Relative energy consumption (Kraft pulping 100%)
LFCP *	180	82.26	45.7	117.74	32.27
Kraft*	180	82.26	45.7	467.9	100
LFCP **	180	110.39	61.33	119.39	27.8
Kraft**	180	110.39	61.33	566.37	100

*: Softwood; **: hardwood

In summary, we concluded that completely remove the water in the woodchips is not cost effective. Instead, if free liquor in the digester is removed but the woodchips are still wet, about 30% of heating energy used in traditional Kraft pulping process can be saved. With this method, the wood pulps have similar properties as that obtained in Kraft pulping.

6. ACCOMPLISHMENTS

- a) An invention disclosure based on dry pulping technology has been filed at Georgia Tech.
- b) One paper based on this study will be submitted for publication. Target journal is Tappi Journal.
- c) One conference presentation was given in 2010 AIChE annual meeting.
- d) Three presentations were given to Georgia Tech pulp paper member companies review meeting
- e) Three invited talks on dry pulping have been given at pulp paper companies.

7. CONCLUSION

The new technology without pulping liquor presenting in the digester was explored. Three different dry pulping methods were investigated in detail. Both softwood and hardwood chips could be pulped into individual fibers with the dry pulping method. Simply baking the pretreated woodchips in an oven resulted in an un-uniform reaction. As a result, wood fiber strengths were poor. This problem was overcome by the Liquid Free Chemical Pulping (LFCP) method in which the free water was removed but the moisture inside the pretreated woodchips remained during the pulping process. Compared to the traditional Kraft pulping method, LFCP saves about 45% of the liquor used in conventional Kraft pulping. Because the pulping liquor in the digester absorbs more than 90% of heating energy during the pulping, removing free liquor before pulping resulted in a decrease as high as 55% of cooking energy consumption in the digester. Moreover, LFCP can give close and even slightly higher fiber tensile strength (Table

30) than Kraft pulping with a Kappa number much lower than Kraft pulping. The NaOH charge can be decreased up to 53.3 wt% and Na₂S charge can be decreased 3.11 wt% compared to traditional Kraft pulping. Key characteristics of three dry pulping technologies are summarized in Table 31. LFCP method showed both energy and chemical saving while other properties of pulp close to Kraft one.

Table 31. Comparison of dry pulping technology to Kraft pulping*

Dry Pulping method	At ambient pressure	At reduced pressure**	At elevated pressure***
Screen yield	Higher	Much higher	Close
Kappa number	Much higher	Much higher	Close
Brightness	Higher	Higher	Close
Tensile strength	Much lower	Lower	Close
Pulp bulk	Lower	Lower	Close
NaOH consumption	Lower	Lower	saving Ca. 53 wt%
Na ₂ S consumption	lower	Lower	saving Ca. 3.0 wt%
Energy consumption	Higher		saving Ca. 55%

*: Comparing with Kraft pulping; **: using AQ as additive; ***: Using AQ and triton as additives

8. RECOMMENDATIONS

Our research demonstrated that free liquor in the pulping digester is not necessary if woodchips are pre-soaked with pulping solution. The pulp quality made from this method is similar to that traditional Kraft pulp. However, because no free liquor is required in the digester, up to 55% of heating energy can be saved compared to traditional pulping method. The concept has been proved in this study. Further fundamental study, optimization of the operation conditions and scale up trial are needed for full scale up production.

Future fundamentals study:

a. Heterogeneous chemical reaction of pulping chemicals and woodchips without free liquor: For most chemical reaction, medium is important for both mass and heat transfer within the reactants. Although the moisture is still presented in the woodchips, there is no free liquor as the reaction medium in LFCP. Therefore, the delignification mechanism, heat and mass transfer as well as the reaction kinetics are different from traditional Kraft pulping technique. All these will affect the pulp quality and yield. These need to be fully studied before the technique can be commercialized.

b. Although the handsheet properties of dry pulping pulp have been studied, many other fiber properties, such as chemical composition (lignin, hemicellulose and cellulose), viscosity, molecular weight, fiber length and individual fiber strength have not been fully analyzed or evaluated. Fundamental study on above properties is very important for designing the reactors, controlling chemical and thermal reaction conditions and improving the pulp qualities.

c. Bleaching chemistry of the pulp from dry pulping process has not been studied. It is expected that the pulp made with dry pulping technique has different chemical compositions. Therefore, the bleaching chemistry must be studied and compared with traditional Kraft pulp.

d. Lignin chemistry, including chemical structure, molecular weight, etc. may be significantly different from traditional Kraft pulp. These differences need to be studied so the new applications of lignin may be developed.

e. Black liquor chemistry and chemical recovery in LFCP may be slightly different from traditional Kraft pulp. These also need to be investigated.

f. Chemical and energy consumptions have been calculated in this study. However, these calculations are based on some theoretical assumption. Actually numbers may be different from these simple calculations. Experiments that can directly measure the energy consumption during pulping process need to be conducted. Economic analysis based on actual experimental results need to be done before full scale production.

Scale up trials:

a. The FLCP method developed in this study uses similar digester as currently used in Kraft pulping. This will reduce the difficulty for commercialization of the technology. However, most Kraft pulping plant does not have chemical pretreatment (soaking woodchips in pulping liquor) and filtration (removing the free liquor after pretreatment) units. The pilot trial plant should have capability to add these units.

b. Because there is no free liquor in the digester, the moisture is the only medium for heat transfer. Using vapor as the heat transfer medium is different from that using liquid water. Therefore, the heat transfer in large scale reactor in saturated vapor should be carefully calculated.

c. To fully evaluate the energy and cost saving, the pilot unit should be able to measure energy consumption during the trials.

Commercialization pathway:

Our concept has been proved by laboratory study. We expected that, if the continuous financial support from DOE or pulp and paper industry is available, the technique can be commercialized in four years from now, which includes fundamental study (1.5 years), pilot trials (1.5 year), and preparation of first full scale of ill production test (1 year). After the success of the first full scale production, the technique, energy saving, environmental and economic evaluation will be accomplished in the fifth year. The full assessment analysis will be collaborated with Georgia Tech’s Industrial System Engineering School. The model for such assessment analysis will be developed and used to analyze the energy, greenhouse gas emissions, wastes, and cost. We will develop a process model of integration of new pulping technique, using ASPEN software and available process models, and we will integrate this into an environmental assessment.

We expected to fully commercialize the technology in 2017 if the if the continuous financial support is available. We expect to replace the current Kraft pulp operation by 10% in 2020, 25% in 2025, and 65% in 2030, the energy savings can therefore be calculated, as shown in Table 32.

Table 32. Summary of the energy, economic and environmental benefits of our technique after industrialization

Year	2020	2025	2030
Replacement percentage (%)	10	25	65
US energy savings (Steam energy, Trillion BTU)	0.599	1.50	3.89
US energy savings (Electrical energy, Trillion BTU)	22.39	56.07	154.4

9. REFERENCES

1. http://www.answers.com/topic/kraft-process#Comparison_with_other_pulping_processes.
2. Mansfield S. D.; Weineisen H., Wood Fiber Quality and Kraft Pulping Efficiencies of Trembling Aspen (*Populus tremuloides* Michx) Clones, *Journal of Wood Chemistry and Technology*, 27: 135–151, 2007.
3. <http://oee.nrcan.gc.ca/publications/infosource/pub/cipec/pulp-paper-industry/pdf/pulp-paper-industry.pdf>.
4. Nilsson, L.J., Larson, E.D., Gilbreath, K.R. and Gupta, A., Energy Efficiency and the Pulp and Paper Industry, *American Council for an Energy-Efficient Economy*, Berkeley, CA, 1995.
5. <http://www.kemira.com/en/solutionsproducts/pages/bleachingadditives.aspx>.
6. Danielewicz D, Surma-Slusarska B, Oxygen delignification of high-kappa number pine kraft pulp, *Fibers & Textiles in Eastern Europe*, 14:89-93, 2006.
7. Smook GA, Handbook for pulp & paper technologists, Angus Wilde publications, Vancouver, Bellingham, 1992.
8. <http://www.corrosioncost.com/pdf/pulppaper.pdf>.
9. <http://www.fao.org/DOCREP/005/V9933E/V9933E04.htm>.
10. Gellerstedt, G, Wood and Cellulose Chemistry, Second Edition, pp859-905, 2001.
11. Gratzl, JS; Chen, CL, Lignin : *Historical, Biological, and Materials Perspectives*, 742:392-421, 2000.
12. Hosokawa, J; Yoshihara, K; Nishiyama, M, et al., Cultural Condition for Cell Mass-production of *Aureobasidium-pullulans* from Solvolysis Pulping Waster Liquid, *Journal of the Society of Fermentation Technology*, 64:473-477, 1986.
13. Santiago, AS; Neto, CP, Assessment of potential approaches to improve Eucalyptus globulus kraft pulping yield, *Journal of Chemical Technology and Biotechnology*, 82:424-430, 2007.
14. Renaud, J; Thibault, J; Lanouette, R, et al., Comparison of two multicriteria decision aid methods: Net Flow and Rough Set Methods in a high yield pulping process, *European Journal of Operational Research*, 177: 1418-1432, 2007.
15. Sjobahl, RG; Axelsson, P; Lindstrom, ME, Addition of dissolved wood components to improve the delignification rate and pulp yield in hardwood Kraft pulping, *Appita J*, 59:317-320, 2006.
16. Luthé, C; Berry, R; Parsons, K, Pulping of white birch: How to maximize yield, *Pulp & Paper-CANADA*, 106: 97-101, 2005.
17. United States Patent, 4,869,783.
18. Macleod, JM; McPhee, FJ; Kingsland, KA, et al., Kraft pulping – Pulp Strength Delivery along Complete Kraft Mill Fibers, *Tappi J.*, 78:153-160, 1995.
19. Blain T, Anthraquinone pulping: fifteen years later. *Tappi J.*, 76:137–146, 1993.
20. Berthold F and Lindstrom M, Polysulfide addition as a mean to increase delignification in kraft pulping. *Nord Pulp Paper Res*, 12:230–236, 1997.
21. Duggirala P, Surfactant based digester additive technology for kraft softwood and hardwood pulping. *Appita J*, 53:41–48, 2000.
22. Duggirala PY, Evaluation of surfactants as digester additives for kraft softwood pulping, *Tappi J.*, 82:121-127, 1999.

-
23. Norman E, Olm L and Teder A, Methanol-reinforced kraft pulping. *Tappi J.*, 76:125–130,1993.
 24. Bujanovic B, Cameron J and Yilgor N, Comparative studies of kraft and kraft-borate pulping of black spruce. *J Pulp Paper Sci*, 29:190–196,2003.
 25. Magnotta V, Kirkman A, Jameel H and Gratzl J, High-kappa pulping and extended oxygen delignification to increase yield. *Proc. Breaking the Pulp Yield Barrier Symposium*, Feb. 17–18, Atlanta, pp. 165–182,1998.
 26. Hartler, N; Mohlin, UB, Cellulose Fiber Bonding 2. Influence of Pulping on Interfiber Bond Strength, *Svensk Paperstidning-Nordisk Cellulosa*, 78,:295-299,1975.
 27. Hodges, R; Cullinan, H; Krishnagopalan, GA, Recent advances in the commercialization of NIR (near-infrared) based liquor analyzers in the pulping and recovery area, *Tappi J.*, 5: 3-10,2006.
 28. Allison RW, Wrathall SH, Effect of pulping and Bleaching Conditions on the Strength of Kraft Pulp. 2. Comparison of 3 Commercial Softwoods, *Appita J.*,47:369-374,1994.
 29. Olm L, Tormund D, Kraft pulping with sulfide pretreatment Part 2. The influence of pretreatment and cooking conditions on the pulp properties, bleachability in a TCF-sequence and strength properties, *Nordic Pulp & Paper Research Journal*, 15: 70-79,2000 .
 30. Yawalata, D, Paszner, L, Characteristics of NAEM salt-catalyzed alcohol organosolv pulping as a biorefinery, *Holzforschung*, 60: 239-244,2006.
 31. Watson PA, Wright LJ, Fullerton TJ, Reactions of metal-ion Complexes with Lignin Model Compounds .1. CO(TSPP) as a Single-electron Transfer Catalyst and Implications for Mechanism of AQ Pulping, *Journal of Wood Chemistry and Technology*, 13: 371-389,1993 .
 32. Watson PA, Wright LJ, Fullerton TJ, Reactions of metal-ion Complexes with Lignin Model Compounds . 2. FE(TSPC) Catalyzed Formation of Oxidized Products in the Absence of Oxygen, *Journal of Wood Chemistry and Technology*, 13: 391-409,1993.
 33. Song, Xianliang; Yin, Ning; Pan, Dingru, Review on researches of explosion pulp, *Beijing Linye Daxue Xuebao/Journal of Beijing Forestry University*, 25:75-79,2003.
 34. Dimmel DR, Althen E, Savidakis M, Courchene C, Bozell JJ, New quinone-based pulping catalysts, *Tappi J.*, 82:83-89,1999.
 35. United States Patent, 4,229,251.
 36. Hynynen, J; Palomaki, A; Merilainen, JJ, et al., Pollution history and recovery of a boreal lake exposed to a heavy bleached pulping effluent load, *Journal of Paleolimnology*, 32: pp351-374,2004.
 37. United States Patent, 6,641,699.
 38. Fullerton, TJ; Watson, PA; Wright, LJ, Catalysts for Alkaline Pulling-Beyond AQ, *Tappi J.*, 43:23-28,1990.
 39. United States Patent, 4,100,016.
 40. Yawalata D, Paszner L, Cationic effect in high concentration alcohol organosolv pulping: The next generation biorefinery, *Holzforschung*, 58: 7-13, 2004.
 41. United States Patent, 6,143,130.
 42. United States Patent, 4,152,197.
 43. United States Patent, 6,913,672.
 44. United States Patent, 4,347,103.

-
45. United States Patent, 6,913,672.
 46. United States Patent, 6,267,841.
 47. United States Patent, 6,267,841.
 48. Li W, Tschirner U, Phosphonates as additives in kraft pulping - a preliminary investigation, *Tappi J.*, 1: 22-27,2002.
 49. http://www.industry.siemens.com/industrysolutions/global/en/paper/mechanical_pulp/Pages/Default.aspx?stc=wwiis120362.
 50. [http://en.wikipedia.org/wiki/Pulp_\(paper\)#Mechanical_pulp](http://en.wikipedia.org/wiki/Pulp_(paper)#Mechanical_pulp).
 51. http://valveproducts.metso.com/nees/ApplicationReports/2621_Paper/2621_06_01en.pdf.
 52. http://www.tappsa.co.za/archive3/Journal_papers/Minimizing_TMP_Energy_Consumpt/minimizing_tmp_energy_consumpt.html.
 53. Jonsson Johanna; Ruohonen Pekka; Michel Gregory; et al., The potential for steam savings and implementation of different biorefinery concepts in Scandinavian integrated TMP and paper mills, Conference: 13th Conference on Process Integration, Modelling and Optimisation for Energy Saving and Pollution Reduction Location: Prague, Czech Republic Date: AUG 28-SEP 01, 2010.
 54. Zelm R.; Gailat T.; Weber P. -G.; et al., ETMP technology brings more than 30% Energy savings in TMP production *Wochenblatt Fur Papierfabrikation* Volume: 139 Issue: 8 Pages: 659-+ Published: AUG 2011.
 55. Chang X. F.; Bridges C.; Vu D.; et al., Saving Electrical Energy by Alkaline Peroxide Treatment of TMP Prior to Low Consistency Refining *Journal of pulp and paper science*, 36, 129-134, 2010.
 56. Wang Zhaorong; Li Xinping; Luo Qing; et al., The influences of pretreatment of masson woodchips by cellulases on refining energy consumption and properties of pulp in TMP Processes Conference: International Symposium on Emerging Technologies of Pulping and Papermaking Location: Guangzhou, Peoples R China Date: Nov 08-10, 2010.
 57. Walter Karin; Paulsson Magnus; Wackerberg Eva, Energy efficient refining of black spruce TMP by using acid hydrogen peroxide: Part 1. A pilot plant study, *Nordic Pulp & Paper Research Journal*, 24, 255-265, 2009.
 58. Dong Jixian; Liang Qianhua, New energy saving refiner plate Conference: 2nd International Papermaking and Environment Conference Location: Tianjin, Peoples R China date: May 14-16, 2008.
 59. Law KN; Lanouette R; Yang KC, A breakthrough in energy reduction in thermomechanical pulping of white birch, *Paperi JA Puu-Paper and Timber*, 82,327-330,2000.
 60. Gorski Dmitri; Morseburg Kathrin; Axelsson Patrik; et al., Peroxide-based ATMP refining of spruce: energy efficiency, fibre properties and pulp quality, *Nordic Pulp & Paper Research Journal*, 26, 47-63,2011.
 61. Bian Yuzhou; Ni Yonghao; Yuan Zhirun; et al., Improving TMP rejects refining through alkaline peroxide pretreatment for value-added mechanical papers, *TAPPI Journal*, 6, 24-32, 2007.
 62. [http://en.wikipedia.org/wiki/Pulp_\(paper\)#Chemithermomechanical_pulp](http://en.wikipedia.org/wiki/Pulp_(paper)#Chemithermomechanical_pulp).
 63. http://publications.gc.ca/collections/collection_2007/nrcan-rncan/Fo143-3-2007-10E.pdf.
 64. <http://www.tappi.org/Downloads/unsorted/UNTITLED---eng90513pdf.aspx>.
 65. Rachor G; Patt R; Horand D, Energy savings in the production of CTMP, *Papier*, 44, V1-V10, 1990.

-
66. Sankari Minna; Aksela Reijo; Ilomaeki Anna; et al., Silicate Free P-RC APMP and CTMP Bleaching Solutions, Proceedings of International Conference on Pulping, Papermaking and Biotechnology 2008: ICPPB '08, VOL I Pages: 418-423 Published: 2008.
 67. Li Dong; Han Qing; Wang Ya-Juan; et al., Microwave pretreatment of logs for saving energy and improving paper properties during mechanical pulping, Second International Papermaking and Environment Conference, Proceeding, books A and B, 346-349, 2008.
 68. Grossmann H; Salmen L, Exploration of new scientific ideas for significant electricity savings in mechanical upgrading of pulp fibres for papermaking, *Applied Thermal Engineering*, 17, 947-954, 10.1016/S1359-4311(96)00056-7, 1997.
 69. Gilbert CD; Long PX; Hsieh J, Torque correlation and control in mechanical pulping using adjustable speed drive, 1997 Pulping Conference, books 1 and 2 Book Series: *TAPPI Proceedings*, 979-984, 1997.
 70. Stationwala mi, production of high-quality and low-energy chemithermomechanical pulp, *TAPPI Journal*, 77,113-119,1994.
 71. Jansson K; Jakara J; Rampotas C, Chemical kidney technology in mechanical pulp processes 2001 Impc: mechanical pulps - added value for paper and board, Vols 1 and 2, proceedings, 463-476, 2001.
 72. Argyropoulos DS; Heitner C, Ultra-high-yield pulping .7. the effect of ph during impregnation on the quality of lightly sulfonated CTMP journal of pulp and paper science, 17, J137-J143, 1991.
 73. Petit-Conil M; de Choudens C; Espilit T, Ozone in the production of softwood and hardwood high-yield pulps to save energy and improve quality, *Nordic Pulp & Paper Research Journal*, 13,16-22, 1998.
 74. Hasan Jameel, and Kevin J. Knoernschild, Energy considerations in CTMP expansions for board mills. TAPPI Engineering Conference Proceedings (1990) 513-523.
 75. Venketa r. Parthasarathy, Robert c. Grygotis, Keith W.Wahoske, and David M. Bryer, a sulfur-free, chlorine-free alternative to Kraft pulping, *TAPPI Journal*, Vol. 79,189-198, 1996.
 76. Hasan Jameel, Josef Gratzl, Duggirala Y. Prasad, and Sreeram Chivukula, Extending delignification with AQ/polysulfide, *TAPPI J.* 89,151-160, 1995.
 77. Sezgin Koray Gulsoy and Hudaverdi Eroglu, Influence of Sodium Borohydride on Kraft Pulping of European, Black Pine as a Digester Additive, *Ind. Eng. Chem. Res.* 50, 2441–2444, 2011.
 78. Richard Berry, Yujun Sun, and Corinne Luthe, Accelerating kraft pulping with hydroxyethylidene diphosphonic acid (HEDP), *TAPPI Journal*, 9, 9-14, 2010.
 79. Severtson, S.J., Duggirala, P.Y., Carter, P.W., et al., Mechanism and chemical control of CaCO₃ scaling in the kraft process , *TAPPI J.* 82, 167, 1999.
 80. Li, W., and Tschirner, U., Phosphonates as additives in kraft pulping - a preliminary investigation, *TAPPI J.* 1, 22, 2002.
 81. Tschirner, U. and Smith, T., Phosphonates as additives in kraft pulping, paper presented at the Spring Technical and International Environmental Conference, Atlanta, May 2–5, 2004.
 82. D. Kanungo; R. C. Francisa; N. -H. Shin, Mechanistic Differences Between Kraft and Soda/AQ Pulping. Part 2: Results from Lignin Model Compounds, *Journal of Wood Chemistry and Technology*, 29, 227–240, 2009.
 83. Knoernschild KJ; Jameel H, Energy considerations in CTMP expansions for board mills,

-
- TAPPI Journal*, 74, 145-150, 1991.
84. <http://oee.nrcan.gc.ca/publications/infosource/pub/cipec/pulp-paper-industry/pdf/pulp-paper-industry.pdf> .
 85. Jameel H; Knoernschild KJ, Energy considerations in CTMP expansions for board mills, 1990 Engineering Conference, Book 1 and 2 Book Series: *TAPPI Proceedings*, 513-523, 1990.
 86. David R. Morris, Frank R. Steward, Chris A. Gilmore, Comparative analysis of the consumption of energy of two wood pulping processes, *Energy Conversion & Management*, 41,1557-1568, 2000.
 87. http://books.google.com/books/about/Improvement_of_pulp_mill_energy_efficien.html?id=JB_tAAAACAAJ.
 88. http://www.energystar.gov/ia/business/industry/downloads/Pulp_and_Paper_Energy_Guide.pdf?3d7d-b40f.
 89. Gruber, T., Drying of woodchips with optimized energy consumption and emission levels, combined with production of valuable substances, 3rd European COST E15 Workshop on Wood Drying 2001. Proceedings : With the theme: softwood drying to meet needs of further processing and specific end-uses. 11-13 June 2001, at Scandic Hotel Kalastajatorppa, Helsinki, Finland Helsinki, 2001.
 90. <http://www.northernwoodheat.net/htm/news/Finland/Symposiumpres/Dryingofwoodchips.pdf>.
 91. http://www.engineeringtoolbox.com/specific-heat-solids-d_154.html.